DOE/BC/10375

THE FATE OF HAZARDOUS AND NONHAZARDOUS WASTES IN USED OIL DISPOSAL AND RECYCLING

Final Report

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August 1983

Prepared for

Bartlesville Energy Technology Center
U.S. Department of Energy
Bartlesville, Oklahoma

Under

DOE Contract No.
DE-AC19-81BC10375

Funding provided by
Waste Products Utilization Branch
Office of Industrial Programs
DOE/Conservation and Renewable Energy
Washington, D.C. 20585

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ABSTRACT

The primary objective of this program, sponsored by the U.S. Department of Energy, Office of Industrial Programs, was to identify the hazardous and nonhazardous compounds that might reasonably be found in used oil and to establish, by experimentation if possible, their fate under a variety of disposal and recycling scenarios. Those considered were sewer disposal, road oiling, combustion as a fuel, reprocessing by physical methods to produce a specification fuel, and various re-refining processes. A secondary objective was to assess the potential environmental impact of the contaminants in the waste and product streams associated with each scenario.

The hazardous and nonhazardous compounds of major interest in waste oil were identified by literature review, interviews with participants in waste oil activities, and by laboratory analysis (standard physical parameters, elements, and organic compounds representing major contaminants) of 24 samples of waste oils obtained from recyclers and users. The contaminants were prioritized according to their concentrations in the oil and their health impacts, as determined by threshold limit values, drinking water standards, or other measures of multimedia health impacts. The prioritized listing formed the basis for the preparation of the COMPOSITE oil used in the experimental simulation studies of the waste oil disposal and recycling scenarios. The experimental simulation studies were designed to establish the fate, through material balance if possible, of specific contaminants under conditions that were representative of those normally encountered in each situation.

In addition to the laboratory simulation studies, computer simulations were conducted to assess the physical transport of specific compounds during typical re-refining operations such as dehydration, light end removal, and vacuum distillation. Correlation of the computer-generated results with the results of the laboratory simulations and analyses of samples collected from an operating re-refinery was also attempted with some success.

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ACKNOWLEDGEMENTS

The authors gratefully acknowledge the technical guidance and support provided by Dennis W. Brinkman, DOE Technical Project Officer. The authors further acknowledge the contribution of the following individuals who provided technical and editorial reviews and made helpful revisions to this document; Bruce Cranford, DOE Program Manager in the Office of Industrial Programs; Donald A. Becker of the National Bureau of Standards; Michael Petruska of the U.S. Environmental Protection Agency, Office of Solid Waste; and members of the Peer Review Board at DOE, BETC, Bartlesville, OK.

Robert E. Hall of EPA's Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina deserves special thanks for making available to GCA the atomizing space heating unit tested in this program. For their helpful advice and cooperation, thanks are also extended to William L. Bider and Suzanne Metzler, Franklin Associates Ltd; Henry Aho, State of Maine Department of Environmental Protection; John Purves, New Jersey Department of Environmental Protection; Gil Holland and Thomas Vernon of the PROP facility in North Carolina; several other personnel within other state agencies in California, Massachusetts, and New York; and the numerous industrial recyclers and re-refiners who submitted samples for analysis.

Finally, the authors gratefully acknowledge the contributions of several GCA personnel who participated in the program. Special commendations are extended to: Mark McCabe, John Fitzgerald, and Richard Graziano who made major contributions to the laboratory simulations and field sampling studies; Howard Schiff who played a major advisory role in designing the laboratory simulations; Rebecca Sommer of our North Carolina office for assistance in the computer simulation studies; and to members of the analytical laboratory, Mary Kozik, Deborah McGrath, Gary Hunt, Marilyn Hoyt, Joanna Hall, Andrea Cutter, and many others who worked diligently in support of this project.

EXECUTIVE SUMMARY

This report, prepared by the GCA/Technology Division for the Department of Energy, Office of Industrial Programs, provides data identifying contaminants and their concentrations in waste oil and follows the fate of these contaminants when the used oil is subjected to a number of disposal and recycling scenarios. The contaminants in waste oil and their concentrations were determined by analysis of 24 samples of representative used oils supplied to GCA by collectors, users, and recyclers of used oils. Based on the results of the analyses, a COMPOSITE test oil was prepared by blending four of the representative oils and adding spike contaminants representing organic compound classes of environmental interest. Laboratory simulations of the disposal and recycling scenarios of interest were then conducted with this spiked COMPOSITE oil, and the waste and product streams resulting from these simulations were sampled and analyzed to determine the fate of the contaminants. The scenarios studied were land and sewer disposal, combustion in a small commercial furnace and in two residential size space heaters designed for waste oil combustion, reprocessing to meet specifications for use as a fuel, and several re-refining processes, i.e., solvent treatment/distillation/finishing; distillation/hydrofinishing; and acid/clay processes.

In addition to the laboratory simulations, field activities were conducted to collect samples of flue gas from a commercial boiler and samples of process and waste streams from two operating re-refining facilities for chemical characterization. Computer simulation studies were also conducted to model the transport of specific contaminants through typical re-refining operations and to provide a check on the results of the laboratory simulations and field studies.

The results of the simulations and field studies were used to assess the potential hazard associated with the disposal and recycling scenarios and their component waste and product streams. The assessment of potential hazard was based on health and ecological effects data. This procedure involved summing the ratios of the concentration of each contaminant in a discharge stream to the concentration of that contaminant representing a potential hazard and multiplying the sum by the flow rate of the discharge to determine a stream severity factor. The results are highly dependent upon the presence or absence of compounds of a highly toxic nature such as polychlorinated biphenyls (PCBs) and polynuclear aromatics (PNAs) such as benzo(a)pyrene, a recognized carcinogen, because of the low concentration levels used to denote the presence of hazard or risk for these compounds.

BACKGROUND

Under the provision of Section 3001 of the Resource Conservation and Recovery Act (RCRA) and the Used Oil Recycling Act, EPA prepared a report to Congress in January 1981 which presents the basis of the EPA administrator's intent to list used automotive and industrial oils as hazardous wastes. EPA's decision to classify used automotive oils and used industrial oils as hazardous will lead to regulations for their transportation, treatment, storage, disposal, and recycling; possible reversal of a current RCRA regulation exempting facilities that burn waste in an energy-producing unit from complying with a provision that the facility demonstrate 99.99 percent destruction of the principal organic hazardous constituents in the waste; and generally change existing patterns of used oil disposal. This study estimates that 2.9 billion gallons of oil are sold and that 1.2 billion gallons of used oil are generated annually. Over 50 percent of the 1.2 billion gallons generated is burned as fuel, 30 percent is discharged to land or to sewers, and the remainder is either re-refined to produce a lube oil basestock (~8 percent) or used for road oiling (~6 percent). Although data are limited, it is felt that the sharp increase in the cost of fuel oil in recent years has led to an increase in the amount of used oil burned as a fuel. Regulatory actions, in addition to the cost of fuel oil and other petroleum products, can affect future disposal and recycling patterns as well as drastically alter the practices of used oil recyclers by requiring more advanced treatments to meet specifications for use, or at a minimum, demonstration through chemical analysis that potentially harmful contaminants are not present at specified levels.

CHARACTERIZATION OF USED OIL

Samples of 24 used oils obtained from collectors, recyclers, and users of waste oil were analyzed to determine physical properties and the concentrations of 29 inorganic elements and numerous specific organic compounds. Although the representative oils were collected and analyzed in two groups, with 14 oils tested in the first group and 10 in the second group, no significant differences were noted between the two series of tests. The results show that lead concentrations average about 1100 μg/g, a factor of over 6 times lower than an average value of 7100 μg/g reported by DOE in a study published in 1977 in which 30 used oils were analyzed. The drop in lead content is attributable to regulated reductions of lead in gasoline during the time interval between the two studies. The results of this study further show that chlorinated organic solvents such as trichloroethylene, tetrachloroethylene and 1,1,1-trichloroethane were present in most samples of used oil at total average concentrations of over 1600 μg/g. Polychlorinated biphenyls (PCBs) were found in 4 of the 24 samples, one at 65 μg/g and the others at 7, 13, and 18 μg/g. Polynuclear aromatics (PNAs) were present in all samples. However, PNAs such as benzo(a)pyrene and benz(a)anthracene, which are considered hazardous, were generally not present at detection limits of the order of 5 to 10 μg/g. The average values and the range of concentrations of contaminants found in the representative oils are shown in Table 1.

TABLE 1. CONCENTRATIONS OF SELECTED CONTAMINANTS IN THE 24 REPRESENTATIVE OILS AND THE COMPOSITE OIL

Contaminant	Representative oils Concentration (μg/g) Average	 Range	COMPOSITE oil Concentration (μg/g)
Elements			
Aluminum	45	1 - 640	31
Arsenic	12	<1 - 100	8
Barium	66	10 - 160	61
Cadmium	1	<1 - 2.8	1
Chlorine	2260[a]	50 - 27,000	2,600
Chromium	6	<1 - 37	8
Iron	240	60 - 980	210
Lead	1100	350 - 2060	1,100
Magnesium	260	5 - 590	210
Vanadium	3	<1 - 13	4
Zinc	800	90 - 1550	730
Volatile Organics			
Trichlorotrifluoroethanes	410	<20 - 1900	110
1,1,1-trichloroethane	700[a]	<20 - 14,800	1,500
Trichloroethylene	600	<20 - 4900	2,000
Tetrachloroethylene	400[a]	<20 - 13,000	670
Toluene	3100	380 - 12,000	2,800
Semivolatile Organics			
Phenol	25	<5 - 70	11
2,4,6-trichlorophenol	<5	<5 - <10	40[b]
N-nitrosodiphenylamine	<5	<5 - <10	116[b]
Benz(a)anthracene	20	<5 - 40	40
Benzo(a)pyrene	<5	<5 - 30	<10
4,4'-DDE	<5	<5 - <10	94[b]
PCBs	<5	<0.1 - 65	34[b]

[a] Average value does not include maximum value shown in range.

[b] Spike contaminants in COMPOSITE.

The reduced concentration of lead in used oil was anticipated because of the drop in consumption of leaded gasoline. However, the frequent presence of chlorinated solvents in used oil and the lower, but still relatively high, frequency of PCB occurrence were not anticipated. This suggests that greater attention to segregation of oil wastes by users and collectors will be necessary to reduce commingling of contaminants and oil. This may be necessary to more readily achieve compliance with proposed regulations. These proposed regulations generally will require lower levels of chlorinated organic compound concentrations than were generally found in this study.

LABORATORY SIMULATIONS

As a result of the analyses of the first set of 14 used oils, 4 of those oils were blended and spiked with four organic compounds of interest to produce a COMPOSITE oil. The spikes added at a level of about 90 µg/g were: (1) 2,4,6-trichlorophenol, (2) N-nitrosodiphenylamine, and (3) the pesticide, 2,2 bis(p-chlorophenyl)-1,1-dichloroethylene (4,4'-DDE). The fourth spike, consisting of polychlorinated biphenyls (PCBs) in a mineral oil, was added to the blended oil at a level of about 40 µg/g. The fate of these spike compounds and of the other contaminants naturally present in the blended COMPOSITE used oil (see Table 1 for concentration data) was followed throughout the laboratory simulations discussed below.

Sewer System Disposal

The results of a recent national survey indicate that only 7 million gallons of the 340 million gallons of oil drained annually from automobiles by people who change their own automotive oil are discarded into sewer systems. However, in at least one location, it has been reported that the petroleum in urban storm sewer runoff resembles used crankcase oil in composition.

The concentrations of hydrocarbons in urban sewer systems have been measured at levels ranging from 1 to 24 mg/l, levels not inconsistent with those obtained by calculation using the value of 7 million gallons of oil discarded annually and rough estimates of nationwide flows in combined and storm sewer systems. Most of the oil (~85 percent) measured in sewer systems is associated with suspended particulate.

Simulation of the sewer disposal scenario involved laboratory determinations of the distribution of the oil (200 g) when mixed with water (200 g) and suspended particulate (20 g), followed by analysis of the water fraction. In agreement with other studies, most (approximately 90 percent) of the used oil constituents were associated with the particulate matter in the water. The water soluble fraction of the COMPOSITE used oil as determined under the conditions used in this study was less than 20 mg/l. Compounds identified were phenol, naphthalene, and toluene. None of the higher molecular weight PNA compounds present in the COMPOSITE were found in the water phase at concentrations above the detection limit of about 0.01 mg/l. Only two elements, iron (2 mg/l) and magnesium (1.6 mg/l), were detected at levels exceeding 1 mg/l.

Because the concentration of phenol (11 mg/l) exceeds the value of 5 µg/l suggested by EPA as a concentration goal for waste stream discharge, sewer disposal may be potentially hazardous despite the high level of dilution ($\sim 10^6$) one would expect, given reported flow rates within sewer systems.

Road Oiling

The most recent study of the use of waste oil as a dust suppressant for dirt roads estimates that 50 to 80 million gallons are used annually for this purpose. This represents roughly 5 percent of the total used oil generated in the United States. According to the study, road oiling is banned in 8 states and formally regulated in 13 other states.

The laboratory simulation study involved examining the fate of specific contaminants in the COMPOSITE oil following application to a simulated roadbed and exposure to outside weather conditions over a 30-day period. Soil taken from a dirt road was used to construct the roadbed which was then oiled at a suggested level of 0.05 gallon/ft^2.

Rainfall runoff from the bed was collected and analyzed for inorganic elements and organic compounds. Soil samples from various bed depths were also taken and analyzed to determine oil concentration as a function of bed depth. Almost all of the oil left in the soil was retained within a few millimeters of the surface. The oil concentration measured at the surface was 35,000 µg/g; the concentration fell to a value of about 1,000 µg/g at a depth of 1 cm. Below a depth of 1 cm, the organic content of the soil was indistinguishable from the background level of the untreated soil (~100 µg/g).

The used oil constituents in the runoff (~3 percent of the oil applied) were associated primarily with soil that was entrained and carried from the roadbed surface to the collection vessel. The water-soluble fraction, measured at a concentration of about 5 mg/liter, represented only about 1 percent of the oil lost by runoff.

The water-soluble compounds found are similar to those found in the sewer disposal partitioning study and were largely phenols. Volatile compounds such as the chlorinated hydrocarbons were present only in trace amounts. The transfer of inorganic elements from the oil to the rainfall runoff was also low. Although certain elements such as sodium and aluminum were measured at concentrations that could have been the result of transfer from oil to water, it is also possible that these elements could have been present in the rainfall or extracted from soil constituents in the roadbed.

Combustion of Waste Oil in a Commercial Combustion System and in Small Space Heaters

Samples of flue gas were collected and analyzed during combustion of used crankcase oil in a commercial unit (operating at 6×10^6 Btu/hr) and in separate tests during combustion of the same crankcase oil and the COMPOSITE oil in two space heating units (250,000 Btu/hr). One of the space heating units used an air atomizing burner, the other used a vaporizing pot burner.

The results of the commercial system tests were consistent with results conducted at the same unit by the owners of the system. However, several elements, particularly lead, were emitted at levels in excess of those considered potentially hazardous. Ambient concentration levels have been monitored by the facility operators, and atmospheric dispersion is apparently sufficient to reduce ground level ambient lead concentrations to acceptable levels.

Consistent with the results of a similar EPA study, several elements were emitted from the air-atomizing unit at levels indicating potential hazard. The trace element emissions from the vaporizing unit were more than an order of magnitude lower than those emitted from the air-atomizing unit. While trace element emissions from the vaporizing unit were below levels considered hazardous, high and potentially hazardous levels of organic compound emissions, including emissions of benzo(a)pyrene, were detected in one test on this unit. This result was similar to that reported by EPA, who also noted that high PNA concentrations were found in the pot residue.

Reprocessing to Produce a Specification Fuel

Several treatment methods (i.e., settling, filtration, centrifugation, clay contacting, and the vacuum distillation of the oil to remove water and light organics) were also studied in the laboratory. Centrifugation was the most effective of the first three methods, with approximately 25 percent of the trace elements removed by centrifugation. The water phase from the vacuum distillation simulation was low in trace element content but did contain organics at the 600 ppm level, a concentration that would require treatment before discharge. The product of the vacuum distillation operation, essentially free of water and volatiles, was used as the base stock for the subsequent re-refining simulations.

Re-Refining Processes

Three different re-refining processes were simulated in the laboratory using the pretreated COMPOSITE oil prepared by vacuum distillation of the COMPOSITE oil to remove water and light ends. Processes studied were solvent treatment/distillation using hydrofinishing or clay finishing as the final process step; distillation/hydrofinishing; and acid/clay. Hydrofinishing was conducted by Hydrocarbon Research Inc. at their pilot plant facility in Trenton, NJ.

All processes yielded products that were appreciably lighter in color than the feedstock and were essentially odor free. Material balances were obtained for all contaminants for all process streams, with moderate success in the case of the elements and with less success for the organic compounds.

A few observations of interest were made during the conduct of this phase of the program. First, processes using distillation yield products that are essentially free of trace elements; second, hydrofinishing is an effective means of removing chlorine from the final product, including that associated with PCBs; third, most PNAs are not eliminated from the main process stream and are contained in the final products; and fourth, PNA formation can occur during distillation under conditions which lead to coking of the oil.

SAMPLING AND ANALYSIS OF COMMERCIAL RE-REFINERIES

Field sampling programs were conducted at two operating facilities, the PROP facility in Garner, North Carolina and an East Coast commercial re-refinery. Collected samples were returned to GCA's laboratory in Bedford, MA for analysis. Both processes produce lubricating oil feedstocks that are essentially free of trace element contamination. However, as with the other re-refining processes studied in the laboratory, PNAs are retained with the product oil. A tendency for PNA concentrations to increase during distillation, as previously noted for the laboratory simulations, was also observed in the data for the East Coast facility.

COMPUTER SIMULATIONS

Computer simulations of oil re-refining operations were used to aid in the determination of the fate of organic contaminants in waste oil for the commercial facility in New York and for the processes studied in the laboratory. The simulations were carried out using the PROCESS® program developed by Simulation Sciences Inc., Fullerton, California. The process allows simulation of most chemical reactions and separation processes for which the degree of completion is determined by thermodynamic equilibrium. Thus, it was possible to simulate the flash drums, evaporators, distillation columns, and condensers in the processes but not the clay treatment and pretreatment steps such as the demetalizing operations.

The results of the computer simulations were compared with the laboratory and field sampling and analysis data. With the exception of a few anomalies, the distributions of the organic compounds among the process and waste streams as determined by the computer programs were in good agreement with the analytical data, given the uncertainties in the accuracy of the analyses and in defining process variables. This means relevant interpolation of the data generated in the experiments is possible so as to fit other process conditions.

HAZARD ASSESSMENT OF DISPOSAL AND RECYCLING SCENARIOS

A matrix table was prepared, which presents a numerical estimate of the potential hazard of each major process and waste stream associated with the disposal and recycling of used oil. This numerical estimate, termed a weighted discharge severity factor, was based on estimates of the potential hazard associated with each contaminant and the stream flow rate. The hazards associated with key contaminants, as determined by the ratio of the contaminant concentration in the stream to that generally considered to represent a hazard based on either health or ecology, are first summed to obtain an overall hazard factor for the stream. The weighted discharge severity is defined as the product of the overall stream hazard factors times the flow rate of the stream.

The results of the analysis are summarized in Table 2 for discharges to air, water, and land. As indicated in the table, the relative ranking of the stream discharges to water and land is extremely sensitive to the contaminants used to determine the stream hazard factor and their concentrations. Small changes in the concentrations of extremely hazardous pollutants such as PCBs (and lead and carcinogens such as certain PNAs) can drastically affect the stream discharge severity. The hazard potential of these contaminants, as derived from toxicity data, can be as much as seven orders of magnitude greater than that estimated for many of the other common contaminants. Despite its shortcomings, the rating system uses a standard methodology to achieve a ranking of potential hazard and provides a baseline for assessment of hazardous waste streams resulting from used oil disposal and recycling.

CONCLUSIONS AND RECOMMENDATIONS

The major objectives of this study were, first; to establish the identity and range of concentrations of contaminants in used oils and, second; to determine the fate and potential impact of these pollutants during disposal and recycling. Conclusions and recommendations relevant to the above objectives are presented below.

Conclusions

Several conclusions regarding specific pollutants in used oil and their disposition during disposal and recycling can be drawn from the results of this study. These conclusions are presented below.

- Used oil contains a myriad of pollutants at the part per million level, including a number of EPA priority and RCRA pollutants.

- Organochlorine solvents are frequent contaminants in waste oils. All but 2 of the 24 representative oils tested contained one or more of these compounds. The absence of these materials in virgin oils suggests that these contaminants are introduced during collection and storage. The chlorinated aliphatics, such as trichloroethylene and tetrachloroethylene for instance, are degreasing agents commonly used for cleaning machinery and engine parts.

- Lead contents of used oil decreased almost tenfold over the past 10 years, as shown by a comparison of the average value measured in this study with those determined in earlier studies.

- The barium content of used oil has also decreased in recent years. An average value of about 60 μg/g was found in this study compared to an average of about 300 μg/g found by DOE in a study of 30 used oils published in 1977. Only one oil in the DOE study had a barium content less than this study's average.

- Some PNAs, such as pyrene, benzo(a)pyrene (BaP), and benz(a)anthracene, are present in used oil at μg/g (ppm) levels. While it is generally agreed that the concentrations of PNAs naturally present in virgin

TABLE 2. RELATIVE RANKING OF WASTE STREAMS BY WEIGHTED DISCHARGE SEVERITIES

Waste stream	Ranking with 11 pollutants		Ranking with 10 pollutants (minus PCBs)	
	Ranking	Weighted discharge severity	Ranking	Weighted discharge severity
Air				
Vaporizing unit	1	1500×10^9	1	1500×10^9
Atomizing unit	2	750×10^9	2	750×10^9
Commercial facility	3	300×10^9	3	300×10^9
Water				
Sewer disposal	1	45×10^9	2	5×10^9
Sedimentation - water discharge	2	18×10^9	1	18×10^9
Dehydration - water phase	3	0.2×10^9	3	0.2×10^9
Land				
Acid clay process - clay sludge	1	1050×10^6	11	$<15 \times 10^6$
Physical treatment - clay contacting	2	400×10^6	6	$<100 \times 10^6$
Road oiling	3	120×10^6	7	$<60 \times 10^6$
PROP process - clay sludge	4	86×10^6	5	6×10^6
Solvent treatment process - solvent sludge	5	85×10^6	4	10×10^6
Physical treatment - filtration	6	80×10^6	1	40×10^6
Solvent treatment process - clay sludge	7	72×10^6	3	12×10^6
Acid/clay process - acid sludge	8	40×10^6	8/9/10	$<20 \times 10^6$
PROP process - DAP sludge	9	33×10^6	2	22×10^6
Commercial process - clay sludge	10	$<48 \times 10^6$	13	$<6 \times 10^6$
Distillation/hydrofinishing process - distillate residue	11/12	$<20 \times 10^6$	8/9/10	$<20 \times 10^6$
Solvent treatment process - distillate residue	11/12	$<20 \times 10^6$	8/9/10	$<20 \times 10^6$
Commercial process - distillate residue	13	$<13 \times 10^6$	12	$<13 \times 10^6$

lubricating oils (at a reported level of 0.03 to 0.28 μg/g), are increased as a result of use, the available data base is limited, and it was not demonstrated in this study that an increase in PNA content does result from use. PNA concentrations in used oil are comparable to those found in fuel oils.

- The data here establish that PCBs are not normally found in used oils. However, their measured presence, at levels ranging from 7 to 65 μg/l in 4 of the 24 representative oils tested, suggests that deliberate contamination of used oils does occur.

- The results of the analyses of the representative oils indicate that, of the contaminants normally found in waste oil and identified in this study, B(a)P and lead are the most significant from a health standpoint. Other PNAs may be significant, and metals such as aluminum and zinc are of concern because of ecological effects.

- Physical treatments to produce a specification fuel do not appreciably reduce the elemental content (maximum reduction achievable in the study was 35 percent) nor are they effective in eliminating PCBs and PNAs from the product oil. Volatile organics, including the chlorinated organic compounds which are common contaminants in waste oil, are removed during distillation as normally conducted to eliminate water and light organic fractions.

- The effectiveness of clay contacting as a means of significantly reducing the concentrations of specific organic compounds, such as the PNAs and PCBs identified in this study, was not demonstrated in laboratory simulations.

- Catalytic hydrofinishing appears to be the most effective means of PCB destruction if those compounds are present in the used oil feedstock prior to re-refining operations. The PCBs, if not destroyed by hydrofinishing, tend to remain with the lube oil fraction during re-refining.

- Re-refining processes can produce a product similar in most respects to virgin lube oils. A possible distinguishing chemical feature is the increased concentration of PNAs such as benz(a)anthracene and benzo(a)pyrene in the used oil. These contaminants are largely contained within the lube oil fraction during re-refining and, as observed in this study, may possibly be created under certain conditions during high temperature distillation operations.

- Computer simulations of certain re-refining operations such as dehydration and vacuum distillation can be used to predict the fate of certain compounds, provided their thermodynamic properties are known and chemical modifications do not occur.

Recommendations

The following recommendations are intended to identify suggested areas of activity not undertaken or successfully resolved in this study. They identify both data gaps and shortcomings in existing analytical protocols for characterizing waste oils.

- A methods development program should be undertaken to improve the recoveries and detection limits of the analytical procedure for semivolatile organics in oils. Fractionation procedures should be emphasized. This is a major undertaking that will be feasible only if a predefined list of components of interest can be established.
- Better resolution of the differences in the contaminant levels of virgin and waste oils is needed, particularly for organic constituents such as chlorinated hydrocarbons and PNAs. A sampling and analysis program that utilizes direct collection from generators is recommended as a means of avoiding uncertainties associated with possible contamination during collection and storage of used oils.
- The additive package and the physical/chemical states of its components need better definition. Although changes in the elemental content of the additive package over time can be inferred from the results of this study, little can be said about the nature of the additives and their breakdown products for both elemental and organic constituents.
- Analytical activities are needed to confirm or deny the presence of contaminants such as nitrosoamines and chromium VI in waste oil. Work will be required, at least in the case of chromium VI, to develop analytical methods.
- There is a definite requirement for the development of a simple analytical technique for chlorine content determination, preferably one that can be applied in the field.

The following recommendations for future activities are presented as a means of more effectively assessing the fate of contaminants in used oils and their environmental impacts during recycling. They supplement those recommendations discussed above which are largely directed at developing techniques for better characterizing the physical and chemical form of known (and suspected) contaminants of significance.

- Partitioning coefficients of contaminants between aqueous and organic fractions should be developed. As noted previously, the laboratory simulations conducted in this study showed only a limited degree of water solubility of major hazardous contaminants found in waste oil. This finding was in contrast to some literature sources which reported appreciably higher contaminant levels (at least of metal contaminants) resulting from the commingling of water and oil.

- The fate of contaminants in used oils applied to road surfaces is not well defined. It is recommended that additional laboratory simulation studies be devised and conducted under carefully defined conditions with well characterized soils, rainfall, and oils to study pollutant transport, particularly that attributable to solubility. Experiments using artificially generated rainfall in a contaminant free environment or percolation type studies should be considered, possibly using traceable amounts of known contaminants similar to those found in used oil.

- Although EPA has undertaken several programs to establish the fate of wastes or contaminants burned in small combustion systems, the results of the combustion activities undertaken in this program, particularly with the vaporizing space heater, indicate that further attention should be given to this class of combustion unit. The question of whether or not vaporizing units are significant sources of PNA emissions should be resolved for the benefit of both manufacturers and users of such equipment. The fate of chlorine during combustion is another area of uncertainty requiring further study.

- Because the effectiveness of clay contacting was not demonstrated in this study, there is a need for additional data concerning the effectiveness of clay contacting over the range of conditions practiced industrially. The removal of key organic species of interest, including those present as additives, could be determined in a series of parametric experiments.

- Questions have been raised in this program with regard to PNA formation during distillation. A number of experimental routes, including systematic checks of existing units or further laboratory or pilot studies under controlled conditions, should be considered to determine the cause, frequency, and extent of such chemical transformations.

SECTION I

INTRODUCTION

The presence of hazardous materials in used oil is a problem of growing concern. Many contaminants found in used oil are present as a natural result of use, while others are introduced, either accidentally or deliberately, during collection and storage. There is very little definitive information concerning the fate of contaminants when the oil is discarded, burned, or recycled. This program, sponsored by the U.S. Department of Energy, Office of Industrial Programs, was undertaken to develop some of this information; thus providing a data base to be used in assessing the potential hazards associated with used oil disposal and recycling options.

OBJECTIVES

The primary objective of this program was to identify the hazardous and nonhazardous compounds that might reasonably be found in used oil and to establish, by experimentation if possible, their fate under a variety of disposal and recycling scenarios. Scenarios considered were sewer disposal, road oiling, combustion as a fuel, reprocessing by physical methods to produce a specification fuel, and various re-refining processes. A secondary objective was to assess the potential environmental impact of the contaminants in the waste and product streams associated with each scenario. Other objectives were to identify the routes of introduction of hazardous contaminants into waste oil, evaluate the singular and interactive effects of these materials on the recycling scenarios, evaluate methods/needs for detecting potentially harmful contaminants, and determine the degree of removal of the hazardous constituents in waste oil for all recycling scenarios.

APPROACH

The hazardous and nonhazardous compounds of major interest in waste oil were identified by literature review, interviews with participants in waste oil activities, and by laboratory analysis of 24 samples of waste oils obtained from recyclers and users.

The oils were analyzed for standard bulk physical properties and for specific elemental and organic compound constituents by techniques representing both standardized and state-of-the-art methods under study by EPA, NBS, and others for determination of priority and other pollutants in multimedia samples. Liquid chromatography fractionation was required for all oil samples prior to organic analysis to reduce background resulting from the presence of the multitude of compounds found in waste oil.*

Elemental analyses were conducted by Inductively Coupled Argon Plasma Emission Spectroscopy (ICAP) for 27 elements, with chlorine and sulfur determined in addition by other procedures. Because of the frequent occurrence of chlorinated solvents in waste oil, emphasis was placed on identifying the chlorinated constituents (organic and inorganic) contributing to the total chlorine content of the oil. Although good closure of the chlorine balance was achieved, the methods used for chlorine analysis require appreciable investment in laboratory equipment and instrumentation. A review of spot test methods currently being used for chlorine contaminant identification was undertaken, but all were deemed inadequate for oils with chlorine contents less than 0.5 percent.

The results of the analysis of the representative oils combined with the results of previous studies were used to establish a listing of hazardous and nonhazardous compounds in waste oil. The compounds were prioritized according to their concentrations in the oil and their health impacts, as determined by threshold limit values, drinking water standards, or other measures of multimedia health impacts.

The prioritized listing formed the basis for the preparation of the COMPOSITE oil used in the experimental simulation studies of the waste oil recycling scenarios. Although polychlorinated biphenyls (PCBs) are not naturally present in significant quantities in waste lubricating oils, they and other compounds representing organic species of potential interest, such as nitrosamines and chlorinated organics, were deliberately added at 40 to 100 ppm levels to this COMPOSITE waste oil to enhance detectability at various points along each scenario.

The disposal and recycling scenarios studied experimentally are shown in Figure I-1. In addition to laboratory simulation studies, field programs were conducted at three facilities to collect samples of process and waste streams for laboratory analysis. The facilities sampled were a commercial boiler burning waste crankcase oil, the North Carolina re-refining plant which uses the Phillips Re-refined Oil Process (PROP) to produce a lubricating oil base stock from waste crankcase oil, and a commercial re-refining facility which uses a wiped-film distillation process to produce a lubricating oil base stock from used automotive and industrial oils.

The experimental simulation studies were designed to establish the fate, through material balance if possible, of specific contaminants under

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*The American Petroleum Institute's Project 6 and Project 60 studies of the constituents in crude oil have demonstrated that the number of individual compounds in crude oils is in the hundreds of thousands, probably approaching a million discrete compounds. Results of these studies have been summarized in References 1 and 2.

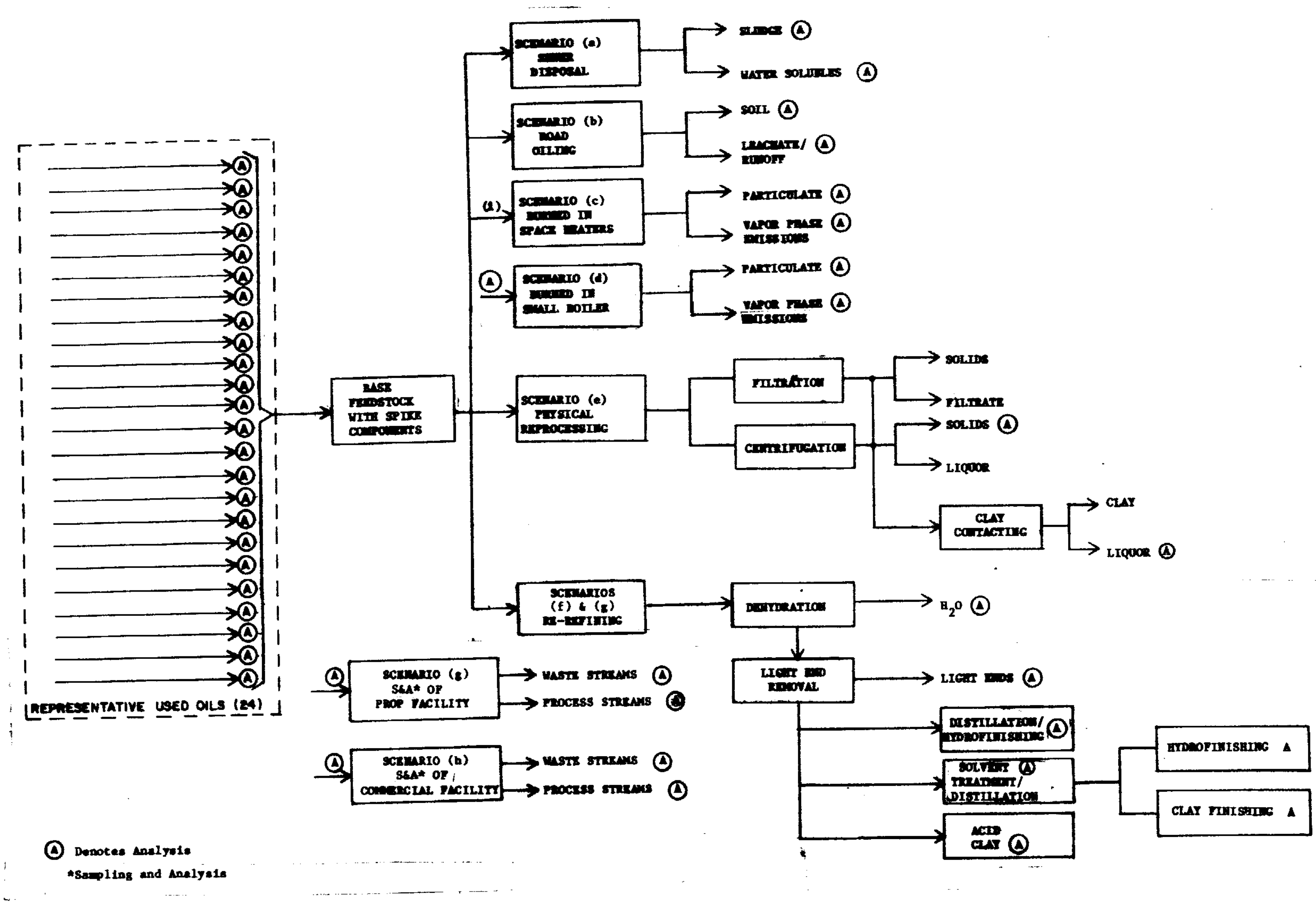

Figure I-1. Experimental simulations of used oil disposal and recycling.

conditions that were representative of those normally encountered in each disposal and recycling scenario. They provide, generally for the first time, a real measure of the transport of specific compounds within each scenario studied. Unfortunately, because of the complexity of the oil matrix and other factors affecting the accuracy of the analysis, the detection limits for organic compounds were generally in the ppm range. Thus, because most organic compounds detected in waste oil were present at concentration levels generally of the order of 100 ppm or less, it was not possible in most cases to demonstrate contaminant removal efficiencies at levels greater than 90 to 99 percent.

In addition to the laboratory simulation and field sampling studies, computer simulations were conducted to assess the physical transport of specific compounds during typical re-refining operations such as dehydration, light end removal, and vacuum distillation. Correlation of the computer-generated results with the results of the laboratory analyses of samples collected from an operating re-refinery was also attempted with some success. These computer programs, of varying complexity to match the degree of process refinement, could be of value in addressing re-refining design and operating procedures, as well as evaluating scenarios somewhat different than the experiments presented here.

REFERENCES

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SECTION II

POLLUTANTS IN USED OIL

As a prerequisite to determining the fate of contaminants in waste oil during the recycling scenarios, it was necessary to establish the nature of the contaminants normally present or frequently found in waste oils. The approach to identifying the contaminants and their concentrations was a two-fold, phased approach. First, a review of the existing data base was conducted to assess the available information concerning contaminants in used oil. Secondly, a number of samples of used oil were obtained from collectors of waste oil throughout the country and analyzed for the physical and chemical parameters of interest (generally as indicated by the assessment of the existing data base).

Although the data base concerning the physical characteristics and the trace element contents of waste oils exhibits variability due to a number of factors, including inherent differences in waste oils, commingling and contamination during collection and storage, differences in additive packages, and regulations reducing the lead content of gasoline, the parameters of interest are reasonably well defined. Such is not the case with the organic contaminants in waste oil. The general deficiency of the organic contaminant data base reflects both the tremendous potential for contamination of oil with a myriad of specific organic compounds due to the mixing of wastes during storage and collection, and the analytical difficulties associated with identifying a specific organic contaminant contained in a multicomponent organic matrix.

Due to the lack of organic compound contaminant data, the analyses of the "representative" waste oils, in addition to focusing on those organics identified in the existing data base as common contaminants (e.g., chlorinated hydrocarbons and polynuclear aromatics (PNAs)), emphasized a search for the EPA "priority pollutants." Although time and resources did not allow quantitative analysis for all 129 priority pollutants, the analytical phase of this task involved screening of the representative oils (and the appropriate process and waste streams analyzed during the studies of the recycling scenarios) for a large number of these pollutants. These included all of the 31 volatile organic compounds, a selected 18 of the 57 extractable compounds (semivolatile organics), 25 of the 26 pesticides and PCBs, and 12 of the 13 elements (mercury excluded) comprising the priority pollutant list. In addition to the determination of 15 additional elements by ICAP analysis, screening was conducted for several other volatile organics such as trichlorotrifluorohydrocarbons, dibrominated ethanes and ethenes, and alkylated benzenes, cyclopentanes, and cyclohexanes. Analyses were also conducted for chlorine, sulfur, and 1,2-glycols. Analytical test methods (other than ASTM methods) are described in Appendix B.

The existing data base in conjunction with health effects data provided the basis for a preliminary prioritization of the contaminants in waste oil. This prioritization, as will be discussed in subsequent sections, was reassessed on the basis of new data developed from the analysis of the representative oils and from other ongoing studies to establish the final priority listing.

EXISTING WASTE OIL CHARACTERIZATION DATA

Sources of Existing Waste Oil Characterization Data

Physical characterization and inorganic element data for waste oils have been obtained by DOE,[1-4] EPA,[5,6] NBS,[7,8] State Agencies,[9,10] and the American Petroleum Institute.[11] Other sources of information include the petroleum refineries and re-refineries, although much of their information remains unpublished. Data relating to the organic characterization of waste oils are much more limited. However, some information is available for organic categories and specific organic compounds.[3-7,9] Recent data for PCBs, halogens, sulfur, volatile organic compounds, and heavy metals in 31 virgin fuel oils and 42 waste oils were recently reported by a study group sponsored by the New York Environmental Protection Agency.[12]. In addition to unpublished and, therefore, not readily available data, there are several ongoing EPA and state sponsored programs which are concerned with measurement of specific organic compounds in waste oil. Analytical methods development and the determination of the fate of organics during combustion and road oiling are the major subjects of concern to EPA.[13] Similar concerns have been expressed by State Environmental Protection Agencies in States such as Maine, Massachusetts, New Jersey, and New York (and by most other state agencies) with emphasis being placed on analytical techniques to identify contaminants and regulate recycling.

Lubricating Oils

As a first step in understanding the nature and origin of contaminants in used oil, it is important that the composition of lubricating oil basestocks and the additive packages be understood. Unfortunately, the identity of specific organic components and their concentrations are not readily discerned from the open literature. Analytical difficulties can be appreciated if it is recognized that crude oils contain several hundreds of thousands of organic compounds.[14,15] Typically, the hydrocarbons found fall in the categories of: straight-chain paraffinic compounds (n-paraffins); branched-chain paraffinic compounds; aromatics, both mononuclear and polynuclear (unsaturated ring structures); polycyclic and fused-ring saturated hydrocarbons based on cyclopentane and cyclohexane, known collectively as the naphthenes; and mixed compounds. A smaller fraction of lubricating oil basestock consists of compounds containing nitrogen, sulfur, and oxygen which are generally more chemically active than are the hydrocarbon-basestock constituents. Compounds defined in the priority pollutant listing as volatile should not be present in significant quantities in lubricating oil basestocks. However, many of the semivolatile components, including PNA compounds, are generally present. A more complete discussion of the composition and properties of lubricating oils may be found elsewhere in the literature.[1,5,16-18]

Modern automotive lubricating (crankcase) oils and industrial oils contain additive packages which may comprise 15 percent or more of the oil by volume.[2] The additives, which augment the natural properties of the oil basestock, may include nitrogen-containing dispersants, metal-containing detergents, rust and corrosion inhibitors, anti-wear additives, and oxidation inhibitors. Table II-1 lists the many functions these additives perform and the types of chemical compounds that are used. Generally, these additives contain highly polar and functionalized molecules which significantly increase the performance and life of both oil and equipment. However, their introduction into crankcase oils makes re-refining, or oil disposal in general, much more difficult. Such elements as Ba, Ca, Mg, Zn, Na, S, N, and P which are found in used crankcase oils often come primarily from the additive package.

Industrial Oils

Industrial oils may be divided into two large categories; lubricating oils, including metalworking oils, and nonlubricating oils such as hydraulic, transformer, turbine, and quenching oils. It is difficult to generalize and identify a set of contaminants of concern in these oils. Industrial oils, unlike automotive lubricating oils, perform a wide variety of functions. Contaminants found in these oils vary with each function (e.g., metals found in metalworking oils depend on the type and composition of the metal being machined, etc.). The additive package also varies for industrial oils and some additive packages are custom-blended depending on the particular function of the oil. In addition, data on the contaminants found in these oils are scarce, although some contaminants have been identified. EPA[5] has identified some compounds of potential concern in used industrial oils. These include barium, other metals, PCBs, and nitrosamines.

Industrial oils have been recommended for listing as hazardous wastes[5]. However, used industrial oil will be listed as a hazardous waste based mainly on its aromatic oil component (basestock) since EPA deems it inappropriate to generalize that all industrial oils will eventually become contaminated with hazardous substances found in certain types of used oils. Until more data are available, it may be assumed that contaminants in industrial oils derived from the oil's petroleum (aromatic) basestock will be similar to those for automotive oils and the priority listing developed in this section may be assumed to apply to industrial oils as well as automotive oils.

Used Oils

During service, the constituents present in crankcase oils can undergo physical and chemical changes and the oil itself becomes contaminated from both internal and external sources. Used crankcase oils contain a broad

TABLE II-1. TYPICAL LUBRICATING OIL ADDITIVES[a]

Type	Typical compounds	Reason for use
Detergents, Dispersants	Succinimides, neutral metallic (Ba, Mg) sulfonates, phenates, phosphates, polymeric detergents, amine compounds.	Keep sludge, carbon, and other deposit precursors suspended in the oil.
Oxidation inhibitors	Zinc dialkyl dithiophosphates. Compounds of nitrogen and sulfur. Hindered phenols. Bis-phenols. Aromatic amines.	Prevent or control oxidation of oil, formation of varnish, sludge, and corrosive compounds. Limit viscosity increase.
Alkaline compounds	Overbased metallic sulfonates and phenates.	Neutralize acids, prevent corrosion from acid attack.
Extreme Pressure (EP) antiwear, friction modifiers	Zinc dialkyl dithiophosphates. Tricresyl phosphates. Organic phosphates. Chlorine compounds. Lead compounds and amines.	Form protective film on engine parts. Reduce wear; prevent galling and seizing.
Rust inhibitors	High base additives, sulfonates, phosphates, organic acids, esters, amines, or fatty acids.	Prevent rust on metal surfaces by forming protective surface film or neutralizing acids.
Metal deactivators	Zinc dialkyl dithiophosphates, phenates, organic nitrogen compounds.	Form film so that metal surfaces do not catalyze oil oxidation.
Viscosity index improvers	Polyisobutylene, methacrylate, acrylate polymers. May incorporate detergent groups.	Reduce the rate of viscosity change with temperature; reduce fuel consumption. Maintain low oil consumption. Allow easy cold starting.
Pour point depressants	Methacrylate polymers.	Lower "freezing" point of oils, assuring free flow at low temperatures.
Antifoamants	Silicone polymers	Reduce foam in crankcase and blending.

[a]Source: Adapted from Automotive Engine Oils - what they are and how they work. Chevron Research Bulletin (1975) cited in Mascetti and White (1978).[2]

variety of contaminants, several classes of which are potentially hazardous to human health or environmental quality. Some of these substances are already present in refined petroleum; others are formed during oil use. Used oils have been recommended for listing as hazardous wastes by the U.S. Environmental Protection Agency.[5] Among the types of contaminants reported to be present in used oils are PNAs, nitrosamines, chlorinated hydrocarbons, and various trace metals and other substances, such as chlorine. These contaminants result from chemical action among oil constituents (e.g., oxidation and halogenation), or breakdown of the additive package. Physical contamination of crankcase oil includes introduction of soot and lead compounds from engine blow-by, dirt and atmospheric dust, engine wear metal particles, rust, gasoline from incomplete combustion, coolant from imperfect engine seals, or water from blow-by vapors.[2]

A comprehensive study characterizing the composition of used crankcase oils was the work of Cotton et al.[1] at the DOE-Bartlesville Energy Technology Center (BETC). Thirty waste oil samples were collected from 20 states. These samples were analyzed by standard physical and chemical tests to characterize contaminant levels. Chromatographic and mass spectral techniques were used to provide qualitative or semiquantitative data relative to organic compound structure and distribution.

The results of the BETC study by Cotton et al.[1] reveal that comparison of physical and chemical properties of the 30 used crankcase oils analyzed shows few significant variations on either a seasonal or geographical basis. The results were generally similar to those found in the API study of the geographical and seasonal variability of waste oils.[11] Levels of inorganic contaminants did vary somewhat among the 30 samples. The average concentrations for lead, zinc, and barium were 7100, 1050, and 290 ppm, respectively. Barium, calcium, magnesium, sodium, phosphorus, and zinc are commonly associated with the additive package. The wear and contaminant metals include aluminum, chromium, copper, iron, potassium, manganese, lead, silicon, and tin. Data in Table II-2 reveal that the metallic contaminant in greatest concentration is lead. Lead accumulates in the automotive crankcase as the oil becomes contaminated with leaded gasoline and combustion products. Lead content in some samples reached almost 14,000 ppm. These results agree with previous analyses conducted by the same research group.[18] The wear metal in the largest concentration was iron; one sample contained 655 ppm Fe.

The data for lead shown in Table II-2 are outdated and do not reflect the marked reduction in the production and use of leaded gasolines. According to statistics compiled by the Bureau of the Census, production of leaded gasoline for domestic use fell from 79 percent of the total produced (on the average) in 1976, to 60 percent in 1979, and this trend continues. In 1970, the gasoline pool contained approximately 2.4 grams of lead per gallon; approximately 1.6 grams of lead per gallon was reported for 1975; and about 0.8 grams per gallon in 1978 to 1979. A maximum value of 0.5 grams of lead per gallon of gasoline produced (approximately 150 ppm) became effective October 1, 1979. The maximum allowable lead content in gasoline is expected to be even lower by 1985.

TABLE II-2. METALS AND PHOSPHOROUS CONTENT OF 30 USED AUTOMOTIVE LUBRICATING OILS[a]

Sample No.	Element (ppm)															
	Ba	Ca	Mg	Na	P[a]	Zn	Al	Cr	Cu	Fe	K	Mn	Ni	Pb[b]	Si	Sn	V
1465	180	1775	311	64	1080	1201	12	9	33	137	31	3	1	4,720	<15	6	0
1466	693	1480	325	42	1118	1267	27	22	33	306	13	4	1	13,885	<15	7	0
1467	286	1245	236	142	889	1000	15	12	27	200	34	3	1	7,070	<15	2	0
1468	175	1393	323	41	1006	952	12	14	27	162	33	8	1	5,225	<15	2	0
1469	131	1260	138	55	740	629	41	7	17	164	9	8	1	3,730	<15	5	0
1470	148	1308	384	132	1012	1239	13	10	26	222	26	6	1	8,460	<15	6	0
1471	229	1315	236	207	782	1023	10	10	39	151	72	3	2	5,860	<15	3	0
1473	176	1675	425	54	1138	1316	15	12	20	249	20	3	1	10,560	19	4	0
1474	204	1295	312	79	1074	1151	15	12	31	212	16	3	1	8,450	<15	3	0
1476	124	1413	599	8	895	1169	12	21	6	170	5	2	1	11,575	<15	3	0
1477	430	1401	225	115	871	990	13	7	22	119	41	3	0	6,495	43	NA[c]	0
1478	485	1317	165	72	672	668	14	8	43	203	79	4	0	7,595	25	NA	0
1479	428	1072	259	95	815	780	13	5	41	150	24	2	0	6,560	39	NA	0
1480	260	1431	227	660	764	860	10	7	41	129	20	8	0	4,890	38	NA	0
1481	203	1358	458	102	1015	1233	12	8	38	212	33	3	0	10,410	36	NA	0
1482	144	1267	261	89	708	910	7	6	37	116	25	2	0	4,165	27	NA	0

(continued)

TABLE II-2 (continued)

Sample No.	Element (ppm) Ba	Ca	Mg	Na	P[a]	Zn	Al	Cr	Cu	Fe	K	Mn	Ni	Pb[b]	Si	Sn	V
1483	278	1008	297	357	778	1040	21	24	37	655	83	8	0	8,005	87	NA	0
1484	520	1170	182	100	674	660	11	8	18	179	57	4	2	4,560	37	NA	0
1485	333	1704	209	81	996	1140	13	8	41	173	37	3	2	7,680	32	NA	0
1486	319	1435	375	125	961	980	20	11	31	216	36	4	2	7,570	51	NA	0
1487	185	2225	999	45	1393	2500	17	8	7	153	5	2	4	7,730	25	NA	0
1488	494	1263	286	127	747	933	11	12	37	181	45	3	5	7,825	40	NA	0
1489	200	969	171	150	675	705	14	11	13	178	15	2	4	6,885	8	NA	0
1492	494	3126	220	23	982	1409	19	6	56	171	17	3	<1	6,980	16	6	0
1493	10	3986	8	67	81	80	4	8	13	88	14	1	<1	19	14	0	0
1494	297	1620	520	59	880	1029	13	10	28	192	48	3	<1	4,855	26	4	0
1495	377	983	147	34	1197	1527	6	5	12	102	6	2	<1	1,362	15	3	0
1496	547	1050	233	64	857	725	18	12	27	216	24	4	1	8,655	25	1	0
1497	213	1505	310	169	881	1150	18	10	37	272	37	4	2	9,420	17	8	0
1498	59	2670	338	69	1341	1574	25	14	16	342	29	4	1	11,165	14	14	0
Avg.	287	1557	306	114	901	1053	15	10.6	28	201	31	3.7	1.1	7,079	24	4.5	0
Std. Dev.	162	657	177	123	243	377	3.9	4.7	12	103	21	1.9	1.3	2,938	17	3.3	0

[a] Analytical method used was ASTM D1091-64; all other values by atomic absorption.

[b] Lead data not representative of present levels.

[c] Not analyzed (NA).

Source: Cotton et al.[1]

As noted, the composition of the petroleum-based materials of these 30 used oil samples was characterized by Cotton et al.[1] by the use of a chromatographic separation procedure which produced saturate, monoaromatic, diaromatic, and polyaromatic fractions. Saturate fractions were analyzed by mass spectral techniques that produced data relative to the naphthene ring structure and abundance of these compounds. Similar analyses of the aromatic fractions gave semiquantitative distributions of compound types. Data presented in this report show that the expected ranges and types of compounds present in all structural categories are quite similar among the 30 samples tested regardless of source or season. That is, the bulk organic composition of waste crankcase oils composited for re-refining or other disposal options can be identified within a narrow range based on the BETC work.

More recent studies such as those conducted by the State of Maine[9] and by Booz, Allen, and Hamilton[4] for DOE have placed greater emphasis on the identification of specific organic contaminants, as well as providing physical characterization and elemental concentration data. These data were helpful in preparing a listing of contaminants of potential concern in waste oil and served as a focus for the development of analytical protocols. Also helpful in arriving at a "hit list" of contaminants for analysis were discussions held with representatives of EPA and the States of Massachusetts, New Jersey, and New York, all of whom were concerned that many foreign substances were apparently finding their way into used oil.

Contaminants of Potential Concern in Waste Crankcase Oils

Data contained in the existing relevant technical literature were used in compiling an initial list of contaminants of potential concern to human health or environmental quality. These contaminants of potential concern are listed on Table II-3. Included in Table II-3 are indications of the source of these contaminants in used oils and their reported concentrations, when available.

Polynuclear aromatic hydrocarbons--

As previously mentioned, polynuclear aromatic hydrocarbons have been shown to be present in the petroleum basestock of lubricating oils. In addition, new PNA compounds are produced during oil use. Peake and Parker[19] estimated that of the PNAs produced by the automobile engine, about 85 percent are retained in the crankcase oil. According to NBS analyses reported by EPA,[5] benzo(a)pyrene levels in used motor oils may be as much as 900 times those found in unused motor oil basestocks (28 versus 0.03 μg/g). Hermann et al.[20] reported an even higher B(a)P level in used oils compared to unused samples: 62,000 versus less than 5 μg/l for crankcase oils and 25,000 versus less than 5 μg/l in new and used steel hardening oils. Total PNA concentrations in the new and used steel hardening oils were 8.3 and 2.6 g/l, respectively. Despite these impressive ratios, B(a)P concentrations in used oil are still in the low ppm region. Moreover, the concentrations of B(a)P in used automotive oil (12 ppm) as determined by NBS[7] were similar to those determined by NBS in No. 6 fuel oil (3 to 34 ppm).

Several PNAs are known mutagens and/or carcinogens in man and animals.[19-23] Hermann et al.[20] concluded from their study that the components responsible for the observed mutagenic activity of used oil are

TABLE II-3. SOME CONTAMINANTS OF POTENTIAL CONCERN IN WASTE CRANKCASE OILS

Organic contaminants	Probable source	Approximate concentration range (µg/l)[a]
Polynuclear aromatic hydrocarbons including:	Petroleum basestock	
benzo(a)pyrene		360-62,000
chrysene		2480
benzo(c)phenanthrene		120
benz(a)anthracene		870-30,000
pyrene		1670-33,000
Monoaromatic hydrocarbons		
alkyl benzenes	Petroleum basestock	900,000
Diaromatic hydrocarbons		
naphthalenes	Petroleum basestock	440,000
alkylnaphthalenes		
alkyl biphenyls		90-740
alkyl benzofurans		minor contaminant
Chlorinated hydrocarbons[b]		
1,2-dichlorobenzene	May be formed chemically during oil use/ contamination of oil by solvents in holding tanks can add appreciably to values provided	60-160
2-chloronapthalene		8.8
2-chlorophenol		24-2200
methylene chloride		2.5-92
chloroform		2-100
di- and trichloroethanes		18-1800
trichloroethylenes		18-2600
tetrachloroethylene		3.3-1300
chlorobenzene		4-500
Nitrosamines	Possibly formed during oil use	No data
Polychlorinated biphenyls (PCBs)[b]	Contamination of oil from outside sources	<1000-9700

(continued)

TABLE II-3 (continued)

Organic contaminants	Probable source	Approximate concentration range (μg/l)[a]
Other priority pollutants[b] including:		
benzene	Contamination of oil from outside sources	18-890
toluene		120-5800
phenol	Present in petroleum basestock/formed during oil use	5100-99,000
phthalates		1-280
nitrophenols		24-550
nitrobenzenes		1100
various pesticides	Contamination of oil from outside sources	minor contaminants
Metals[c]		
barium	Additive package	59-693
calcium		983-3126
magnesium		138-999
zinc		629-2500
aluminum	Engine wear and contamination by soot and dust	4-41
chromium		5-24
copper		6-56
iron		102-665
lead	Contamination from leaded gasoline/lead-containing additives	3730-13,885[d]

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[a] Concentration data are from References 1, 3, 4, 19, and 20.

[b] Concentration data are from re-refining process streams and may not reflect true concentrations in used oil feedstocks. Other data from Reference 9 indicate some waste oils contain appreciably higher levels (approximately 1000X) of chlorinated hydrocarbons; high levels of PCB (approximately 500,000 to 810,000 μg/kg) were also detected in two samples of waste oil.

[c] All concentrations are in mg/kg (ppm).

[d] Higher levels not anticipated now due to Federal regulation of lead in gasoline.

4-, 5-, and 6-ring PNAs. They report that B(a)P was the most important identified individual contributor to this mutagenic activity. Among the known mutagens or carcinogens found in used oil extracted with DMSO by Peake and Parker[19] were benzo(a)pyrene, chrysene, benzo(c)phenanthrene, benz(a)anthracene, cyclopenta(c,d)pyrene, and benzo(g,h,i)perylene. Other potential contributors to the observed mutagenicity were not identified in this study; however, the authors speculated that compounds other than PNAs in the 166 to 302 molecular weight range could be responsible. Possible compound types include: heterocyclic aromatic compounds, higher molecular weight aromatic hydrocarbons, or polar PNA derivatives (e.g., keto, hydroxy, and nitro derivatives). Some of the more important used oil contaminant PNAs are listed in Table II-3.

Chlorinated hydrocarbons--

When the mixtures of hydrocarbons present in the petroleum basestock of automotive lubricating oils are exposed to the significant levels of halogens introduced during automotive use, halogenated hydrocarbons may be formed. A variety of chlorinated hydrocarbons has been detected in byproducts of used oil recycling processes.[4] Some of these substances probably would not be formed during oil use (e.g., methylene chloride and chloroform). These solvents may have been introduced as contaminants during oil recycling or in oil feedstock holding tanks. As noted in Table II-3, the high levels found in the Maine study[9] are representative of concentration levels now being found in Massachusetts and New York.

Polychlorinated biphenyls (PCBs)--

It is unlikely that PCBs would be found in modern used crankcase oils unless these oils were contaminated in holding tanks through addition of other, older oils (e.g., transformer oils, etc.) known to contain these substances. However, because of the recognized adverse health and environmental impacts of PCBs,[5] it is prudent to assume that waste crankcase oils contain PCBs as contaminants. The EPA regulations under the Toxic Substances Control Act imply that all used oils are contaminated with PCBs and PCB contamination was considered in the EPA recommendation to list waste oils as hazardous wastes.[5] Measurable levels of PCBs have been reported in byproducts of used oil recycling processes[4] and by Maine.[9] Moreover, in the recent New York study[12] PCBs were detected in 4 of the 42 waste oil samples analyzed at levels above the detection limit of 3 μg/g. One sample contained over 3000 μg/g of PCBs.

Nitrosamines--

Nitrosamines are formed when secondary amines react chemically with NO_2^-, NO_3^-, or NO_x. Both nitrogen compounds and amines are found in used oils. Since these precursors are present, the formation of nitrosamines in used oil is possible. However, no data were available to quantify the probable levels of nitrosamines in used oil.

Metals--

As noted previously, trace metals of potential concern are present in used oils. These metals are part of the additive package in crankcase oils or are oil contaminants resulting from internal or external sources. Some of these metallic species, and the concentration ranges measured in used oils, are listed in Table II-3. The lead data, as noted earlier, are outdated.

NEW DATA ACQUISITION

The review of the literature and discussions with EPA, State agency, and industrial personnel continued throughout the program. Although waste oil study activity is high and appreciable amounts of data will be forthcoming as these activities mature, this section is concerned solely with data obtained in this program through analyses of 24 samples of waste oil supplied by collectors and recyclers throughout the country. The analytical activity was conducted in two stages. Initially, 14 samples were obtained and analyzed; an additional 10 samples were later tested with the intent of both adding to the data base and resolving apparent problems with the organic data, primarily the volatile chlorinated-organic compound data. The physical and chemical parameters that were selected for analysis following a review of the literature and a preliminary analytical screening of priority pollutants in a few samples of waste oil are shown in Table II-4, II-5, and II-6 for the physical, elemental, and organic parameters, respectively.

As noted earlier, the measurement of physical characteristics and the determination of the concentrations in waste oil of the 27 elements and chlorine and sulfur is relatively straightforward. Accuracy and precision of measurement are generally well within ± 10 percent.

Such is not the case with organic compound measurement. Analysis of the multitude of organic compounds present in waste oil is essentially restricted to those volatile compounds that can be introduced into detection systems. Resolution of individual compounds also requires fractionation (by liquid chromatography) to reduce interferences and improve detection limits. Analytical techniques are available, as demonstrated by the API projects 6 and 60 studies of compounds in petroleum. However, given the time and budgetary constraints of this study and the large number of samples to be analyzed, the analytical procedures (described in Appendix B), involved a tradeoff between analytical simplicity and precision and accuracy (see Appendix C for quality control data).

Major difficulties were encountered initially in dealing with the analysis of the volatile organic priority pollutants. Recoveries, using a modified headspace method, were low, with the result that chlorine balances based on a comparison of the chlorine content of individual chlorinated hydrocarbons in the oil with the total chlorine content (from ion chromatography) were of the order of 10 to 50 percent. The headspace technique was replaced with a new EPA-developed technique involving transfer of volatiles from the oil to a tetraglyme solution before introduction into the detection system. The use of the tetraglyme method appears, within the limitations of compound recoveries as determined by quality control procedures, to have solved the chlorine balance problem. Thus, as will be shown in a following discussion, the sum of the organic chlorine present in specific volatile compounds does approach the total chlorine content as accurately determined by ion chromatography.

TABLE II-4. PHYSICAL PARAMETERS MEASURED[a]

Parameter	ASTM test method
Sulfated ash, %	D874
Ash, %	D482
Water by Dist., %	D95
Water & Sediment, %	D1796
Specific Gravity, API	D287
Flash Point, °F	D93
Pour Point, °F	D90
ASTM Dist., % Initial Boiling Point, °F 10% Recovery at, °F 50% Recovery at, °F	D1160
Viscosity, cSt. @ 100°F	D445
Copper Corrosion	D130
Sulfur, %[b]	D2622

[a] Physical property data reported in this study were determined by E. W. Saybolt & Co., Inc., Kenilworth, N.J.

[b] Also measured by Ion Chromatography (see Appendix B).

TABLE II-5. ELEMENTAL PARAMETERS MEASURED[a]

Element
<u>ICAP Analysis</u>
Aluminum
Antimony
Arsenic
Barium
Beryllium
Boron
Cadmium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Magnesium
Manganese
Molybdenum
Nickel
Selenium
Silicon
Silver
Sodium
Strontium
Thallium
Tin
Titanium
Vanadium
Zinc

[a] Also chlorine by ion chromatography following Parr bomb oxidation and absorption in a sodium carbonate solution (see Appendix B); sulfur by ASTM D2622 and ion chromatography.

TABLE II-6. ORGANIC PARAMETERS MEASURED[a]

Purgeables (volatiles)[b]	Extractables (semivolatiles)	Pesticides/PCBs[c]
chloromethane	phenol	aldrin
dichlorodifluoromethane	chlorophenol	α-BHC
bromomethane	dichlorobenzene	β-BHC
vinyl chloride	nitrobenzene	γ-BHC
chloroethane	nitrophenol	Δ-BHC
methylene chloride	naphthalene	chlordane
acrolein	2-chloronaphthalene	4,4'-DDD
acrylonitrile	2,4,6-trichlorophenol	4,4'-DDE
trichlorofluoromethane	acenaphthene	4,4'-DDT
1,1-dichloroethylene	N-nitrosodiphenylamine	dieldrin
1,1-dichloroethane	hexachlorobenzene	endosulfan I
trans-1,2-dichloroethylene	phenanthrene/anthracene	endosulfan II
chloroform	dibutyl phthalate	endosulfan sulfate
1,2-dichloroethane	butyl benzyl phthalate	endrin
1,1,1-trichloroethane	Bis(2-ethylhexyl) phthalate	endrin aldehyde
carbon tetrachloride	pyrene	heptachlor
bromodichloromethane	benz(a)anthracene	heptachlor epoxide
bis-chloromethyl ether	triphenyl phosphate	toxaphene
1,2-dichloropropane	benzo(a)pyrene	PCB-1016
trans-1,3-dichloropropene		PCB-1221
trichloroethylene		PCB-1232
dibromochloromethane		PCB-1242
cis-1,3-dichloropropene		PCB-1248
1,1,2-trichloroethane		PCB-1254
benzene		PCB-1260
2-chloroethylvinyl ether		
bromoform		
tetrachloroethene		
1,1,2,2-tetrachloroethane		
toluene		
chlorobenzene		
ethylbenzene		

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[a] Analyzed by gas chromatography/mass spectrometry (GC/MS) unless otherwise noted.

[b] Determinations also made for the nonpriority pollutants: trichlorotrifluoroethanes, dibromoethanes, dibromoethenes, and alkylated benzenes, cyclopentanes, and cyclohexanes, in addition to the priority pollutant volatiles listed in the table.

[c] PCBs analyzed by gas chromatography with electron capture detection (GC/ECD).

Results of the Analyses of Representative Waste Oils

To augment the limited data base and to provide a meaningful basis for experimentally examining the fate of hazardous and nonhazardous contaminants in used oil during recycling scenarios, samples of waste oil were obtained from various suppliers across the country. The collection and analysis of the representative waste oil was conducted in two stages. In the first stage, oils were collected by 14 established collectors and/or recyclers of waste oil in the Spring of 1982 and shipped in 55-gallon drums to GCA for analysis. With the exception of "representative" oil No. 14, which was taken from the inlet to a combustion chamber after pretreatment by sedimentation and filtration, all oils were supplied in an "as is" condition, generally from holding tanks at the facility. Although bias in sampling as conducted in this study is a possibility, the analytical results confirm the presence of a number of contaminants in most oils, with many organic compounds measured at levels exceeding those found in the existing data base (see Table II-3 for the existing data base values). Nevertheless, to reduce the possibility of bias, sample collection was modified somewhat in the second stage of sample collection conducted in the Fall of 1982. At that time 10 samples were collected. With the exception of waste oil sample Nos. 16, 22, 23, and 24, all samples were collected in the field by GCA personnel.

The results of the analyses for physical properties, inorganic elements, and trace organics are shown in Tables II-7, II-8, and II-9, respectively for the first series of waste oils. As a result of these analyses, oils 1, 5, 6, and 10 were blended to provide the base for a "COMPOSITE" used oil to be utilized in the laboratory simulations of the disposal and recycling scenarios. The following spikes representing classes of organic compound of environmental interest were also added to this blended base at a level of about 90 ppm in order to determine the fate of these compounds through the laboratory simulations: (1) 2,4,6-trichlorophenol, (2) N-nitrosodiphenylamine, and (3) the pesticide, 2,2 bis(p-chlorophenyl)-1,1-dichloroethylene (4,4'-DDE). Polychlorinated biphenyls (PCBs) were added to the COMPOSITE oil at a level of 40 ppm.

The used oil samples were analyzed for 27 elements by Inductively Coupled Argon Plasma Emission Spectrometry (ICAP). The average lead content for this first series was 1,220 μg/g of oil, a value appreciably lower than values of about 10,000 μg/g reported in studies conducted in the early 1970s,[24] as would be expected with the declining use of leaded gasoline. Several preparation modes were studied at the outset of this analytical activity (dry ashing at 550°C for 24 hours, dry ashing with magnesium nitrate flux, and low temperature plasma ashing), with excellent agreement obtained for almost all elements. The data presented in Table II-8 were obtained from ICAP analysis of samples prepared by low temperature ashing.

The organic analyses were much more complex than the inorganic analyses. Sample preparation techniques were tailored for each organic species, and an extensive quality control effort was required for compound identification and quantification. The measurement of volatile organic compounds was particularly troublesome, and is the subject of extensive and current methods development by the EPA.[25,26] The data, as determined by a tetraglyme

TABLE II-7. RESULTS OF PHYSICAL PROPERTY ANALYSES OF USED OIL SAMPLES--FIRST SERIES

Parameter	ASTM Test Method	Representative oil No.															
		1[a]	2	3	4	5[a]	6[a]	7	8	9	10[a]	11	12	13	14	COMP[b]	Avg
Sulfated ash, %	D874	0.77	1.1	0.85	1.0	0.9	0.67	0.57	0.73	0.82	0.66	0.84	NA	0.87	0.99	0.8	0.83
Ash, %	D482	0.71	1.1	0.81	0.86	0.67	0.67	0.5	0.66	0.74	0.66	0.79	NA	0.84	0.84	0.68	0.76
Water by dist., %	D95	7.2	3.6	11.4	2.2	8.4	12.0	6.8	2.5	3.5	2.0	4.6	NA	0.2	5.0	7.1	5.3
Water & sediment, %	D1796	9.0	6.6	10.0[c]	11.0	10.0	16.0	9.0	11.0	9.0	16.0	8.0[c]	NA	0.1	6.0[b]	12.0	9.3
Specific gravity, API	D287	26.3	27.6	23.5	27.0	24.6	24.2	26.8	26.4	26.5	24.6	27.4	NA	28.1	26.2	24.6	26
Flash point, °F	D93	186	200+	194	174	130	200+	160	168	200+	188	188	NA	200+	192	180	-
Pour point, °F	D90	-25	-15	-25	-15	-10	-10	-10	-10	-10	-15	-30	NA	-30	-30	-25	-
ASTM dist.	D1160																
Initial boiling point, °F		403	210	310	194	206	210	210	378	475	210	210	NA	218	210	315	-
10% recovery at, °F		581	504	341	580	450	212	260	715	684	214	401	NA	598	407	648	-
50% recovery at, °F		811	804	862	794	784	779	866	855	832	780	795	NA	817	781	827	-
Viscosity, cSt. at 100°F	D445	44.2	60.1	62.0	59.1	56.4	56.9	58.1	55.8	59.8	56.2	42	NA	48.0	46.0	54	-
Copper corrosion	D130	3B	3A	3A	3A	3A	3A	3B	3A	3B	3B	3B	NA	3A	3A	3B	-
Chlorine, %	d	0.26	0.18	0.16	0.16	0.34	0.67	0.1	0.19	0.10	0.24	0.10	0.12	0.05	0.12	0.37	0.21
Sulfur, %	D2622	0.44	0.48	0.37	0.40	0.40	0.43	0.42	0.46	0.49	0.45	0.46	NA	0.57	0.44	0.43	0.45

[a] Used for COMPOSITE oil.

[b] COMP = COMPOSITE.

[c] Sediment

[d] Analyzed by ion chromatography technique (see Table II-5).

NA = Not analyzed; insufficient quantity available for analyses.

TABLE II-8. RESULTS OF ELEMENTAL ANALYSES OF USED OIL SAMPLES (μg/g)--FIRST SERIES

	Representative oil No.															
Element	1[a]	2	3	4	5[a]	6[a]	7	8	9	10[a]	11	12	13	14	C[b]	Average[c]
Aluminum	8.4	8.0	15	16	21	18	15	13	17	77	12	8.3	8.4	11	31	18
Antimony	<0.3	<0.3	1.1	1.4	<0.2	0.9	3.7	9.3	2.0	1.9	0.3	<0.3	<0.2	1.0	0.6	1.5
Arsenic	9	100	11	13	4.6	5.5	3.7	14	11	16	6.5	17	<0.4	17	8.1	16
Barium	68.0	44	44	22	100	23	49	160	62	82	43	150	9.2	95	61	68
Beryllium	0.04	0.02	0.03	0.06	0.03	<0.04	<0.04	0.04	0.04	0.22	0.03	0.04	<0.01	0.03	<0.1	0.4
Boron	8.0	20	19	16	7.7	6.2	7.7	15	14	22	13	6.6	26	11	6.2	14
Cadmium	1.5	1.4	1.3	1.9	1.2	0.7	0.8	2.3	1.0	2.8	1.1	0.8	0.6	1.6	1.3	1.0
Calcium	690	1,100	900	1,120	940	540	650	900	910	1,790	1,360	610	1,210	1,060	990	990
Chromium	3.4	2.9	5.7	6.3	4.7	3.0	3.3	5.2	3.8	37	3.3	3.4	0.3	4.1	7.7	6.2
Cobalt	0.2	<0.06	<0.07	<0.04	0.6	0.9	0.2	<0.1	<0.06	2.6	0.2	0.2	<0.04	<0.1	0.8	0.4
Copper	31	32	30	36	18	21	27	39	73	110	26	13	91	23	34	41
Iron	130	120	180	290	150	110	100	180	140	980	160	110	58	170	210	210
Lead	1,300	1,250	1,420	1,590	580	690	510	1,630	1,280	2,000	880	2,060	23	1,890	1,090	1,220
Magnesium	93	190	350	380	87	170	260	380	310	530	280	280	590	320	210	300
Manganese	6.2	5.2	11	19	10	14	3.1	11	12	31	6.6	13	1.4	14	14	11
Molybdenum	2.4	1.6	4.4	6.8	1.1	2.2	1.4	8.7	2.9	12	7.2	1.4	3.5	4.5	3.2	4.3
Nickel	2.1	1.1	1.7	1.3	6.3	0.5	0.7	1.1	1.4	16	1.3	0.6	0.3	1.2	3.7	2.5
Selenium	<0.5	<0.5	<0.5	<0.3	<0.3	<1.0	<1.0	<0.8	<0.5	<1.0	<0.4	<0.4	<0.3	<0.7	<1.0	<1.0
Silicon	11	20	22	19	15	36	34	21	20	210	15	22	8.2	14	40	33
Silver	<0.02	<0.02	<0.02	<0.01	<0.01	<0.04	<0.04	0.2	0.3	<0.04	<0.02	<0.04	<0.01	0.03	<0.1	<0.1
Sodium	55	85	140	140	68	170	150	93	110	570	140	60	24	100	260	140
Strontium	1.1	1.1	1.3	1.2	2.1	1.3	1.1	2.4	1.2	4.1	2.1	0.1	0.7	1.4	1.9	1.5
Thallium	<0.9	<0.9	<1.0	<0.6	<0.6	<2.0	<2.0	<2.0	<0.9	<2.0	<0.8	<1.7	<0.5	<2.0	<1.0	<1.0
Tin	110	5.5	8.5	11	8.9	3.0	3.1	8.4	21	10	18	2.2	16	8.6	16	17
Titanium	0.1	0.1	0.5	0.3	0.10	2.1	1.1	0.3	0.4	33	0.6	2.2	<0.01	0.2	7.8	3.0
Vanadium	1.0	<0.1	<0.1	<0.1	13	<0.2	<0.2	<0.2	<0.1	3.4	1.4	<0.2	<0.1	0.2	4.1	1.4
Zinc	830	1,100	940	1,150	390	470	660	1,020	920	1,530	1,000	630	1,550	1,000	730	940

[a] Used for COMPOSITE C

[b] COMPOSITE

[c] < = 0

TABLE II-9. RESULTS OF ORGANIC ANALYSES OF USED OIL SAMPLES--FIRST SERIES (μg/g EXCEPT AS NOTED)

Component	Representative oil no.														C^b	Average
	1^a	2	3	4	5^a	6^a	7	8	9	10^a	11	12	13	14		
1,2-Glycols^c	N	N	N	P	P	P	P	P	N	N	N	N	N	N	-	-
Chlorine	2,600	1,800	1,600	1,600	3,400	6,700	1,000	1,900	1,000	2,400	1,000	1,200	500	1,200	3,700	2,000
Volatile Organics																
Trichlorotrifluoroethanes	160	<20	1,350	<20	80	<20	530	<20	<20	160	<20	<20	<20	<20	110	160
Dibromoethanes	NA	<20	<20	<20	NA	NA	<20	<20	NA	NA	<20	<20	<20	NA	NA	<20
Dibromoethenes	NA	<20	<20	<20	NA	NA	<20	<20	NA	NA	<20	<20	<20	NA	NA	<20
Methyl cyclopentane	NA	<20	<20	150	NA	NA	970	<20	NA	NA	<20	<20	<20	NA	NA	-
Methyl cyclohexane	NA	<20	<20	150	NA	NA	630	<20	NA	NA	340	110	<20	NA	NA	-
Chloromethane	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	-
Dichlorodifluoromethane	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	6
Bromomethane	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Vinyl chloride	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Chloroethane	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Methylene chloride	<20	<20	<20	<20	90	50	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Acrolein	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Acrylonitrile	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Trichlorofluoromethane	<20	<20	360	<20	110	<20	<20	<20	<20	<20	<20	<20	<20	<20	30	30
1,1-Dichloroethylene	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
1,1-Dichloroethane	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Trans-1,2-Dichloroethylene	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Chloroform	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
1,2-Dichloroethane	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
1,1,1-Trichloroethane	1,700	910	210	100	1,250	1,560	210	950	120	1,500	150	<20	<20	130	1,500	620
Carbon tetrachloride	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Bromodichloromethane	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Bis-chloromethyl ether	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
1,2-Dichloropropane	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Trans-1,3-dichloropropene	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Trichloroethylene	570	<20	<20	<20	740	4,900	220	<20	<20	800	<20	<20	<20	130	2,000	510
Dibromochloromethane	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Cis-1,3-dichloropropene	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
1,1,2-Trichloroethane	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Benzene	110	90	120	100	110	50	80	<20	180	80	100	90	100	70	70	45
2-Chloroethylvinyl ether	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20

(continued)

TABLE II-9 (continued)

Component	1[a]	2	3	4	5[a]	6[a]	7	8	9	10[a]	11	12	13	14	C[b]	Average
	Representative oil no.															
Volatile Organics (cont.)																
Bromoform	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Tetrachloroethylene	530	650	270	700	1,250	1,100	<20	900	<20	80	230	<20	<20	<20	670	380
1,1,2,2-Tetrachloroethane	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	400
Toluene	5,000	2,400	970	1,650	5,300	1,200	2,800	1,400	1,200	1,000	4,400	670	1,700	2,300	2,800	2,500
Chlorobenzene	34	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<4	<20
Ethylbenzene	1,200	540	300	800	120	20	730	580	320	200	500	160	260	840	570	530
Dimethylbenzenes	NA	1,300	1,070	2,300	NA	NA	2,400	2,200	NA	NA	1,900	710	880	NA	NA	1,600
Alkylbenzenes (C_9H_{12})	NA	23,000	20	2,700	NA	NA	<20	33,000	NA	NA	48,000	<20	6,600	NA	NA	-
Semivolatile Organics																
Phenol	<10	<10	<10	<20	<10	<10	<10	<10	<10	<10	<10	<40	<10	<10	11	<10
Dichlorobenzene isomers	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	80	-
Nitrobenzene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	10	<10
2-Nitrophenol	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	<20	-
Naphthalene	780	330	110	560	800	260	170	260	240	290	260	280	490	580	440	360
2-Chloronaphthalene	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	<10	-
2,4,6-Trichlorophenol	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	40	<10
Acenaphthene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
N-Nitrosodiphenylamine	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	120	<10
Hexachlorobenzene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Phenanthrene/Anthracene	350	150	40	150	780	120	130	40	80	180	230	130	140	210	150	180
Dibutyl phthalate	<10	<10	160	230	<10	<10	<10	190	<10	<10	<10	<10	<10	500	60	-
Butylbenzylphthalate	<10	<10	40	400	<10	<20	<10	20	600	200	60	60	330	<10	<10	-
Bis(2-ethylhexyl) phthalate	740	60	20	50	360	<10	<10	80	130	30	70	70	70	<10	2,200	-
Pyrene	50	30	10	110	30	20	10	10	20	40	20	20	40	40	60	45
Benz(a)anthracene	30	20	<10	<10	<10	<10	<10	<10	20	30	10	10	40	20	40	18
Triphenyl phosphate	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Benzo(a)pyrene	20	<10	<10	<10	<10	<10	<10	<10	<10	30	<10	<10	<10	<10	<10	<10
4,4'-DDE	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	90	<10
PCBs	<0.1	<0.5	<0.5	<0.1	<0.1	7	<0.1	<0.1	13	<0.1	<0.1	<0.1	<0.1	<0.1	34[d]	<2

[a] Used for COMPOSITE oil.
[b] C = COMPOSITE from used oil Nos. 1, 5, 6 and 10.
[c] N ≤ 0.1%; P ≥ 0.1%.

[d] Aroclor 1260 (as spike).
NA = Not analyzed (analyses for these compounds not always conducted in first series)

analysis procedure described by Battelle,[25] confirm the presence of chlorinated solvents and volatile organics such as benzene and toluene in most samples of the first series of representative oils.

A number of semivolatile compounds were also detected in most of the samples comprising the first series of analyses. These included several PNA compounds, e.g., phenanthrene/anthracene, pyrene, and benz(a)anthracene. Benzo(a)pyrene was positively identified in only two of the 14 samples at the 20 and 30 μg/g levels. Polychlorinated biphenyls were also detected in two samples at levels of 7 and 13 μg/g. No priority pollutant pesticides, other than the spiked compound 4,4-DDE, were found in the representative oils.

The second series of samples collected in the Fall of 1982 were analyzed using identical analytical procedures. However, the number of volatile and semivolatile organics subjected to quantification by analysis was increased either as part of the effort to improve the chlorine balance or to provide data on compounds of interest (e.g., the dibromoethanes and the dibromoethenes). Volatile compounds looked for in the analyses were expanded to include, in addition to the dibromo compounds, analyses for alkylated benzenes, cyclopentanes, and cyclohexanes. The "hit list" of semivolatile compounds analyzed was also increased slightly to include some chlorinated phenols, naphthalenes, and benzenes. These compounds were included as part of the analytical effort to improve the chlorine balance. Concentration values for these compounds, although listed in Table II-9, are generally noted as NA (not analyzed).

The results of the analyses of the second series of representative oils are summarized in Tables II-10, II-11, and II-12 for the physical properties, the elements, and the organic components, respectively. Variations in the detection limits shown in Tables II-9 and II-12 for the organics are principally due to the amount of sample either introduced onto the fractionation column during the sample preparation step, or extracted with tetraglyme; matrix interferences also affect detection limits. On the average, the results are not appreciably different from those found for the first series of oils. PCBs were detected in two samples: one at 18 μg/g and the other at a relatively high level of 65 μg/g. Benzo(a)pyrene was identified in only one sample, at a level of 7 μg/g. To facilitate comparison of the results of the two series of analyses, average concentration values for the two series are presented in Table II-13. As noted in the table, the averages for chlorine and some of the volatile organics from the second series of samples do not include data from sample 15 because of its high chlorinated hydrocarbon content. The total chlorine content of this oil was 2.7 percent.

Despite moderately successful efforts to establish a chlorine balance (as described below), correlative comparisons between the presence of specific hazardous materials and more general analytical data are difficult to discern from the data. Relationships among other factors such as volatile compound content, flash point, ASTM distillation, and total chromatographic organics are obscure. Thus, simple physical tests do not seem to offer much promise as screens for hazardous wastes, although they have been addressed in the literature.[18,27,28]

TABLE II-10. RESULTS OF PHYSICAL PROPERTY ANALYSES OF USED OIL SAMPLES--SECOND SERIES

Parameter	ASTM test method	Representative oil No. 15	16	17	18	19	20	21	22	23	24	Avg.
Sulfated ash, %	D874	0.13	0.53	0.1	0.76	0.61	0.48	0.67	0.68	0.36	1.3	0.56
Ash, %	D482	0.12	0.48	0.1	0.69	0.58	0.45	0.61	0.63	0.23	1.2	0.51
Water by Dist., %	D95	0.1	1.0	0.1	4.2	8.4	9.9	9.1	9.0	1.5	15	5.8
Water & Sediment, %	D1796	0.1	7.0	0.1	10.0	11.0	9.0	9.0	8.1	1.0	25	8.0
Specific Gravity, API	D287	28.6	28.2	41.2	26.3	25.6	28.0	26.7	26.8	27.2	23.6	28.2
Flash Point, °F	D93	128	104	116	-	-	104	200	108	172	-	-
Viscosity, cSt. @ 100°F	D445	12	27.2	2.2	43.9	52.6	16.3	57.2	58.1	18.1	52.0	-
Chlorine, %	a	2.7	0.36	0.17	0.51	0.23	0.18	0.25	0.12	0.11	0.34	0.25
Sulfur, %	D2622	0.59	0.61	0.27	0.69	0.75	0.36	0.66	0.62	0.65	0.67	0.59

[a] Analyzed by ion chromatography techniques (see Table II-5).

TABLE II-11. RESULTS OF ELEMENTAL ANALYSES OF USED OIL SAMPLES (μg/g)--SECOND SERIES

Element	Representative oil no.										Average
	15	16	17	18	19	20	21	22	23	24	
Aluminum	52	15	1.5	17	47	11	13	15	20	640	83
Antimony	1.8	1.0	1.7	0.9	0.7	0.4	0.5	<0.4	<0.4	1.1	8
Arsenic	<1.0	10	0.9	6.2	6.2	7.1	5.0	8.8	7.4	4.5	6
Barium	51	70	84	32	54	30	71	64	100	84	64
Beryllium	0.2	0.1	<0.1	<0.1	0.9	<0.1	<0.1	<0.1	<0.1	0.4	0.1
Boron	1.3	7.6	3.8	5.8	8.2	4.1	4.1	14	14	11	7
Cadmium	0.8	1.6	0.2	1.5	0.8	1.0	1.3	1.4	1.2	1.0	1
Calcium	350	530	63	890	620	500	610	1,020	920	1,030	650
Chromium	17	3.8	1.2	4.8	5.4	3.3	4.0	4.9	4.4	18	7
Cobalt	1.0	1.0	0.3	0.2	0.4	0.2	<0.1	<0.1	0.1	0.2	1
Copper	19	34	12	36	40	19	45	37	32	130	40
Iron	490	150	84	170	200	100	120	150	160	1,300	290
Lead	1,070	1,170	170	810	810	950	660	1,800	1,500	350	930
Magnesium	43	190	4.6	300	210	78	430	280	280	240	210
Manganese	10	6.4	1.2	11	7.6	5.6	7.3	8.4	7.5	28	9
Molybdenum	2.5	3.6	0.4	7.6	3.4	2.3	2.9	3.9	3.7	13	4
Nickel	12	2.3	0.6	15	7.6	3.0	1.8	1.7	1.5	86	7
Selenium	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Silicon	26	20	<0.1	41	35	19	20	12	20	200	38
Silver	<0.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sodium	24	130	14	160	510	250	85	100	170	450	190
Strontium	1.0	0.8	<0.1	1.2	1.3	0.7	1.3	1.8	1.6	3.4	1
Thallium	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9
Tin	2.6	7.9	<0.7	11	3.8	4.3	3.9	8.5	7.8	17	7
Titanium	1.3	0.8	<0.1	7.0	4.2	1.5	1.1	1.0	1.3	21	4
Vanadium	11	0.6	0.9	0.3	13	3.1	<0.1	0.1	0.1	7.5	4
Zinc	170	690	91	890	620	430	850	1,050	900	340	600

TABLE II-12. RESULTS OF ORGANIC ANALYSES OF USED OIL SAMPLES--SECOND SERIES (μg/g)

Component	Representative oil no.										
	15	16	17	18	19	20	21	22	23	24	Average
Chlorine	27,000	3,600	1,700	5,100	2,300	1,800	2,500	1,200	1,100	3,400	2,500[a]
Volatile Organics											
Trichlorotrifluoroethanes	230	<30	860	1,900	1,300	940	<20	620	380	1,400	760
Dibromoethanes	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Dibromoethenes	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Methylcyclopentane	<20	670	<30	<20	80	360	<20	270	190	<30	160
Methylcyclohexane	730	980	<30	230	170	440	110	280	160	280	340
Chloromethane	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Dichlorodifluoromethane	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Bromomethane	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Vinyl chloride	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Chloroethane	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Methylene chloride	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Acrolein	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Acrylonitrile	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Trichlorofluoromethane	<100	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
1,1-Dichloroethylene	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
1,1-Dichloroethane	<100	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Trans-1,2-dichloroethylene	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Chloroform	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
1,2-Dichloroethane	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
1,1,1-Trichloroethane	14,000	2,000	500	880	670	840	110	390	310	1,700	820[a]
Carbon tetrachloride	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Bromodichloromethane	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Bis-chloromethyl ether	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
1,2-Dichloropropane	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Trans-1,3-dichloropropene	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Trichloroethylene	1,600	370	730	3,700	170	<100	<20	<90	<90	790	740
Dibromochloromethane	<20	<30	<30	<20	<20	<30	<20	<20	<20	<20	<30
Cis-1,3-dichloropropene	<20	<30	<30	<20	<20	<30	<20	<20	<20	<20	<30
1,1,2-Trichloroethane	<20	<30	<30	<20	<20	<30	<20	<20	<20	<20	<30
Benzene	<100	<100	<30	100	90	190	<90	190	170	<100	100
2-Chloroethylvinyl ether	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30

(continued)

TABLE II-12 (continued)

Component	Representative oil no. 15	16	17	18	19	20	21	22	23	24	Average
Volatile Organics (cont.)											
Bromoform	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Tetrachloroethylene	13,000	640	<90	620	200	190	210	610	490	690	380[a]
1,1,2,2-Tetrachloroethane	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Toluene	9,700	3,100	380	4,400	1,000	12,000	510	3,500	2,500	1,400	3,850
Chlorobenzene	<20	<30	<30	<20	<20	<30	<20	<20	<20	<30	<30
Ethylbenzene	<330	3,700	560	570	390	1,500	180	840	670	440	30
Dimethyl benzenes	1,300	2,600	3,300	1,800	1,100	6,400	650	3,400	2,500	1,400	2,400
Alkylbenzenes (C_9H_{12})	42,000	<30	<30	<20	4,100	<30	36,000	<20	<20	<30	-
Semivolatile Organics											
Phenol	70	40	<5	35	25	<5	<5	18	14	45	25
Chlorophenol isomers	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Dichlorobenzene isomers	10	<5	<5	10	7	<5	<5	20	<5	15	6
Nitrobenzene	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
2-Nitrophenol	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Naphthalene	990	430	1,400	230	750	990	210	420	340	270	600
2-Chloronaphthalene	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
2,4,6-Trichlorophenol	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Acenaphthene	60	<5	<5	10	50	95	<5	7	<5	10	23
N-Nitrosodiphenyl amine	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Hexachlorobenzene	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Phenanthrene/Anthracene	260	100	330	80	390	380	80	100	100	150	200
Dibutyl phthalate	10	10	<5	6	6	15	7	<5	<5	<5	5
Butyl benzyl phthalate	<5	<5	<5	<5	<5	<5	<5	60	45	<5	<5
Bis(2-ethylhexyl) phthalate	50	<5	10	40	45	<5	<5	90	60	30	30
Pyrene	30	30	20	15	70	40	<5	45	35	20	30
Benz(a)anthracene	35	12	10	30	60	<5	<5	25	8	20	20
Triphenyl phosphate	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Benzo(a)pyrene	<5	<5	<5	<5	<5	<5	<5	7	<5	<5	<5
4,4'-DDE	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
PCBs	<5	65[b]	<5	<5	<5	<5	<5	<5	<5	18[c]	8

[a] Average for oils 16-24; < values = 0

[b] Aroclor 1260

[c] Aroclor 1242

TABLE II-13. COMPARISON OF THE RESULTS OF THE ANALYSES OF THE TWO SERIES OF REPRESENTATIVE OILS

Contaminant	Average concentration (μg/g) First series (14 oils)	Average concentration (μg/g) Second series (10 oils)
Ash	0.76	0.51
Water and sediment	9.3	8.0
Elements		
Arsenic	16	6
Barium	68	64
Cadmium	1	1
Chlorine	2,100	2,500[a]
Chromium	6	7
Copper	41	40
Iron	210	290
Lead	1,220	930
Magnesium	300	210
Nickel	3	7
Sulfur	4,500	5,400
Vanadium	1	4
Zinc	940	600
Volatile Organics		
Trichlorotrifluoroethanes	160	760
1,1,1-trichloroethane	580	820[a]
Trichloroethylene	490	740
Tetrachloroethylene	380	400[a]
Toluene	2,500	3,850
Dimethyl benzenes	1,600	2,400
Semivolatile Organics		
Phenol	<10	25
Naphthalene	360	600
Phenanthrene/Anthracene	180	200
Pyrene	45	30
Benz(a)anthracene	18	20
Benzo(a)pyrene	<10	<5
PCBs	<2	8

[a] Does not include oil No. 15 because of its excessively high chlorine level (27,000 μg/g).

Chlorine Balance for the Representative Oils

As noted above, the chlorine balance, as given by the ratio of the sum of the chlorine content of specific organic compounds to the total chlorine value obtained by ion chromatography (IC), was low due to the poor compound recoveries obtained using a modified headspace technique for the analysis of volatiles. The chlorine balance was significantly improved when the head space procedure was replaced with the procedure based on a tetraglyme extraction of the volatile organics from the oil.[25] With few exceptions, the closure is essentially complete if the total of the specific organic compound chlorine content is adjusted for the compound recoveries found as a result of the program quality control procedures. Analytical procedure recoveries, as shown in Appendix C (Quality Control), were generally 70 to 85 percent for the chlorinated compounds.

The chlorine balance data is summarized in Table II-14. The table includes a total chlorine value as determined by IC, the chlorine contribution of major chlorine-containing compounds, the results of an IC analysis of an aqueous extract of the oil, and the calculated chlorine balance recovery in percent.

The measured chlorine content of the aqueous extract is termed inorganic chlorine, although the extent to which this is a measure of inorganic chlorine is unclear. Although some portion is probably organic, it has been assumed that the chlorine in the aqueous fraction is largely inorganic and has been added to the chlorine content of the specific organics in arriving at the calculated closure.

The frequency with which chlorinated organic solvents are found in waste oils underscores the need for quick, reliable, and economical methods of analysis. Unfortunately, such a method has not been found. The Beilstein spot test method was examined in this study. The test was unsatisfactory for chlorine loadings less than 5000 μg/g. While of value in identifying high concentrations of chlorine in waste oils, such as the 2.7 percent chlorine found in representative oil No. 15, the test is not an adequate screening technique for most of the waste oils tested in this program.

PRIORITIZATION OF POLLUTANTS IN USED OILS

Determination of Relative Hazard of Contaminants

Contaminants in used oils range from those substances which possess the potential to significantly affect human health or environmental quality (benzo(a)pyrene, PCBs, etc.), to those that are relatively innocuous. Any attempt to rank a large population of chemical substances by potential toxicity necessitates selection of a methodology which can translate experimental toxicological data from diverse sources into numerical values that are comparable within the group. Also, since the hazard potential of chemical substances varies according to media (i.e., some substances will be much more hazardous in air than in water), the ranking methodology should be flexible enough to differentiate relative hazard in air, water, or in solid

TABLE II-14. CHLORINE BALANCE FOR THE REPRESENTATIVE OILS

Representative Oil No.	A: Specific Organic Compound Contribution[a] (μg/g) 1	2	3	4	5	Subtotal 1-5	B[b]: Chlorine in Aqueous Extract (μg/g)	C: Total Chlorine A+B (μg/g)	D[b]: Total Chlorine (μg/g)	Chlorine Balance, Percent Recovery C/D x 100
1	100	1,200	405	405	40	2,150	500	2,650	2,600	102
2	ND	730	ND	560	ND	1,290	700	1,990	1,800	111
3	830	170	ND	230	220	1,450	500	1,950	1,600	122
4	ND	80	ND	600	ND	680	300	980	1,600	61
5	50	1,000	600	1,070	120	2,840	300	3,140	3,400	93
6	ND	1,360	4,290	1,020	50	6,720	NA	6,720	6,700	100
7	400	170	180	ND	ND	750	100	850	1,000	85
8	ND	760	ND	770	ND	1,530	400	1,930	1,900	102
9	ND	100	ND	ND	ND	100	300	400	1,000	40
10	100	1,200	650	50	10	2,010	NA	2,010	2,400	84
11	ND	120	ND	200	ND	320	700	1,020	1,000	102
12	ND	ND	ND	ND	ND	0	800	800	1,200	67
13	ND	ND	ND	ND	ND	0	200	200	500	40
14	ND	100	100	ND	10	210	400	610	1,200	51
15	140	11,200	1,300	11,100	50	23,800	NA	23,800	27,000	88
16	ND	1,600	300	550	ND	2,450	NA	2,450	3,600	68
17	530	400	590	50	ND	1,570	NA	1,570	1,700	92
18	1,180	700	3,000	530	ND	5,410	NA	5,410	5,100	106
19	810	540	140	170	ND	1,660	NA	1,660	2,300	73
20	580	670	50	160	ND	1,460	NA	1,460	1,800	81
21	ND	90	ND	180	ND	270	NA	270	2,500	11
22	390	310	50	520	ND	1,270	NA	1,270	1,200	106
23	240	250	50	420	ND	960	NA	960	1,100	87
24	870	1,360	640	590	ND	3,460	NA	3,460	3,400	102

[a] 1 = trichlorotrifluoroethanes
2 = 1,1,1-trichloroethane
3 = trichloroethylene
4 = tetrachloroethylene
5 = other chlorinated compounds.

[b] By IC.

waste material. This differentiation by media is especially relevant to waste oil recyling or disposal options. Chemical species of high relative hazard in air would be of interest in waste oil disposal through incineration, for example. Pollutants which are toxic in water or are leachable into water following disposal on land would be of interest in recycling options resulting in large amounts of wastewater, or in cases where waste oils are applied directly to soils (e.g., road oiling).

The methodology selected to rank pollutants in waste oil according to potential hazard to human health or the environment was the Multimedia Environmental Goal (MEG) format[29,30] which initially formed an integral part of the environmental assessment efforts of the EPA-Industrial Environmental Research Laboratory (EPA/IERL), Research Triangle Park, NC. This methodology was developed to the point where it provided a workable system for evaluation and ranking of pollutants according to relative hazard. However, its use has been deemphasized because of uncertainties concerning the significance of the relative rankings obtained by summing the contribution of individual contaminants and its applicability across the media of air, water, and land.

Nevertheless, using the MEG methodology, a discharge goal may be calculated for each pollutant for release into air, water, or solid waste. Goals may be calculated using data relative to both protection of human health and protection of environmental quality. These numerical factors were calculated using appropriate model equations for which data were available. All factors were calculated using toxicity data derived from similar sources; among these were:

- Drinking Water Regulations[31]
- Water Quality Criteria[32,33,34]
- Lethal and toxic dose information from animal studies and human exposures. Such data were lagely provided in the NIOSH Registry of Toxic Effects of Chemical Substances, 1980 Edition;[35] Patty's Industrial Hygiene and Toxicology;[36] and the IARC Monographs on Evaluation of Carcinogenic Risk.[37]
- Threshold Limit Values (TLVs)--as established by the American Conference of Governmental Industrial Hygienists (ACGIH).[38]

Table II-15 lists selected chemical pollutants of concern in used oils ranked according to potential hazard. They are listed in order of descending concern; that is, the pollutants of highest priority head the list. Numerical ranking factors were calculated for each substance using the MEG model equations and appropriate toxicity data. Data for toxicity in air and water were considered separately. Where sufficient data existed to calculate factors for both human health and environmental protection, the more stringent value was used to rank the substance. It was assumed that adverse effects due to disposal of waste oil as a solid waste would be limited to leaching or

TABLE II-15. PRIORITIZATION OF SELECTED POLLUTANTS IN WASTE OIL ACCORDING TO RELATIVE HAZARD BY MEDIA

Air		Water and solid waste	
Pollutant	Relative hazard[a]	Pollutant	Relative hazard[a]
Benzo(a)pyrene[b]	1	Polychlorinated biphenyls (PCBs)[b]	1
Polychlorinated biphenyls (PCBs)[b]	50	Benzo(a)pyrene[b]	60
Benz(a)anthracene[b]	2,250	Aluminum (E)[c]	100
Cadmium	2,500	Phthalate esters (E)	300
Cobalt	2,500	Phenol	1,000
Nitrosamines[b]	3,250	Nitrophenols	1,000
Nickel	5,000	2-chlorophenol	1,000
Lead[b]	7,500	Cadmium	2,000
Benzo(c)phenanthrene[b]	11,200	Selenium	2,000
Barium	25,000	Lead (E)	10,000
Chromium	25,000	Chlorobenzene (E)	20,000
Benzene[b]	36,450	Dichlorobenzene (E)	20,000
Copper	50,000	Zinc (E)	20,000
Iron	50,000	Chromium (Cr^{+6})[b]	50,000
Phenanthrene	80,000	Phenanthrene	80,000
Chrysene[b]	1.1×10^5	Benz(a)anthracene	1.3×10^5
Zinc	2.5×10^5	Nitrosamines	2.0×10^5
Phthalate esters	2.5×10^5	Benzene[b]	2.0×10^5
Toluene	2.3×10^5	Alkyl benzenes (E)	2.0×10^5
Nitrobenzenes	2.5×10^5	Nitrobenzenes (E)	2.0×10^5
Aluminum	2.6×10^5	Trichloroethane (E)	2.0×10^5
Chloroform	5.0×10^5	Tetrachloroethylene (E)	2.0×10^5
Nitrophenols	5.0×10^5	Toluene (E)	2.0×10^5
Ethylene glycol	5.0×10^5	Chloroform (E)	2.0×10^5
Phenol	9.5×10^5	Arsenic	2.0×10^5
Dichloroethane	1.0×10^6	Cobalt	2.0×10^5
2,4,6-Trichlorophenol	1.9×10^6	Copper	2.0×10^5
Naphthalene	2.5×10^6	Silver	2.0×10^5
Pyrene	10^7	Barium (E)	5.0×10^5
Alkyl napthalenes	10^7	Benzo(c)phenanthrene	6.7×10^5
Methylene chloride	10^7	Ethylene glycol (E)	1×10^6
Chlorobenzene	10^7	Dichloroethane (E)	1×10^6
Dichlorobenzenes	10^7	Trichloroethylene (E)	1×10^6
Alkylbenzenes	10^7	Methylene chloride (E)	1×10^6
Trichloroethane	10^7	Naphthalene	2.5×10^6
Trichloroethylene	10^7	Chrysene[b]	7×10^6
Tetrachloroethylene	10^7	Pyrene	10^7
		Alkyl naphthalenes	10^8

[a] Indicates the relative hazard potential of each listed substance compared to the substance determined to be most "hazardous" which has been arbitrarily assigned the value of 1. Most hazardous values are 0.02 $\mu g/m^3$ of B(a)P in air; 0.005 μg/liter of PCBs in water; and 0.1 $\mu g/g$ of PCBs as solid waste.

[b] Indicates that the substance is a known or suspected carcinogen in man and/or animals.

[c] (E) indicates that hazard potential is mainly as a detriment to the ecology or environmental quality; other substances are hazards to human health, or both human health and environmental quality.

runoff of contaminants into ground waters or surface waters. Relative hazard factors were obtained by normalizing all calculated numerical ranking-factors to the value for the most hazardous species in each media, which was arbitrarily set equal to 1. That is, the calculated numerical ranking factor for release of benzo(a)pyrene into air was 0.02 $\mu g/m^3$. This was multiplied by 50 to provide a normalized value of 1.0. Factors for all other species of concern in air were likewise multiplied by 50 and relative hazard is listed on this basis. The potential of the contaminants to adversely impact human health is seen to vary over seven orders of magnitude.

It must be remembered that the numerical ranking factors derived through the MEG model equations are based on empirical data presently available in secondary references. Obviously, as new experimental data become available, these values may be revised and updated. It is worth reemphasizing the fact that the numerical ranking factors and indications of relative hazard are only useful in the context of relative toxicity ranking within the population of chemical substances on the list developed for this study. They should not be misconstrued as representing a true measure of potential detrimental or toxic impact to human health or environmental quality.

Based on the lists in Table II-15, there appear to be several specific chemical contaminants, or groups of contaminants whose hazard potential in waste oil could be significant. A brief summary of the toxic effects of some of these substances in man and animals is presented below.

Nitrosamines--

As noted previously, there is a potential for formation of various nitrosamines during oil use if the oils contain both nitrites and amine compounds. Both aliphatic and aromatic species are toxic in man and animals. The biological activity of N-nitrosodimethyl- and N-nitrosodiethylamine (and their metabolites) include acute and chronic toxicity, carcinogenicity, and teratogenicity in experimental animals. Acute effects include central necrosis of the liver, bleeding, and jaundice. There is some experimental evidence which suggests that acute toxicity of alkyl nitrosamines decreases with increases in the length of the alkyl chain. All mammals which have been studied are susceptible to carcinoma induction by at least one nitrosamine.

The American Petroleum Institute in its critique of EPA's report to Congress[5] takes exception to the contention that formation of nitrosamines is likely. According to the API report,[39] most manufacturers of oils are replacing the precursors of nitrosamines (nitrites and amines) with substitutes or are using only one of the two precursors to limit the possibility of nitrosamine formation. (The API critique also discusses and generally downplays the significance of contaminants such as chromium (VI), PCBs, and PNAs because of their low concentration levels in oil and their lack of mobility in the environment.)

Polynuclear aromatic hydrocarbons--

As noted in Table II-15, several PNAs are of potential concern in considering waste oil reuse or disposal options. Specifically, these are B(a)P, benz(a)anthracene, benzo(c)phenanthrene, and chrysene. The toxic actions of PNAs are usually most pronounced in air; however, the hazards associated with B(a)P are also relevant to the presence of this contaminant in water or solid waste. B(a)P is considered to be an active carcinogen.[21] It has been shown to cause chromosomal aberrations in mammalian cells; experimental evidence also indicates that B(a)P is a mutagenic and teratogenic agent in the mouse.[35] In addition to B(a)P, benz(a)anthracene, chrysene, and benzo(c)phenanthrene and eight of its alkyl derivatives are carcinogenic in mice.

Polychlorinated biphenyls (PCBs)--

The adverse health effects of polychlorinated biphenyls are numerous and varied. The adverse health effects in experimental animals as well as those observed in man, accidentally and occupationally exposed, point to a risk for the general population. In addition, the cumulative potential of PCBs is of great concern in considering toxicity to aquatic life or man. PCBs at 0.01 μg/l in water have been known to accumulate in fish up to 200,000 times the water concentration. Also of importance for recycling or disposal of PCB-contaminated oils is their resistance to destruction. Despite the observations that mammalian systems have some capacity to metabolize many PCBs, they are still among the most resistant chemicals to biodegradation.

Metals--

Among the metallic species of high priority in considering waste oil reuse or disposal options are chromium (as Cr^{+6}), lead, aluminum, and barium. Discussions below are summaries of information contained in various sources (including the IARC Monograph Series; Patty, Sax, Fairchild, et al.).

Chromium--The known harmful effects of chromium in man are primarily attributable to the hexavalent form. The concentration of hexavalent chromium in used oil is extremely low according to API sources.[39]

Health effects associated with hexavalent chromium are mainly effects on skin and the respiratory tract. Cutaneous injury from chromium includes corrosive ulcers, scars, and nonulcerative contact dermatitis as well as allergic effects such as eczematous and noneczematous contact dermatitis. Hexavalent chromium is irritating to the respiratory tract and produces ulceration and perforation of the nasal septum. Respiratory effects such as lung fibrosis have also been reported. Of greater significance is the role of chromium in the production of lung cancer. In many experiments, various chromium compounds have been shown to induce tumors in mice and rats. Calcium chromate (VI) has been found to be carcinogenic by several routes of administration. Data have also revealed that there is an excessive risk of lung cancer among workers in the chromate-producing industry.

Lead--Lead compounds are toxic when ingested or inhaled. Ingested lead is largely captured by the liver and excreted in bile. Lead absorbed through inhalation results in toxic effects at lower lead concentrations when compared to ingestion. Lead poisoning results in hemolysis of red blood cells, lesions of the liver, kidneys, and male gonads, and adverse central nervous system effects. Lead is also a cumulative poison; the biological half-life of lead is reported to be 6 months.

Several lead salts are reported to cause oncogenic effects in animals. There is some evidence that exposure to lead increased the incidence of abortion and stillbirth; lead is known to cross the human placenta. Exposure to lead has resulted in teratogenic effects in animals.

Lead has also been shown to be toxic to aquatic organisms, with the degree of toxicity varying according to factors such as water temperature. Reproductive impairment of Daphnia magna has been observed at lead concentrations of 30 $\mu g/l$.

Aluminum--Although aluminum is not a highly toxic element to humans, it is of high priority in protection of aquatic life. Aluminum is highly toxic to fish, especially at low pH. Aluminum is reported to be concentrated 10,000 times in fish muscle and 15,000 times in benthic algae. Aluminum compounds may adversely affect benthic organisms (e.g., clams, crabs, oysters, lobsters). Aluminum would especially be of concern in land disposal of used oils where leaching (especially at acid pH) and runoff could ultimately affect aquatic species.

Barium--Soluble barium compounds (including the acetate, halides, hydroxide, thiocyanate, and thiosulfate) are highly toxic when ingested; insoluble barium compounds are generally nontoxic. Barium stimulates all muscle types, causes vasoconstriction, and initially stimulates, then paralyzes the central nervous system. BaO and $BaCO_3$ have caused respiratory injury and fatalities in man. The fatal dose of $BaCl_2$ for man is 800-900 mg (550-600 mg as Ba). However, barium is readily excreted and probably noncumulative. As noted in Table II-15, barium is of greater concern in air than in water (regarding human health). Barium is of lower priority as an environmental contaminant; the existence of soluble barium compounds toxic to fish or other aquatic species is unlikely under normal ambient aquatic conditions.

Ranking of Contaminants in Waste Oils Based on Weighted Relative Hazard

The compilation of the list of pollutants of concern in waste oil as provided in Table II-15 was only an initial step. Concentration data were incorporated to assess whether the listed hazardous pollutants are of concern. Whenever possible, data from the analysis of the 24 representative waste oils were used as the measure of the concentration in the oil.

The degree of hazard of major contaminants, along with their concentrations in waste oil, are shown in Table II-16. The weighted relative hazard, as defined in the table, is the ratio of the reported concentration in waste oil to its relative hazard factor given in Table II-15. The weighted relative hazards will be used to assess the potential environmental significance associated with waste and process streams for the various recycling options examined in this program.

TABLE II-16. WEIGHTED RELATIVE HAZARD FOR SOME CHEMICAL CONTAMINANTS OF INTEREST IN WASTE OIL

Contaminant	Concentration (mg/kg)	Weighted Relative Hazard[a]
Benzo(a)pyrene	< 5	< 5000
Polychlorinated biphenyls	< 2	< 2000
Aluminum	40	400[b]
Lead	1100	110
Phenol	25	25
Toluene	3100	16
Benz(a)anthracene	15	7
1,1,1-trichloroethane	700	3.5[b]
Zinc	800	3.2
Phenanthrene	200	2
Benzene	70	2
Tetrachloroethylene	400	2
Trichloroethylene	600	0.6
Cadmium	1	0.5
Chromium	7	0.3
Dichlorobenzene	5	0.25
Naphthalene	460	0.2
Dibutylphthalate	50	0.2

[a] Weighted Relative Hazard $= \frac{\text{Concentration in Waste Oil } (\mu g/kg)}{\text{Relative Hazard Factor}}$

[b] Based on ecology.

The ranking by relative hazard in Table II-16 assumes worst case impact; i.e., impact of these pollutants would be on the most sensitive species in the appropriate medium (air, water, soil). Using the ranking methodology described, weighted relative hazard was noted to span four orders of magnitude (naphthalene's hazard in waste oils relative to PCBs or B(a)P).

The concentration data are average values for those compounds as determined by analysis in this study. PCBs were found in 4 samples of oil, although their presence in waste oil as a natural contaminant is unlikely. For lack of data, compounds such as nitrosamines and hexavalent chromium have not been listed in the table. API feels their presence is unlikely.[39]

Lead, despite a tenfold reduction in concentrations in waste oil over the past 10 years, remains a contaminant of some concern. Further reduction in lead concentrations should continue and will eventually reduce the significance of lead in waste oil.

It is interesting to note the relatively low priority attached to the chlorinated hydrocarbons, many of which are present in relatively high concentrations. (The use of maximum rather than average concentrations would raise the weighted relative hazard of 1,1,1-trichloroethane to 70). As discussed, initial ranking of chemical contaminants was accomplished through models which translated existing emission standards or criteria or relevant toxicity data into numerical ranking factors. Review of the toxicity data and existing exposure limitations (including Threshold Limit Values), revealed that the toxicity of the majority of these types of compounds manifests itself in similar ways. Very detectable reactions to these substances occur following inhalation of high concentrations. Toxic signs or symptoms usually include irritation of the eyes, nose or upper respiratory tract. Some substances are also skin irritants. Prolonged exposure to these halogenated hydrocarbons sometimes results in central nervous system (CNS) depression or liver or kidney impairment. Inhalation or accidental ingestion of high concentrations of these substances has resulted in human death; and some compounds (1,2-dichloroethane, for example) have been reported to produce cancer in test animals. However, on the whole, the toxicity of these componds is usually a result of exposures (e.g., inhalation) which are not relevant in considering their potential toxicity as components in waste oils, except for those involved in the oil recycling industry or possibly involved in road oiling.

Other Pollutant Effects

The above discussion of contaminants in waste oil has focused on health and ecological effects and has not considered the potential adverse impact of contaminants on recycling scenarios. Many contaminants are of interest in this regard. As examples, the presence of chlorine compounds, regardless of their weighted relative hazard, may result in corrosion of re-refining and combustion equipment; metals could lead to coking and fouling problems; gasoline and other volatile, inflammable organics could present fire and explosion hazards, and excessive water could result in a multitude of deleterious effects. These contaminants, and others such as glycols, are often present in appreciable quantities, generally above 1000 ppm and much higher in the case of water. The recycler should be aware of their concentrations in used oil so that corrective measures can be taken to forestall obvious difficulties. However, the need for, and the ability to, take corrective actions is not always obvious or possible. Cumulative effects of many trace contaminants are possible and even trace amounts of certain contaminants, regardless of their health hazard, may affect processing and/or the quality of the final product.

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SECTION III

USED OIL GENERATION AND RECYCLING

USED OIL GENERATION

Several estimates of the quantity of used oil generated in the United States have been made based on surveys generally involving Bureau of Census sales data and information obtained from generators, collectors, and recyclers of used oil.[1-10] Direct comparison of many estimates is difficult because of variations in estimation criteria and methods. At the present time EPA estimates that 1.2 billion gallons of used oil are generated per year.[11] While this estimate is in accord with many of the estimates found in the cited references, a larger value of about 2.5 billion gallons per year has also been proposed.[12] However, this higher estimate includes spills, tank bottoms, wastewater oil recovery, and other nonlubricant sources of oil which are not necessarily sources of readily collectable or re-refinable oil.

Approximately 50 to 60 percent of the lubricating oil sold is potentially recoverable, with the remaining 40 to 50 percent lost through engine combustion, leakage, and handling. The actual amount recovered is less, and is now estimated by EPA at about 775 million gallons per year, with automotive lubricating oils accounting for about 425 million gallons.[13]

USED OIL RECYCLING

About one-third of the used oil generated in the United States is discarded by land or sewer disposal; the remaining two-thirds is recycled in a variety of ways. Major recycling options include reuse as a fuel, as a road oilant to suppress dust emissions from dirt roads, or as a feedstock for the production of re-refined lube oil basestocks. Other uses (e.g., as an asphalt extender or as a carrier for pesticides) have also been reported. There are no totally defensible estimates of the fate of used oil. However, the data provided in Table III-1 are felt to represent a reasonable consensus of opinion concerning sales, generation, collection, and recycling. The sales data for 1980 were taken from Reference 14. The values for the total quantities of used oil generated and collected were also provided by EPA.[11] However, the amounts generated by source and the dispositions of the collected oil were adapted from References 12, 15, and 16. EPA is attempting through additional ongoing survey efforts to update the information presented in the table to obtain as accurate a data base as possible in order to assess present and future impacts of used oil management.

TABLE III-1. USED OIL SOLD, GENERATED, COLLECTED, AND RECYCLED

Activity/disposition	Amount in millions of gallons per year
Oil sold (1980)	
Automotive lubricating oil	1,290
Industrial lubricating oil	1,050
Other industrial oils	530
	2,860
Used oil generated	
Automotive lubricating oil	620
Industrial lubricating oil	480
Other industrial oil	100
	1,200
Used oil disposition	
Oil collected/recycled	
Burned as fuel	640
Road oiling	40
Re-refining	95
	775
Use by private industry	
Burned as fuel	40
Road oiling	30
	70
Land/sewer disposal	355

As shown in the table, approximately 42 percent of the lubricating oils and other industrial oils sold, for example, as transformer oils and heat transfer fluids, appear as used oils (generated). Approximately 65 percent (775 million gallons) of the 1,200 million gallons generated is collected. It has been assumed that all collected oil is burned as a fuel, used for road oiling, or re-refined. The amount burned was determined by difference after subtraction of a reasonably accurate value for re-refined oil and the use of data in Reference 16 to provide road oiling values. The value of 640 million gallons collected and burned is higher than EPA's present estimate of 460 million gallons, but is in good agreement with the value of 621 million gallons provided in Reference 12. Values of waste oil use by private industry were provided by Reference 12 for burning and by Reference 16 for road oiling. The value for land and sewer disposal represents the difference between that generated and the sum of that collected and that used by private industry. The value of 355 million gallons per year is not appreciably different than the value of 342 million gallons per year reportedly discarded by individuals who change their own automotive oil. The latter estimate is based on a recent study for DOE by Market Facts in which a national probability sample of 4805 telephone households across the country was used to identify waste oil disposal practices.[17]

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SECTION IV

SEWER DISPOSAL

BACKGROUND

Based on the result of a recent national survey,[1] it is known that a significant portion of used automobile lubricating oil is generated by individuals who change their own oil. According to this study, a total of 542 million gallons of crankcase oil is drained annually from vehicles operated by American households, with 342 million gallons recovered by the do-it yourself (DIY) households. Most of this used oil is disposed of on the ground or discarded with trash. Reportedly only 2 percent (approximately 7 million gallons) is disposed of in sewers.[1] The potential for sewer disposal appears to be much higher than that reported because, according to the survey, approximately 45 percent of the individuals who change their own automotive oil currently live within the limits of a major city or in the suburbs of a major city, most of which are served by sewer systems.

In at least one location it has been reported that the petroleum in urban sewer runoff resembles used crankcase oil in composition.[2] Deliberate discharge is not the only cause of observed oil levels in urban sewer runoff. Other studies[3,4] have shown that hydrocarbon concentrations in runoff from roadbeds can exceed those in the runoff from sewers draining urban areas. Although wastes from industrial sources also undoubtedly find their way to the sewer system, the relative importance of used oil discarded by DIY households will increase as treatment processes become more prevalent for industrial sources of hydrocarbons.

The concentrations of hydrocarbons in urban sewer systems have been measured at levels ranging from 1 to 24 mg/l, with most of the oil (approximately 85 percent) associated with suspended particulate in the runoff.[3,4,5] The lower value is consistent with values calculated from estimates of crankcase oil disposed of by urban DIYs[1] and overall estimates of nationwide flows in combined and storm sewer systems.[6] According to Reference 6 almost 150 million people live in urban areas. About 25 percent of this population is served by combined sewer systems, 52 percent by storm sewer systems, and the remaining 23 percent live in areas without sewer systems. Calculated petroleum loadings in the combined sewer systems and in the storm sewer systems would be of the order of 1 and 2.5 mg/l, respectively, assuming only 7 million gallons per year are discarded into sewers and there are no losses to walls or sediments. Runoff from roads and industrial sources also contribute to the measured levels.

The discharge from storm sewers is not controlled and any oil discarded into them will flow directly into and contaminate receiving bodies of water. The environmental impact will vary greatly depending upon local conditions. In the case of oil discharged into combined sewers, the oil loading and that of specific compounds may well impact on the-end-of-pipe treatment system. EPA is actively engaged in evaluating the effect of conventional and priority pollutants on the performance of publicly-owned treatment works (POTWs). Reportedly, 50 percent of secondary treatment plants achieve roughly a 75 percent reduction of the priority pollutant metals and organics in the influent.[7]

OBJECTIVES OF LABORATORY SIMULATIONS

Two simple laboratory experiments were conducted to determine the partitioning of specific used oil contaminants in particulate-ladened water and in water alone. The principal objectives were to assess the role of particulates in the transport of oil and its contaminants, and to identify water-soluble constituents and their concentration levels resulting from sewer disposal of used oil. These data, in conjunction with other data in the literature, could then be used to assess the impact of used oil sewer disposal on POTWs.

LABORATORY SIMULATION PROCEDURES

Two similar experiments were conducted. In one, 200 ml of the COMPOSITE used oil, 200 ml of distilled water and 20 g of the soil taken from a local roadbed were mixed in a 1 liter reaction flask outfitted with a mechanical Teflon stirrer for 8 hours. The oil/water/soil mixture was then allowed to separate in a separatory funnel. The water phase, containing most of the particulate, was filtered before being submitted for chemical analysis. The particulate matter collected on the filter was dried for 24 hours, then extracted with methylene chloride. The extract and a methylene chloride extract of the water phase were weighed following room temperature evaporation of the methylene chloride to determine the weight of the methylene chloride-soluble organics associated with the particulate matter and that dissolved in the water phase.

In the second experiment 100 ml of the COMPOSITE used oil was added to 1000 ml of distilled water and gently stirred for 24 hours in a flask using a magnetically operated Teflon stirrer. The water was separated from the oil in a separatory funnel, extracted with methylene chloride and analyzed for total organics gravimetrically after room temperature evaporation of the methylene chloride, and for specific organics by the methods described in Appendix B. The procedure is similar to that attributed to Anderson, et al.[8] as a means of determining the water-soluble fraction of petroleum products.

RESULTS OF LABORATORY SIMULATIONS

The results of the first experiment, in agreement with other studies such as that described in Reference 5, show that most of the oil (approximately 90 percent) which is found in the water phase is associated with the particulate matter in the water. This association with particulate matter is generally responsible for the increased hydrocarbon loading found with increases in sewer flow rates.[5,9] The implications are that the upgrading of primary particulate control technologies employed at wastewater treatment plants can be an effective means of reducing organic loadings to the POTW.

The water soluble fraction of the COMPOSITE waste oil consists of a number of organic compounds as shown in Table IV-1. The concentrations of these compounds are those resulting from the conditions of laboratory simulation; actual concentrations will be dependent upon sewer loading, dilution and other factors. The compounds found are similar for both experiments. However, the number and the concentrations of compounds found in the water phase were generally less in the second experiment, probably reflecting the differences in experimental conditions, e.g., the oil/water ratios, the intensity of mixing and the presence of particulates. Total organic concentrations were less than 20 mg/l and compounds identified were phenol, naphthalene, and toluene. None of the higher molecular weight PNA compounds were detected at levels greater than the detection limits of about 0.01 ppm. The results are consistent with those described in the literature.[10,11]

CONCLUSIONS AND RECOMMENDATIONS

The concentration levels of water-soluble organics and elements found in this study would suggest that discharge into sewers served by secondary treatment plants would result in little or no adverse impact. The concentration levels of organics found are well below those suggested as being harmful to POTW operation,[12] e.g., <100 µg/g oil and grease content. Water-phase inorganic concentration levels do not appear to be of major concern. The contaminant loadings of concern in POTW treated sewer systems appear to be those associated with particulates. Although primary treatment measures such as sedimentation reportedly reduce particulate loadings by 50 percent, the reduction in particulate associated with the oil influent is unknown. Presumably oil removal will be a function of particle surface area rather than volume or weight; thus, oil removal efficiencies of 50 percent will not be achieved by sedimentation. Further work to clarify the role of particulates and the effect of particle size distribution in oil transport is recommended. This information is needed to assess the possibility of reducing the oil influent to subsequent treatment operations by upgrading primary treatment particulate control measures.

Only 25 percent of the urban population is served by combined sewer systems using effective primary and secondary treatment plants.[6,14] The remaining 75 percent of the urban population is served by storm sewer systems or live in unsewered areas.[13] Storm water discharged from storm sewer systems will generally receive no treatment whatsoever. Because the concentrations of some of the contaminants shown in Table IV-1 exceed the EPA suggested concentration goals for stream discharge (notably 5.0 µg/l for phenol),[15] storm sewer disposal of used oil represents a practice which is potentially harmful to the large urban population living in areas which are downstream of storm water discharge points.

TABLE IV-1. CONTAMINANT LEVELS IN AQUEOUS PHASE OF OIL/WATER MIXTURES

	Sample		
Contaminant	COMPOSITE oil (μg/g)	Experiment 1 aqueous phase (mg/1)	Experiment 2 aqueous phase (mg/1)
Organics			
Volatiles			
1,1,1-Trichloroethane	1,500	<1	<1
Trichloroethylene	2,000	<1	<1
Tetrachloroethylene	670	<1	<1
Benzene	70	<1	<1
Toluene	2,800	<1	2
Semivolatiles			
Phenol	11	11.0	1.2
2,4,6-Trichlorophenol	40	2.0	< 0.01
N-Nitrosodiphenylamine	120	1.0	< 0.01
Naphthalene	440	1.4	< 0.002
Phenanthrene/Anthracene	150	< 0.01	< 0.01
Pyrene	60	< 0.01	< 0.01
Benzo(a)pyrene	<10	< 0.01	< 0.01
Pesticide 4,4'-DDE	90	0.5	< 0.01
PCB (Arochlor 1260)	34	< 0.1	< 0.01
Inorganics			
Arsenic	8	< 0.03	< 0.05
Barium	61	0.01	0.003
Cadmium	1	0.02	0.001
Cobalt	1	< 0.00	< 0.003
Chromium	8	< 0.01	< 0.01
Copper	34	< 0.01	< 0.01
Iron	210	2	0.5
Lead	1,090	< 0.02	< 0.02
Magnesium	210	1.6	0.5
Manganese	14	0.01	0.2
Nickel	4	< 0.01	< 0.01
Selenium	< 1.0	< 0.02	< 0.02
Silver	< 0.1	< 0.001	< 0.001
Zinc	730	0.3	0.9

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SECTION V

ROAD OILING SCENARIO

BACKGROUND

Used oil is often applied to rural dirt roads as a dust suppressant by local government agencies or by industries which operate and maintain their own private roads. The practice, once prevalent, is declining for a number of reasons including a decrease in the number of dirt road miles; the availability of substitutes that can be used as dust suppressants; and regulations, based on potential environmental impacts, either banning road oiling or limiting contamination of the used oil with components such as lead or chlorinated hydrocarbons. An early estimate[1] of about 200 million gallons per year of waste oil used for road oiling developed in 1969 has been revised downwards by EPA to a value of about 125 million gallons in 1982.[2] Of this total, it was estimated that 95 million gallons were applied commercially by highway agencies, with the remaining 30 million gallons applied by private road owners. However, it would appear that far less oil is used for road oiling than has been estimated by EPA. A total of only 24 million gallons per year was accounted for in an ongoing study[3] conducted for EPA which involved a comprehensive state-by-state survey of road oiling practices in the United States. According to this survey, road oiling activity is banned in 8 states and formally regulated in 13 other states. Given omissions in the data base, a value of 50 to 80 million gallons per year was estimated as the total for road oiling. The wide range given shows that even this well-documented estimate is only an approximation. Nevertheless, the potential for pollution is appreciable; this estimate is roughly 5 percent of the total used oil generated in the United States.

There is a concern that contaminants in road oil can contribute to the impairment of the health of participants engaged in road oiling activities, road users, or others nearby due to vaporization of some of the volatile components. Another concern is the possibility of contamination of ground and surface waters. These concerns have been heightened by recent incidents in which highly toxic materials such as PCBs and dioxins have been detected in waste oil used for road oiling. The fate of contaminants in used oil is dependent upon a multitude of factors relating to soil, meteorology, road traffic, and oil properties. Very little data exist in the literature with regard to the transport of waste oil contaminants following application to a road surface. Only two studies[4,5] have been conducted which attempted to measure the fate of contaminants following road oiling. The EPA study reported that only about 1 percent of the oil applied to dirt roads over extended periods (approximately 12 years) is retained on the road surface. This same study further determined experimentally that 7 to 18 percent of the oil is lost through evaporation and that 10 to 20 percent of the oil is lost through rainfall runoff, with most runoff occurring during the first rains following application. Although no data were available, it was suggested that other factors such as biodegradation and reentrainment of oil-coated particles by road traffic could account for a large fraction of the long term oil transport from the road surface. Direct penetration of oil beneath the first few millimeters of road surface did not appear to be a major factor.

Similar semiquantitative observations were provided by the California study. The California study concentrated on the fate of heavy metals and PNAs after application to a dirt road surface. Lead and zinc were found to be the metals of primary concern in the oils. Anthracene, benz(a)anthracene, pyrene, and benzo(e)pyrene were found in significant quantities in the oils and selected for analysis in road and soil samples. The results of the study revealed that volatilization, adhesion to vehicles, and biodegradation accounted for 25 to 30 percent of the oil leaving the roadway while runoff and windborne dust particles account for the remainder. Solubilization of many elements under acidic conditions was felt to contribute to the effect of runoff as a transport mode. The work, in general, confirms this study's observations that penetration of contaminants downward through the soil is minimal and that very little PNA material is lost through solubility of these compounds in water. However, despite the existing and present study efforts, further work, as noted below, is needed to fully assess the transport modes of the oil and its constituents and the environmental impact of road oiling.

The environmental impact of volatile air emissions resulting from road oiling is now being assessed under EPA-sponsorship by Franklin Associates Ltd. in conjunction with a research group from PEDCo Environmental Services. Data from this and other studies are being used by the Franklin/PEDCo team to model transport of volatile components and estimate ambient concentrations and resulting impacts.

OBJECTIVES OF LABORATORY SIMULATIONS

Upon consideration of many approaches that could be used to experimentally assess the transport of contaminants in used oil following road oiling, it became apparent that adequate simulation would require extensive experimentation involving many parameters associated with oil, soil, traffic, and meteorology. Because such an extensive study, either in the laboratory or in the field, was not possible, a simple experiment was designed to examine some of the conclusions reached in the earlier studies, and, in addition, to identify the compounds transported from the surface by rainfall. Thus, an experiment was designed using soil panels (roadbeds) that were oiled and exposed to outdoor weathering followed by chemical analysis of the oil and water streams resulting from the penetration and runoff of naturally occurring rainfall.

LABORATORY SIMULATION PROCEDURES

An experimental setup similar to that described by Freestone[4] was used to determine the contaminants present in the rainwater runoff from and that penetrating into simulated oiled roadbeds. One roadbed was prepared from a gravel soil taken from a local dirt road; the other roadbed was prepared from the same soil to which 5 percent bentonite was added. The bentonite was added to reduce water penetration into the soil, thus increasing the potential for transport of the oil with rainfall runoff.

The experiments were conducted in equipment shown schematically in Figure V-1, consisting of two concentric circular containers 2 and 2-1/2 feet in diameter, respectively. A fine mesh stainless steel screen supported on a perforated stainless steel plate separated the inner vessel into two approximately 6-inch deep compartments. The separator retained the soil comprising the roadbed in the upper compartment but allowed water penetrating the soil to enter the lower compartment. Two valves were installed in the lower compartment to facilitate breathing and drainage of penetrating rainfall. Runoff from the crowned (approximately 1-1/2 inches at the center) surface of the roadbed was collected in the outer container.

The roadbed was prepared by compacting the soil to an apparent specific gravity that was shown in a previous series of column permeability experiments, conducted inhouse, to favor runoff rather than penetration. The permeability experiments involved preparing a soil column of known apparent specific gravity in the lower portion of a 2-inch diameter lucite cylinder, adding a constant head of water to the cylinder above the soil column, and measuring the rate of penetration of water into the soil. The rate of penetration decreased as the apparent specific gravity of the soil increased. (Addition of bentonite to the soil also decreased penetration). The apparent specific gravity of the simulated roadbed used in the experiment was approximately 1.8, although large local variations were undoubtedly present due to the gravel-like size distribution of the soil and the method of compaction. In preparing the bed, a weight of soil sufficient to achieve the desired 1.8 specific gravity, given the known volume of the compartment, was added to the container at intervals and compacted manually by tamping with a weighted cylinder. Density of the crowned surface was similarly approximated.

The used COMPOSITE oil was applied to the surface of the roadbed using a small spray can applicator at a level of 0.05 gallons per square foot, a value suggested by Freestone[4] as typical of road oiling practice. The panels were then conditioned for 3 days in a well-ventilated area at a surface temperature of about 100°F to allow volatiles to evaporate before the panels were placed outside. A weight loss of 12 percent was measured on a smaller test panel that was similarly exposed. Rainfall occurred on the third day of outdoor exposure with a water equivalent of 0.68 inches recorded in a 24-hour period. The water was removed from the outer and lower inner compartments following this rainfall and saved for analysis. Rainfall occurred on seven other occasions during the 30-day exposure period (total rainfall was approximately 3.2 inches) and was similarly collected. At the conclusion of the exposure

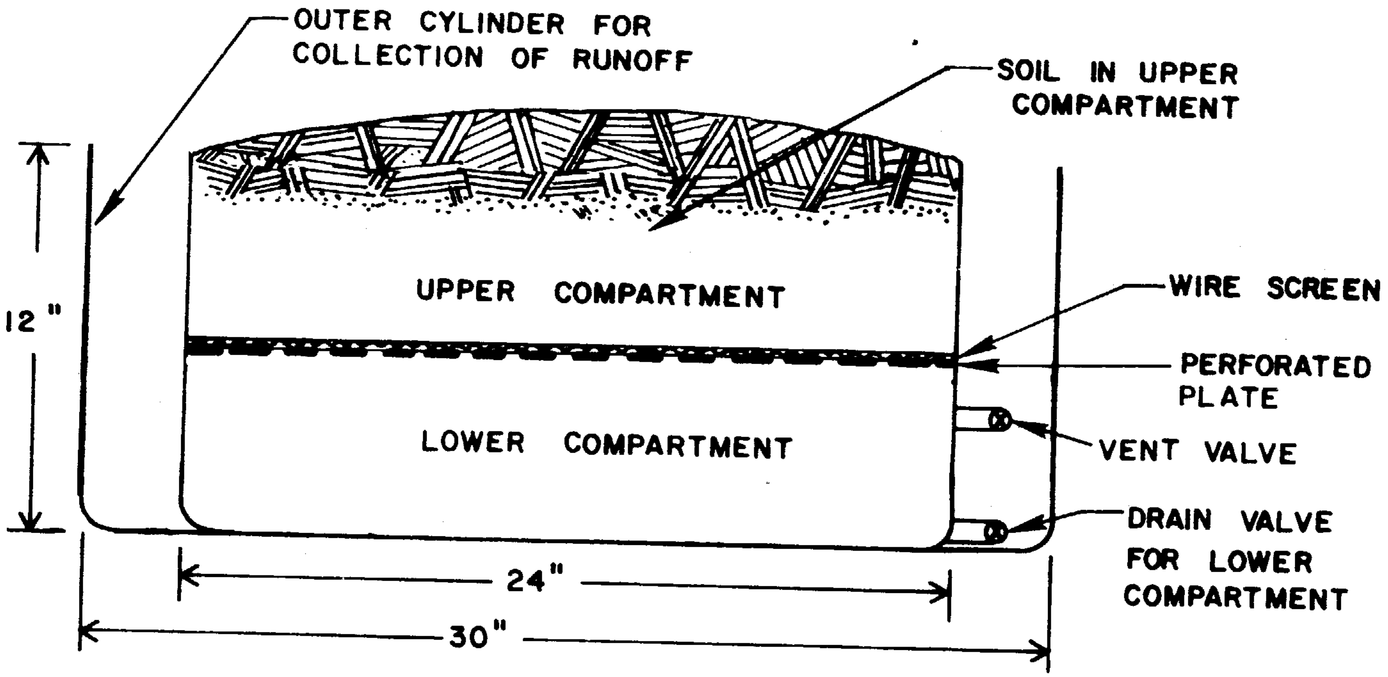

Figure V-1. Schematic of equipment for collection of rainfall impacting upon a simulated roadbed.

period the oil content of the soil was determined gravimetrically as a function of depth in the bed. A weighed quantity of soil, troweled from the surface to a given depth, was extracted with methylene chloride. The extract was then reduced in volume, transferred to a tared aluminum weighing dish, evaporated in a clean fume hood until visually dry, stored overnight in a desiccator, and then weighed to the nearest 0.1 mg to determine oil content. Water samples from the runoff were composited, and along with runoff from an unoiled surface (blank), were submitted for analysis. Only the runoff from the gravel soil (without bentonite) and the blanks were analyzed.

RESULTS OF LABORATORY SIMULATIONS

The results indicate that in addition to oil lost by evaporation (initially 12 percent) another 3 to 5 percent is lost by runoff. Measured runoff loss was 3 to 4 times less than the 10 to 20 percent found in the EPA study,[4] probably resulting from differences in soil density and configuration, namely, the crowning of the surface. Almost all of the oil left in the soil was retained within a few millimeters of the surface. The oil concentration, as measured at the surface by methylene chloride extraction of the top few millimeters of the soil, was 35,000 μg/g; the concentration fell to a value of about 1,000 μg/g at a depth of 1 cm. Below a depth of 1 cm the organic content of the soil was indistinguishable from the background level of the untreated soil (approximately 50 to 100 μg/g).

The used oil constituents in the runoff were associated primarily with soil (particulate) that was entrained and carried from the surface to the outer collection vessel. The water-soluble organic fraction, present at a concentration of only 4 to 6 mg/liter in a total volume of about 25 liters, as determined gravimetrically from a methylene chloride extract of the filtered runoff, represented about 1 percent of the total oil lost by runoff. Rainwater penetration into the lower compartment of the roadbed containment cylinder represented 20 percent of rainfall impacting on the gravel roadbed and only 3 percent of that impacting on the soil to which bentonite was added. In both cases the contamination level of water soluble organics in the rainwater was similar to that found in the runoff water, 4 to 6 mg/liter. The oil lost through water transmitted through the soil was very small, less than 0.1 percent of that lost by runoff (0.02 to 0.2 percent). The distribution of oil in the various streams is summarized in Table V-1, along with information concerning the total rainfall and its distribution in the collection equipment.

Laboratory analyses of the water samples for 27 elements were conducted using ICAP. Organic pollutant analyses were conducted on the water samples using the procedures described in Appendix B.

The results of the elemental analyses shown in Table V-2 indicate that the transfer of some elements from the oil applied to the roadbed to the runoff is small but possibly significant. Assessment of the data shown in the table is difficult because of the lack of temporal data (transfer as a function of time) and the possible influence of external contributions to the concentrations in the runoff. These external factors include sodium in rainfall (and other elements as well at the test location near Boston), pH of

TABLE V-1. DISPOSITION OR FATE OF OIL FOLLOWING APPLICATION TO THE SIMULATED ROADBED SURFACES

Fate of used oil	Percent of total oil applied* Roadbed soil	 Roadbed soil with 5% bentonite
Evaporation	>12	>12
Rainfall runoff		
Insoluble	2.7	3.5
Soluble	0.03	0.04
Rainfall penetration		
Insoluble	Neg.	Neg.
Soluble	0.006	0.001
Remaining in soil	~85	~84

*530 grams of oil applied: total volume of rainfall over exposure period was ~29 liters per panel, with ~25 liters collected from outer cylinder enclosing roadbed soil panel and ~28 liters from cylinder enclosing bentonite containing soil.

TABLE V-2. ELEMENTAL TRANSFER FROM OILED ROADBED TO RAINFALL RUNOFF

Element	Concentration of oil as applied (μg/g)	Weight applied (μg)	Concentration in runoff* (μg/g)	Weight in runoff (μg)	% of weight applied found in runoff
<u>ICAP Analysis</u>					
Aluminum	31	16,700	1.0	25,000	149
Antimony	0.6	320	<0.01	-	-
Arsenic	8.1	4,370	<0.03	-	-
Barium	61	32,900	0.005	125	0.4
Beryllium	<0.1	<55	<0.0012	-	-
Boron	6.2	3,350	<0.004	-	-
Cadmium	1.3	700	0.001	25	4
Calcium	990	535,000	0.6	15,000	3
Chromium	7.7	4,160	<0.003	-	-
Cobalt	0.8	430	<0.003	-	-
Copper	34	18,400	<0.002	-	-
Iron	214	116,000	0.5	12,500	10
Lead	1,090	589,000	<0.02	-	-
Magnesium	212	115,000	0.35	8,750	8
Manganese	14	7,600	0.02	500	7
Molybdenum	3.2	1,730	<0.002	-	-
Nickel	3.7	2,000	<0.005	-	-
Selenium	<1	<550	<0.02	-	-
Silicon	40	21,600	0.6	15,000	70
Silver	<0.1	<55	<0.001	-	-
Sodium	257	139,000	3.8	95,000	68
Strontium	1.9	1,030	0.005	125	12
Thallium	<1	<550	<0.04	-	-
Tin	16	8,640	<0.03	-	-
Titanium	7.8	4,200	0.002	50	1
Vanadium	4.1	2,210	0.005	-	-
Zinc	740	400,000	0.16	4,000	1

*Blank corrected for runoff from unoiled surface: elemental content μg/ml ≅ μg/g

- = Indeterminate; "less than" concentration values could range anywhere from 0 to the given detection limit rainfall, (pH measurements at a nearby location over the same period of time ranged from 4.1 to 4.5), leachates from the soil and its impurities, and windblown contaminants and dustfall.

The results of the organic analyses of the road oil and the rainfall runoff are shown in Table V-3. The major organic constituent of the rainfall runoff appears to be phenol present at levels in excess of recommended environmental goals (5 μg/l).[6] However, many of the comments made above with regard to the significance of the elemental content of the runoff, apply as well to the significance of the other organic components in the runoff. Most of the organics present in the road oil are present in the runoff, if at all, at concentration levels of less than 10 μg/l. Given the ppm concentration levels of compounds such as benzo(a)pyrene and PCBs in the oil applied to the soil, it is doubtful if they are present (in the combined volume of about 25 liters of rainfall runoff, which is approximately 50 times that of the oil applied to the surface) at the ppb level. Nevertheless, the absolute values cannot be determined from the data in Table V-3.

CONCLUSIONS AND RECOMMENDATIONS

The experiments described above are in agreement with semiquantitative observations by EPA and the California study group concerning the transport of used oil from road surfaces. However, the analytical results for specific elements and organic compounds were inconclusive and merely confirm literature observations concerning the limited solubility of major oil components in water. Although the results tend to indicate that the environmental impact of road oiling is not severe, several cases of severity have resulted from road oiling with highly contaminated oils. More work is needed to assess the potential hazard. Given the wide variety of possible local conditions a worst case situation could be assessed, given certain assumptions concerning, for example, the effect of traffic on transport of the oil from the surface of the roadbed and the partitioning of specific compounds in the water phase. Full scale road tests also would be useful in defining the cause of transport and the range of contamination.

There is still a need for carefully controlled laboratory simulation studies to determine the extent of partitioning of key elements and organics between the roadbed surface and rainfall. Rainfall simulation or cylinder permeation studies using rainfall (rather than distilled water because of pH effects) could be used to follow the transfer over time of contaminants (and spikes) from and to carefully characterized soils, oils, and rainwaters. External influences associated with dust and windborne contamination could be avoided and experimental factors adjusted to closely define the sources of contamination within each media.

TABLE V-3. ORGANIC COMPOUND TRANSFER FROM OILED ROADBED TO RAINFALL RUNOFF

Contaminant*	Concentration of oil as applied (μg/g)	Weight applied (μg)	Concentration in runoff** (μg/g)	Weight in runoff (μg)	% of weight applied found in runoff
Phenol	11	5,870	0.6	15,000	>100
Chlorophenol	40	21,400	0.2	5,000	23
2,4,6-trichlorophenol	40	21,400	<0.01	-	-
Nitrobenzene	30	16,000	0.02	500	3
N-nitrosodiphenyl amine	116	62,000	<0.01	-	-
Naphthalene	440	235,000	<0.01	-	-
Phenanthrene/ anthracene	150	80,100	<0.01	-	-
Pyrene	60	32,000	<0.01	-	-
Benzo(a)pyrene	10	5,300	<0.01	-	-
Dibutylphthalate	60	32,000	0.02	500	2
Pesticide:4,4'-DDE	94	50,200	<0.01	-	-
PCBs (Aroclor 1260)	34	18,000	<0.01	-	-

*Volatile compounds not detected

**μg/g ≅ mg/l

- = Indeterminate; "less than" concentration values could range anywhere from 0 to the given detection limit

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SECTION VI

COMBUSTION OF WASTE OIL IN COMMERCIAL COMBUSTION SYSTEMS AND SMALL SPACE HEATERS

INTRODUCTION

The amount of waste oil collected and sold as a fuel was estimated in Section III at 460 to 640 million gallons per year. To improve this estimate and assess the impact of waste oil combustion, the EPA is now conducting survey studies to inventory the generators and collectors/recyclers of used oil and to evaluate the environmental impact of used oil combustion emissions through a number of sampling and analysis programs and associated modeling studies.[1]

Up until now there has been no comprehensive survey of United States facilities burning used oil, although it is reported that most of the used oil is blended with virgin fuel and burned in steam boilers. Reportedly 95 percent of the fuel is burned in boilers with thermal heat inputs in excess of 5×10^6 Btu/hr (approximately 35 gallons/hr).[2] However, in the absence of more definitive information it would appear that potentially smaller sources such as those in apartment houses, greenhouses, warehouses, and service stations consume a significant fraction of the waste oil used as fuel. The sharp increase in the cost of fuel oil in recent years has definitely resulted in an increase in waste oil consumption in small space heaters specifically designed for combustion of waste oils.[3,4]

It has been noted with some concern that current RCRA regulations [40 CFR 261.2(c)(2)] specifically exempt facilities that burn waste in energy-producing operations from complying with rules regarding the incineration of wastes. These rules require that a 99.99 percent removal efficiency be achieved for the principal organic hazardous constituents (POHCs) found in the waste to be incinerated. Boilers and space heaters are not required to comply with this destruction requirement. However, the inadvertent blending of potentially harmful organics in waste oil and the considerable number of recorded incidents indicating that waste oil and other petroleum products are being deliberately used as carriers for known hazardous compounds such as PCBs have raised serious questions about this exemption. These questions have led, among other things, to studies concerning the effect of furnace and boiler size and type upon destruction efficiency and environmental impacts. Although emissions of elements such as lead and most other contaminants will increase directly with combustion system fuel feed rate, other factors must be considered in assessing the environmental impact of organic emissions and their relationship to boiler size and type. Combustion efficiency and products of combustion associated with the contaminant destruction variables of time, temperature and turbulence are factors about which little is definitely known.

To illustrate some of the differences associated with size, it is often assumed that operators of larger boilers generally would efficiently pretreat the oil prior to combustion, would use blends of fuel oil and used oil (due to limited availability of waste oil and potential maintenance problems), would have the analytical capability (or finances) required to identify troublesome contaminants prior to combustion, would tend to provide the conditions of time, temperature, and turbulence necessary for efficient combustion (and destruction of potential hazardous contaminants such as polychlorinated biphenyls (PCBs) which have been detected in used oils), and would discharge emissions from relatively high stacks. Conversely, operators of smaller units, and particularly small space heaters of the type investigated in this study (approximately 250,000 Btu/hr heat input), generally would use untreated or marginally treated and poorly characterized oils, would use unblended oils, would provide less efficient combustion and thus possibly emit significant amounts of hazardous contaminants, and would emit stack effluents at low levels close to human receptors. All of the above factors, supported in at least a qualitative fashion by the existing data base discussed in the following subsection, contribute to the concerns expressed about combustion of waste oil in small systems, and led to the selection of the test activities included in this program.

EXISTING DATA BASE

The data base dealing with the combustion of waste oil in oil-fired combustion systems of all sizes and types is limited, particularly with regard to organic compound emissions. Most environmental studies have focused on the impacts associated with the emissions of lead and other trace elements, with lead of major environmental concern because of its presence in relatively high concentrations in used automotive oil.[5] Despite the limited nature of the data base, existing data, in conjunction with a fairly large body of data dealing with emissions resulting from combustion of conventional fuel oils, can be used to estimate lead and other trace element emissions from waste oil combustion with reasonable accuracy.[6] At a minimum, worst case conditions can be evaluated by assuming lead and all other inorganic elements in the fuel are quantitatively emitted with the flue gases. Such is not the case with organic compound emissions. Existing organic emissions data are sparse for both virgin and waste fuels and the chemical analysis of the large number of potentially harmful compounds that could either be emitted directly as an uncombusted component of the fuel or as a product of incomplete combustion is extremely difficult. Available analytical data are subject to uncertainty with regard to completeness and accuracy of results.[6] The available data does indicate that both thermal destruction and the formation of combustion byproducts are dependent upon fuel composition and boiler size and efficiency. As noted previously, the growing use of waste oil in smaller units is of concern because of the possibility of less efficient combustion and the proximity of discharge to human receptors. These concerns have been heightened by recent evidence indicating that waste oil is being used as a vehicle for other, more hazardous wastes. As a result of these concerns several recent programs, of which this program is one of the first, have been instituted to study organic compound emissions from combustion units. Some of these studies and the available data base are identified in the following discussion.

Large Boilers

There is a small but reasonably definitive body of data dealing with the combustion of waste oil (typically waste oil/fuel oil blends) or fuels containing organic materials such as PCBs in large industrial or utility boilers. For purposes of this discussion, large boilers are defined as those with a heat input rate greater than 25×10^6 Btu/hr. This size definition is not completely arbitrary because it eliminates from this size classification almost all cast iron and firetube systems. Thus, large boilers, as defined here, will consist almost entirely of watertube boilers.[7] Preliminary results of EPA studies indicate that many of these units appear to have sufficient combustion chamber temperatures and residence times to achieve substantial destruction of waste components in used oils.[8,9] This observation will be further evaluated by an EPA program, instituted in 1982 to study thermal destruction of specific organic contaminants in large boilers as a function of boiler time, temperature, and turbulence. Mathematical models will be developed to predict thermal destruction and the models will then be checked with data from a companion sampling and analysis program for hazardous waste co-firing with virgin fuel in industrial boilers.[9] The data obtained from this EPA program will add considerably to the existing data base.

Available data shown in Table VI-1 includes that from test burns of waste oils and contaminated fuels. Data are also available from a Chemical Manufacturers Association (CMA) survey of 20 boilers burning chemical waste materials.[15] Organic compound destruction efficiencies reported in this (CMA) study were in the 99 to 99.99 percent range, although values as low as 97 percent were reported.

It has been suggested that a decrease in combustion efficiency is likely to occur when waste materials are substituted for fuels, implying that the thermal destruction of waste materials can approach but will probably not exceed thermal destruction levels for fuels.[8] In the case of difficult-to-burn materials, such as chlorinated hydrocarbons, destruction efficiencies may be well below these levels. Examination of data dealing with hydrocarbon emissions from 10 oil-fired utility boilers and 12 large industrial and commercial watertube boilers indicate that on the average 99.98 percent of the fuel is fully combusted.[6,16,17] This value is comparable to that calculated from AP-42 hydrocarbon emission factors.[18] Values as low as 99.93 were measured in these recent combustion measurement programs, with 99.99 percent combustion met or exceeded by four of the utility boilers and nine of the industrial and commercial units. The data indicate that achievement of

TABLE VI-1. SUMMARY OF AVAILABLE DATA FOR ORGANIC COMPOUND AND LEAD EMISSIONS FROM LARGE UNCONTROLLED BOILERS

Combustion source	Operating load (10^6 Btu/hr)[a]	Type of virgin fuel	Percent and type of waste oil	Destruction efficiency for organics (%)	Lead emitted (%)	Ref. No.
Shell Oil	63	No. 6 fuel oil	75 percent used automotive oil	-	31	10
Hawaiian Electric Co.	210	No. 6 fuel oil	7.5 percent used automotive oil	-	27	5
Northeast Utilities, Middletown Station	-	No. 6 fuel oil	PCB-contaminated waste oil	-		11
Continental Can Co. Hopewell, Virginia	-	No. 6 fuel oil	PCB-contaminated waste oil	99.1-99.8	-	11,12
Florida Power and Light Co., Sanford, Florida	-	No. 6 fuel oil	60-80 percent PCB	99.999		11,12
Duke Power Co., Riverbend Station	-	No. 6 fuel oil	PCB-contaminated waste oil	99.92	-	11
General Motors Corp. Bay City, Michigan	35	No. 6 fuel oil	PCB-contaminated waste oil	99.99	-	13
Union Electric Co., St. Louis, Missouri	-	No. 6 fuel oil	PCB-contaminated mineral oil	99.99[b]	-	14
Washington Water and Power Co., Spokane, Washington	-	No. 6 fuel oil	500 ppm PCB in mineral oil	-	-	14

[a] One million Btu/hr (MBtu/hr) is equivalent to 1.05 GJ/hr.

[b] Preliminary results.

99.99 percent destruction efficiency for potential hazardous contaminant will not always be possible and individual tests (or modeling) must be conducted to determine performance.*

With regard to lead emissions the two studies shown in Table VI-1 indicate that only about 30 percent of the lead in the waste oil is emitted with the flue gas. EPA has also conducted tests of lead emissions from large boilers and uses an emission factor of 50 percent of the lead concentration in the fuel. Lead not emitted is reportedly deposited on the boiler internal surfaces and is removed either by sootblowing, if practiced, or during cleaning. No problems with boiler operation have been cited as a result of this internal deposition of lead and possibly other elements resulting from used oil combustion.

The concern about lead emissions from waste oil combustion is related to the high lead concentrations in automotive waste oil. An average value of approximately 1100 ppm for waste oil was found in this study compared to average values of roughly 3.5 ppm and 0.35 ppm for residual and distillate fuel oil, respectively.

Lead (and zinc) emissions from oil-fired boilers are largely submicron in size.[5] As a result only high efficiency control devices such as fabric filters and electrostatic precipitators can be expected to effectively (99 percent) capture these particulate emissions. A high efficiency Venturi scrubber would achieve perhaps 85 percent efficiency for particulates 0.5 μm in diameter with 50 percent efficiency or less obtained by most particulate scrubbers.[19] A recent test of a dual alkali controlled oil-fired industrial boiler reported an overall particulate efficiency of 83 percent.[19] Data were not available for lead emissions but the efficiency of control would not exceed the 83 percent figure. Although reduction of lead emissions is desirable, it should be noted that only about 20 percent of oil-fired utility boilers are controlled at an average 50 percent efficiency and less than 10 percent of industrial boilers are controlled at all. The above control application data, although somewhat outdated since they represent data obtained in the early 1970s, were determined from information available in the NEDS, EPA's National Emission Inventory Data Base.[6,16]

Small Boilers/Space Heaters

The existing data base for the emissions of organic compounds and lead and other trace elements is even more limited for small combustors than that for the large boilers. Recent literature includes tests for lead emissions from a 20 x 10^6 Btu/hr firetube combustion unit [20] and EPA-sponsored tests of two

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*It should be recognized that the relationship between hydrocarbon emissions and organic compound destruction is unclear. Research efforts currently underway are attempting to correlate destruction efficiencies with factors such as ignition temperatures, bonding strengths, and ionization potentials.

space heaters; a vaporizing unit and an air-atomizing unit.[3,4] These studies and others are included in Table VI-2. The results of the EPA study will be discussed in conjunction with the results of this study in a later subsection.

As shown in Table VI-2, lead emissions generally correspond to less than 50 percent of the lead in the fuel feed. An exception was noted in the EPA test of the air-atomizing space heater where close to 100 percent of the lead in a truck crankcase oil fuel was found in the flue gas. As expected, the vaporizing unit emitted far less of all elements found in the fuel, with roughly 10 percent of the lead being emitted.

Almost without exception, emissions from small boilers and space heaters will not be controlled. However, long term ambient lead concentration levels measured at the commercial boiler site tested in this study indicated that lead emitted from the source contributes less than 0.1 $\mu g/m^3$ quarterly to downwind concentrations. These results have been interpreted to indicate that it is possible to consider waste oil combustion as a viable disposal option, even from sources where flue gas emissions are uncontrolled. It should be noted that approximately 20 percent of the lead in the waste oil as received is removed by the facility's pretreatment system using settling, filtration, and magnetic separation prior to combustion.[20]

The EPA study indicated that burner design has a marked effect on trace element emissions with the vaporizing unit retaining most of the trace elements with the pot residue. In contrast, several elements were emitted from the atomizing unit well in excess of their Threshold Limit Values.[23] These levels are of particular concern because of their discharge generally from short stacks and, thus, potentially in close proximity to human receptors.

Organic emission data are extremely sparse. The EPA tests of the two space heaters did include some speciation of organics by liquid chromatography fractionation, infrared analysis, and low resolution mass spectroscopic analysis. The presence of significant quantities of PNA materials in the flue gases of the vaporizing unit and in the vaporizing pot residue was indicated. The finding of high PNA levels was confirmed in one run of the vaporizing unit used in this study, as will be discussed in following subsections.

Total organic emissions as measured in the EPA study were similar to those of conventional oil burners. Although the EPA emission factors given in AP-42[18] are similar for all oil-fired combustion systems, independent of size, most studies have indicated that total hydrocarbon emissions are somewhat higher for the smaller firetube units than those from larger watertube boilers.[16,17,24,25] Maximum concentrations were 2 to 3 times higher for the firetube units.[25]

TEST PROGRAM COMBUSTION EQUIPMENT AND FUEL

A sampling and analysis program was conducted to determine the extent of trace element emissions and to identify and quantify the emissions of organic

TABLE VI-2. SUMMARY OF AVAILABLE DATA FOR ORGANIC COMPOUND AND LEAD EMISSIONS FROM SMALL BOILERS AND SPACE HEATERS

Combustion source	Operating load (10^6 Btu/hr)[a]	Type of virgin fuel	Percent and type of waste oil	Destruction efficiency for organics (%)	Lead emitted (%)	Ref. No.
Mobil Oil Co.	19	No. 6 fuel oil	5 percent waste oil	-	50	10
Gulf Oil	0.44	No. 2 fuel oil	25 percent waste oil	-	28	10
Aberdeen Proving Ground, Edgewood Arsenal	5.3	No. 2 fuel oil	30 percent waste oil	-	~3	21
Esso Research and Engineering	~1	None	100 percent waste oil	-	50	22
Skidmore College, Saratoga Spring, NY	5.7 and 11.4	None	100 percent waste oil	-	50	20
U.S.EPA, IERL, RTP, NC	0.096[b] and 0.23[c]	None	100 percent waste oil	-	~10[b] 30-100[c]	3

[a] One million Btu/hr (MBtu/hr) is equivalent to 1.05 GJ/hr.

[b] Vaporizing Unit.

[c] Air-Atomizing Unit.

compounds previously reported in combustion effluents. A combination of three combustion systems and two test oils were included in this program. The three combustion systems were:

1. A 20 x 10^6 Btu/hr heat input commercial combustion system operated at 6.1 x 10^6 Btu/hr during the test period.
2. A 250,000 Btu/hr heat input space heating unit designed for burning waste oil using an air-atomizing burner.
3. A 250,000 Btu/hr heat input space heating unit designed for burning waste oil using a vaporizing pot burner.

The two oils used in the program were (1) a waste automotive lubricating oil used after pretreatment by the commercial source and (2) the spiked COMPOSITE oil used in this program. All three combustion units were sampled during operation with the first oil; only the two space heating units were tested during combustion of the COMPOSITE oil. In the latter case the collected samples were analyzed for spiked compounds, as well as other organic constituents, to determine destruction efficiencies. The results of the analyses will be presented and discussed in a later subsection.

The 20 x 10^6 Btu/hr heat input, 500 hp Cleaver-Brooks firetube unit was sampled during combustion of 100 percent waste crankcase oil. The oil is fed to the combustion unit through a system designed for settling and water removal and subsequently through a series of basket filters of decreasing mesh size containing magnetic inserts to remove additional particulates. Approximately 20 percent of the lead is removed by this pretreatment operation.[20] Following the test runs, additional oil was collected at the burner feed following pretreatment and transported back to the test facility in Bedford, MA for use in one series of runs with the space heaters. No pretreatment was used for the spiked COMPOSITE oil. A comparison of some physical and chemical characteristics of the two test oils is provided in Table VI-3.

FIELD SAMPLING AND ANALYSIS

The fuel feed rate and flue gas physical parameters measured during the two tests of the commercial boiler are provided in Table VI-4. Both the Source Assessment Sampling System (SASS) and a Method 5 train, modified to include an adsorbent (XAD-2 resin) for organic flue gas constituent collection, were used for sample collection (see Appendix A for a description of sampling equipment and methods). However, organic compound analyses were restricted to the components of the SASS train because of the much larger volume sampled and the resulting greater analytical sensitivities. Only the SASS train was used during the tests of the space heaters. Feed rates and flue gas physical parameters during these runs are tabulated in Table VI-5.

Total particulate emissions were obtained from both the SASS and the modified Method 5 train runs in the tests of the commercial unit. Inorganic

TABLE VI-3. PROPERTIES AND ELEMENTAL CONCENTRATIONS OF TEST OILS USED IN COMBUSTION TESTS

	Test oil	
Property	Waste lubricating oil[a]	Spiked COMPOSITE oil
Heating value, Btu/gal	132,800	134,600
API gravity @ 15°C	26.1	24.6
Viscosity, cSt @ 100°F	.896 46	.904 54
Water, wt %	5.0	7.1
Flash point, °F	192	180
Sulfur, %	0.44	0.43
Ash, %	0.84	0.68
Chlorine, %	0.12	0.37
Chromium, ppm	4	8
Lead, ppm	1,900	1,100
Nickel, ppm	1	4
Vanadium, ppm	<1.0	4
Zinc, ppm	1,000	730

[a] Representative Oil No. 14.

TABLE VI-4. FLUE GAS PARAMETERS DURING TESTS OF A COMMERCIAL/INSTITUTIONAL UNIT FIRING AUTOMOTIVE WASTE OIL

Parameter		SASS	Method 5
Oil feed rate, gal/hr		46	46
Flue gas temp., °F		309	317
Flue gas moisture, %		7.3	8.4
Oxygen content, %		7.5	7.7
Carbon dioxide content, %		7.5	7.6
Boiler thermal efficiency, %		82	82
Volumetric flow rate, acfm		2,830	2,540
Percent isokinetic		105	93
Particulate emissions,	gr/dscf	0.098	0.112
	lb/hr	1.52	1.53
	ng/J	108	109

TABLE VI-5. FLUE GAS PARAMETERS DURING SASS TRAIN SAMPLING OF SPACE HEATERS FIRING WASTE OIL AND A COMPOSITE WASTE OIL

Parameter	Waste oil (No. 14)		Spiked COMPOSITE oil	
	Vaporizing unit	Air-atomizing unit	Vaporizing unit	Air-atomizing unit
Oil feed rate, gal/hr	1.3	2.0	1.4	1.8
Flue gas temp., °F	405	494	428	525
Flue gas moisture, %	8.3	10.7	10.5	10.8
Oxygen content, %	9.0	6.5	8.8	6.5
Carbon dioxide content, %	10.0	12.0	8.5	12.0
Carbon monoxide content, %	0	0	0	0
Volumetric flow rate, acfm	289	243	216	248
Percent isokinetic	82	98	98	96
Particulate emissions, gr/dscf	0.0034	0.206	0.0097	0.207
lb/hr	0.0031	0.213	0.0094	0.209
ng/J	7.6	344	11.6	374

analyses of the SASS train particulate fractions and the Method 5 samples were conducted by Inductively Coupled Argon Plasma (ICAP) spectrometry. Chlorine and sulfur were determined by Parr bomb oxidation followed by ion chromatography analysis.

Organic analyses were conducted in accordance with procedures provided in Appendix B. Following methylene chloride extraction of aliquots of the particulate and XAD-2 resin, the extracted organics were concentrated and fractionated by liquid chromatography, in accordance with procedures developed over the course of the program. The fractions were analyzed by gas chromatography/electron capture detection or by gas chromatography/mass spectroscopy as described in Appendix B.

An additional integrated gas sample for fixed gases (O_2, CO, and CO_2) was collected during each sampling run. The procedures for this sampling technique are as specified in Appendix A of 40 CFR 60. The sample was collected in a Tedlar bag at a rate of 1.0 liter per minute and analyzed for O_2 and CO_2 with an Orsat Gas Analyzer. Each bag was analyzed three times as specified in the method.

RESULTS OF COMBUSTION TESTS

This section will present the results of the laboratory analyses for trace elements and specific organics compounds collected during combustion of waste oil. The results will be contrasted with other data resulting from recent studies conducted at the commercial boiler by the owners and with the space heaters by EPA at its Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. A following discussion will evaluate the data, using Threshold Limit Values and other similar measures, to assess the significance of emissions.

Commercial Combustion Unit Study Results

The flue gas parameters during the tests of this firetube unit frequently used for the combustion of waste oil have been presented in Table VI-4. Following the runs the sealed trains were transported to the GCA laboratories and disassembled using EPA-specified QA/QC procedures prior to analyses of train components.

Particulate Emissions--

Particulates collected on the filter and in the probe rinses from both the SASS and Modified Method 5 trains were conditioned and weighed to determine the particulate loading during the test period. Over 86 percent of the particulate collected by the SASS was collected by the filter with most of the remainder found in the probe rinse and only trace amounts in the cyclones preceeding the filter, indicating an average particle size of less than 1 μm. The total amount of particulate collected, the stack flow conditions, and the volume sampled were used to determine particulate emissions (see Table VI-4). In terms of emission concentration, the values obtained were about

225,000 μg/m^3 of flue gas during the SASS run and about 260,000 μg/m^3 during the Method 5 run. Tests conducted by the owners of the boiler in 1980 found loadings of about 200,000 μg/m^3.

Trace Element Emissions--

Inorganic analyses were conducted by ICAP for both SASS particulate fractions and the Method 5 particulate fractions (filter and rinses). The fractions for each unit were combined to determine the elemental emission concentrations shown in Table VI-6. The percent of lead emitted as compared to that fed to the combustion unit (as determined by the fuel feed rate and ICAP analysis of the feed) was 44 percent for the SASS run and 59 percent for the Method 5 run. Comparable values for zinc were 68 percent and 71 percent, respectively. The percent of lead emitted with the flue gas is consistent with that reported in the existing data base and comparable to the value of 52.4 percent measured by the boiler operators as the average for four runs conducted at the facility in 1980. During two of the runs conducted during the 1980 test period, the lead concentration in the flue gases was measured at 19,000 μg/m^3 and 25,000 μg/m^3. Values determined by GCA were two to three times higher (i.e., 43,000 and 65,000 μg/m^3 for the SASS and Method 5 runs, respectively). The differences in flue gas concentration are largely attributable to the difference in lead concentration of the fuel; i.e., 660 μg/g for the 1980 tests and 1890 μg/g as measured in this study. Variation in the results of the runs conducted in this study are most likely due to sample collection differences resulting from single point (SASS) versus multiple point (Method 5) sampling for the two methods.

Organic Emissions--

Organic emissions determined by analysis of the methylene chloride extract of the combined SASS train particulate fractions, XAD-2 resin and module, and the module condensate were similar to those found in the analysis of organic emissions from conventional fuels. Methods of analysis are described in Appendix B. Only a few PNA compounds were found in low concentrations; e.g., 2 to 3 μg/m^3 of flue gas for naphthalene and phenanthrene/anthracene. These two compounds were the only PNAs identified. The only other organic compounds identified were phthalates. These results are in agreement with earlier studies of conventional commercial combustion systems.[17]

Space Heater Combustion Results

The space heaters, unlike the commercial boiler, were tested with both representative oil No. 14 and the COMPOSITE oil. The SASS train was used to collect samples during four test burns of the two units using the two oils. Analytical procedures are described in Appendix B.

Particulate Emissions--

Particulate emissions as determined during the four runs, have been shown previously in Table VI-5. Flue gas particulate loadings for these runs and those obtained by EPA are summarized in Table VI-7. As indicated by the footnotes to the table the same atomizing burner/combustion system unit was

TABLE VI-6. ELEMENTAL EMISSIONS FROM THE COMMERCIAL UNIT DETERMINED BY ICAP ANALYSIS

Element	Concentration ($\mu g/m^3$) SASS train	 Modified Method 5 train
Aluminum	150	340
Antimony	1	<0.2
Arsenic	330	550
Barium	300	1,600
Beryllium	<1	<1
Boron	70	270
Cadmium	40	45
Calcium	10,000	18,000
Chromium	95	95
Cobalt	2	1
Copper	900	1,000
Iron	2,800	3,700
Lead	43,000	65,000
Magnesium	3,600	6,200
Manganese	270	330
Molybdenum	90	100
Nickel	110	55
Selenium	<1	<1
Silicon	NA	NA
Silver	<0.2	<0.2
Sodium	3,100	6,000
Strontium	30	25
Thallium	3	<1
Tin	120	220
Titanium	NA	20
Vanadium	440	150
Zinc	35,000	41,000

NA = Not Analyzed, instrumental difficulties

TABLE VI-7. PARTICULATE LOADINGS FOUND IN TESTS OF WASTE OIL SPACE HEATERS

Burner/oil[a]	Particulate loading, mg/m^3	
	GCA tests	EPA tests
<u>Air-atomizing burner</u>[b]		
No. 2 oil	-	10.3
Automotive waste oil	-	224
Truck waste oil	-	223
Representative Oil No. 14	470	-
COMPOSITE oil	470	-
<u>Vaporizing burner</u>[c]		
No. 2 oil	-	24.2
Automotive waste oil	-	18.2
Truck waste oil	-	26.7
Representative oil No. 14	8	-
COMPOSITE oil	22	-

[a] See Table VI-3 and References 3 and 4 for oil properties.

[b] Same burner used in both studies.

[c] GCA tests with Kroll Model W800L.
EPA tests with Kroll Model W400L.

used at EPA and GCA. The vaporizing burner used at GCA was a new unit rated at twice the capacity of an otherwise similar unit used in the EPA tests.

Although the flue gas loadings for the atomizing unit measured in this study are appreciably greater than those measured at EPA, there is no question that the air-atomizing unit emits an order of magnitude or greater more particulate than the vaporizing units. The average particulate size of the particles emitted by the air-atomizing space heater would appear to be somewhat greater than the average size emitted by the commercial boiler. Roughly, 50 percent of the particulate emitted by the air-atomizing unit is captured by the filter (particle size less than 1 μm diameter) with the bulk of the remainder found in the 1 μm cyclone. Variable results were obtained in the two tests of the vaporizing unit. In the first test with the No. 14 oil, 91 percent of the particulate was captured by the filter; in the second test with the COMPOSITE oil the particle size was greater, with only 25 percent reaching the filter. The reason for this discrepancy is not apparent from other test and combustion parameter data.

Trace Element Emissions--

Trace element emissions in terms of flue gas loadings in $\mu g/m^3$ are shown in Table VI-8 for this study and compared with results obtained by EPA using ICAP analysis. Although somewhat higher values were obtained in the EPA study, the results for lead and zinc are reasonable considering the trace element contents of the three oils. The EPA test oil contained about 3,300 μg of lead per gram of fuel and about 1,100 μg of zinc per gram of fuel; both elements were found in the EPA oil at appreciably higher levels than those found in the two oils used in this study (see Table VI-3).

The percent of lead in the feed to the atomizing unit that is emitted with the flue gas was measured at 81 and 74 percent, respectively, for the representative oil No. 14 and the COMPOSITE oil. Comparable values for zinc were 89 percent and 78 percent. In the EPA study, almost 100 percent of the lead was emitted with the flue gas from the atomizing unit when truck crankcase oil was burned. The percent emissions, however, dropped to roughly 30 percent when automotive oil was burned. Comparable values for zinc were about 60 and 30 percent, respectively, for tests with truck and automotive crankcase oil. In the case of the vaporizing unit, the results of this (and the EPA) study shows that almost all (approximately 95 percent) of the trace elements are retained in the vaporizing pot. Only 4 elements were emitted at levels greater than 10 percent of the amount introduced with the fuel in the two tests of the vaporizing unit. The elements were aluminum, boron, strontium, and chromium. These elements are not particularly volatile and their presence in the flue gas at higher than anticipated concentrations can most likely be attributed to experimental error.

Organic Emissions--

The results of GC/MS analysis of the semivolatile organic emissions collected by the SASS train are shown in Table VI-9. The samples, with the exception of the initial run of the vaporizing unit, are essentially free of

TABLE VI-8. TRACE ELEMENT FLUE GAS EMISSIONS FROM SPACE HEATERS DETERMINED BY ICAP ANALYSIS, $\mu g/m^3$

	Vaporizing unit[a]			Atomizing unit[b]		
Element	Oil No. 14	COMPOSITE oil	EPA test[3,4] with automotive oil	Oil No. 14	COMPOSITE oil	EPA test[3,4] with automotive oil
Aluminum	200	390	25	570	1,900	650
Antimony	3	2	-	40	40	-
Arsenic	3	13	-	700	380	-
Barium	4	90	25	3,800	1,900	1,300
Beryllium	<1	<1	-	3	4	-
Boron	130	-	670	100	-	1,960
Cadmium	<1	3	1	65	60	110
Calcium	380	2,600	25	93,000	59,000	11,900
Chromium	6	50	4,200	250	450	4,950
Cobalt	<1	7	54	5	75	70
Copper	6	30	16	1,200	2,200	2,400
Iron	20	630	15,200	5,300	19,500	22,300
Lead	280	580	1,600	97,000	51,000	144,000
Magnesium	90	-	8	14,500	-	7,000
Manganese	3	30	420	800	100	1,300
Molybdenum	3	20	250	190	210	1,300
Nickel	5	25	21	60	270	3,500
Selenium	<1	<1	<1	<1	<1	<1
Silicon	500	-	-	1,360	-	-
Silver	<1	<1	-	2	<1	-

(continued)

TABLE VI-8 (continued)

Element	Vaporizing unit[a]			Atomizing unit[b]		
	Oil No. 14	COMPOSITE oil	EPA test[3,4] with automotive oil	Oil No. 14	COMPOSITE oil	EPA test[3,4] with automotive oil
Sodium	60	170	-	4,100	14,300	-
Strontium	<1	30	<4	85	150	50
Thallium	<1	<1	7	<1	<1	7
Tin	2	30	340	230	1,400	490
Titanium	8	10	2	30	670	80
Vanadium	<1	30	<1	7	220	16
Zinc	40	250	190	56,000	40,000	66,000

[a] Kroll Model W800L (Model W400L used for EPA Test).

[b] Dravo Hastings Thermoflo Model 20-WO.

- = Emission data not determined for these elements

TABLE VI-9. RESULTS OF GC/MS ANALYSIS OF SASS TRAIN SAMPLES (μg/m^3)

Component	Vaporizing unit		Atomizing unit	
	Oil No. 14	COMPOSITE oil	Oil No. 14	COMPOSITE oil
Chlorobenzene	-	-	-	-
Bischloromethylether	-	-	-	-
Phenol	18	-	0.25	-
Chlorophenol	-	-	-	-
Dichlorobenzene	0.05	-	-	-
Nitrobenzene	-	-	-	-
Nitrophenol	-	-	-	-
Naphthalene	190	0.15	0.70	1.0
Chloronaphthalene	-	-	-	-
Trichlorophenol[a]	-	-	-	-
Acenaphthene	-	-	-	-
N-nitrosodiphenylamine[a]	-	-	-	-
Hexachlorobenzene	-	-	-	-
Phenanthrene/anthracene	160	0.21	1.6	0.15
Dibutylphthalate	-	-	0.37	0.23
Butylbenzylphthalate	3.8	-	-	-
Bis(2-ethylhexyl)phthalate	20	12	-	-
Pyrene	104	0.34	0.87	0.06
Benz(a)anthracene/chrysene	30	-	-	-
Triphenyl phosphate	-	-	-	-
Benzo(a)pyrene	30	-	-	-
Aldrin	-	-	-	-
4,4'-DDE[a]	-	-	-	-
PCBs[a]	-	-	-	-

- Not detected at levels of about 0.15 μg/m^3.

[a] Spike components.

semivolatile organics and the results appear comparable to those found for combustion of conventional fuel oils. None of the components present as spikes were detected in the flue gas at a detection limit corresponding to a flue gas concentration of 0.15 $\mu g/m^3$. The concentration of the contaminant in the flue gas can be related to its concentration in the fuel (assuming all of the contaminant in the fuel is emitted) by the following expression:

$$\text{Emission Concentration } (mg/m^3) = \text{Fuel Concentration (ppm)} \times \frac{1-4.762\ (O_2/100)}{24.04\ F}$$

O_2 is the flue gas concentration of oxygen in percent. F is the number of gram moles of dry effluent per gram of fuel burned under stoichiometric conditions. The value of F is 0.46 for an average distillate oil and 0.44 for an average residual oil. A typical F value for used lubricating oil would be in the same range; a value of 0.45 was used in the above equation to calculate the emission concentrations. Given the initial concentration in the oil feed of 34 $\mu g/g$ of oil for the PCB spike, the calculated destruction efficiency achieved at a detection level of 0.15 $\mu g/m^3$ in the flue gas is 99.993 percent. At a concentration level in the fuel of 100 $\mu g/g$ the destruction efficiency would be 99.9977 percent. Although the HCl content of the flue gas was not measured, a recent study has indicated that the chlorine present in chlorinated organic contaminants is emitted quantitatively as the acid.[26]

The one run in which high concentrations of PNAs were found, including the compound benzo(a)pyrene, was the first run of the series with the vaporizing unit. The manufacturer has suggested that the nominal break-in period of about 5 hours for the unit prior to the test was not sufficient and that excessively high heat losses may have reduced burner efficiency and led to the high organic emissions. This contention is supported by the low emissions found in the subsequent test of this unit with the COMPOSITE oil. However, the EPA study, although not quantitative in nature, also identified PNAs in the flue gases and pot residues of the vaporizing unit.

DATA ASSESSMENT AND CONCLUSIONS

Data Assessment

The emission concentrations in $\mu g/m^3$ found in the flue gas stacks of the commercial boiler and the space heaters during combustion of the used crankcase oil (representative oil No. 14) are shown in Table VI-10. To assess the significance of these concentrations, two indicators of potential environmental impact are provided in the table. The first indicator, designated as the environmental impact index, is defined as the primary national ambient air quality standard for particulates; the Threshold Limit Values (TLVs) as reported by the American Conference of Governmental Industrial Hygienists[23] for the trace elements; and as the Discharge Multimedia Environmental Goals (DMEG) values for the specific organic compounds.[27] The second measure of environmental impact, the source severity factor developed by Monsanto Research Corporation[28], was used in the emissions assessment of conventional stationary combustion systems test

TABLE VI-10. MEASURED EMISSIONS AND CALCULATED SEVERITY FACTORS FOR SOME POLLUTANTS

	Environmental[a] impact index ($\mu g/m^3$)	Commercial unit		Vaporizing space heater		Air-atomizing space heater	
		Emissions ($\mu g/m^3$)	Severity[c] factor	Emissions ($\mu g/m^3$)	Severity[c] factor	Emissions ($\mu g/m^3$)	Severity[c] factor
Particulates	75[b]	225,000	0.11	7,840	< 0.001	473,000	0.006
Cadmium	50	40	0.03	1	< 0.001	65	0.013
Chromium	500	95	0.008	6	< 0.001	250	0.005
Cobalt	50	2	0.002	1	< 0.001	5	< 0.001
Copper	200	870	0.15	6	0.005	1,200	0.6
Iron	1,000	2,850	0.12	20	< 0.001	5,300	0.055
Lead	150	42,700	11	280	0.015	97,000	7
Nickel	100	110	0.04	5	< 0.001	60	0.006
Zinc	5,000	34,800	0.28	40	< 0.001	55,700	0.114
Naphthalene	50,000	3	< 0.001	190	< 0.001	1	< 0.001
Phenanthrene	1,600	2	< 0.001	160	<0.001	2	< 0.001
Pyrene	230,000	ND	-	100	< 0.001	1	< 0.001
Benz(a)anthracene	45	ND	-	30	0.005	ND	-
Benzo(a)pyrene	0.02	ND	-	30	11	ND	-

[a] TLV values for trace elements; DMEG values for organic compounds.

[b] Primary national ambient air quality standard for particulates.

[c] Underlined values indicate factors in excess of 0.05.

ND = Not Detected.

program[6] to evaluate the significance of emissions. The source severity factor was defined as the ratio of the calculated maximum ground level concentration of the pollutant species to the level at which a potential environmental hazard exists. A source severity factor equal to or greater than 0.05 was considered indicative of potential hazard. The simple Gaussian plume equation for ground level receptors at the plume centerline was the dispersion model used for determining the ground level concentration. The potential environmental hazard was taken to be the TLV divided by 300 for noncriteria pollutants and the ambient air quality standard for particulates. The source severity factor for noncriteria pollutants is calculated as follows:

$$S = \frac{5.5Q}{(TLV)R^2}$$

where Q = emission rate, g/sec

TLV = threshold limit value, g/m^3

R = stack height, m.

For particulates the source severity factor is:

$$S = \frac{70Q}{R^2}$$

The source severity factors shown in Table VI-10 were calculated assuming a stack height of 10 meters for the commercial unit and 4 meters for the space heaters. Emission rates were as measured during the test program. The trace elements selected for inclusion in the table were those for which emission concentrations exceeded TLVs in the recent EPA study of space heaters.[3,4]

Conclusions

The use of the source severity factor as a measure of environmental impact would indicate that lead from the commercial unit and from the atomizing space heater is the trace element emission of most concern. Other elements of possible concern are copper, iron and zinc. Depending upon their concentrations in the waste oil, other elements could also have potential impact. Leaky flues or excessive contact with the flue gas due to down drafts or low level discharges could lead to greatly elevated human exposures.

The vaporizing burner was not a significant source of particulate or lead emissions although it did emit more organics than the other systems tested. Benzo(a)pyrene was emitted in significant amounts as determined by the source severity factor. An extremely low hazard index factor is used for benzo(a)-pyrene due to the known carcinogenic nature of the compound. Benz(a)anthracene was the only other organic measured of possible significance.

The emissions data provided in this study confirm certain information regarding the effect of burner design and fuel composition on the emissions of inorganic elements. Elemental emissions from the atomizing burner are one to two orders of magnitude higher than those from the vaporizing unit. Unfortunately, the data are too limited to determine whether or not organic emissions from the vaporizing burner, which were measured at an appreciably higher level in one run than those from the atomizing units, are due to an inadequate break-in period or inherent to the design concept. The organic emissions from the atomizing units appear to be similar to those from conventional combustion systems.

Disposal of pot residue from the vaporizing burner can be a problem because of the high trace element content and PNA content of the residue. This residue, representing about 3 percent of the feed, contains over 90 percent of most trace elements and a variety of organic components including PNAs. Additional study of the vaporizing unit to establish flue gas emissions and pot residue characteristics appears warranted.

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SECTION VII

REPROCESSING TO PRODUCE A SPECIFICATION FUEL

CURRENT STATUS

The pretreatment of waste oils prior to their use as fuels is designed to minimize potential problems associated with the effect of contaminants, including metals, water, and chlorinated compounds, leading to inefficient combustion, high emission levels, and erosion and corrosion of the combustion system. The seriousness of these potential problems has not been studied in any detail. Most reports indicate that, at least over the short term, no serious effects are apparent even when waste oil is burned alone without blending with virgin fuels.[1,2] Lead emissions, despite the reduction in the lead content of used oil over recent years, appears to pose the most significant environmental problem associated with used oil combustion. Unfortunately, most current physical pretreatments practices will not significantly reduce the lead content in used oil.

The most common physical treatment methods are the gravity-assisted procedures such as settling, filtration, and centrifugation. Appreciable amounts of water and sediment are removed by settling followed by filtration or centrifugation. Water and sediment when present in large quantities may cause clogging of pipes and nozzles, corrosion, and fuel line freezing. Consequently, almost every collector provides for physical separation of water and gross particulates through sedimentation. Environmentally, discharge of water from sedimentation operations is of concern because of the presence of water soluble components, e.g., phenols. It has also been proposed that metals in the water phase may be a problem.[3,4]

DOE[5] has studied the use of physical techniques to reduce water, sediment, ash, and metal levels in waste oil, and the results are summarized in Table VII-1. The solvent extraction treatment in the table refers to diluting the used oil with hexane and 2-propanol, followed by centrifugation. Coyle and Siedle[6] have conducted an interesting review of these studies and others, with emphasis on metals and the implication of their physical and chemical states on pretreatment and applications such as combustion and road oiling. They interpret existing data to show that significant quantities of metals, and particularly about 50 percent of the lead, occur as particulates. In their citation of Reference 4, they note that more than 90 percent of the lead, cadmium and zinc passed through a filter with a pore size of 0.05 µm in diameter. A major conclusion of the study was that there is a definite

TABLE VII-1. EFFECT OF PHYSICAL TREATMENTS ON ASH, SEDIMENT, AND LEAD IN WASTE OIL

Treatment process	Concentration				
	BS&W[a] % v/v	Water % v/v	Sediment % v/v	Ash[b] % w/w	Lead[b] % w/w
No treatment	10	8	5	3	1
Settling pretreatment	1	0	2.5	2.3	0.9
Centrifugation	1.5	1	1.7	1.5	0.75
Solvent extraction	0.3	0	0.3	0.3	0.1
Vacuum distillation	0	0	0	0	0

[a] Bottom sediment and water.

[b] Referred to as v/v in Reference 5 and assumed to be w/w.

Source: Reference 6.

need for better characterization of the physical and chemical forms in which metals occur in used oil and their distribution among water-soluble, oil-soluble, and particulate fractions. Such data would be useful in developing more efficient pretreatment processes and in assessing the potential for transport of metals into the environment.

Despite a great deal of uncertainty about pretreatment methods and their effectiveness, it is apparent that most used oil is reprocessed by physical methods (e.g., settling, filtering, centrifuging, clay contacting, and thermal processing for removal of water and light ends) to produce a product meeting specifications for use as a fuel (or as road oilant). The nature of the processing will depend upon the intended use of the oil, its composition, and the nature of regulations, if any, governing their use. Recently proposed regulations, such as that under consideration for the burning of waste oil in the State of New York, will generally necessitate more stringent processing measures to meet the proposed fuel requirements. At a minimum, a distillation step appears necessary to meet the proposed maximum concentration levels of 25 ppm for lead, 5 ppm for total halogens, and 5 ppm for PCBs.

As will be noted in Section VIII, it is unlikely that any physical processing method, including distillation and steam stripping, will remove PCBs once they have been added to the waste oil (hydrofinishing was the one method tested in this study which successfully destroyed PCBs). Athough PCBs are not normally found in waste oil, lead (in waste automotive oils) and volatile halogenated organics are nearly always present, and if both are present, a fractionation process will be needed to meet the required concentration levels. In any event, the new regulations, if promulgated, will place the burden of analysis on the recycler, further emphasizing the need for quicker and cheaper methods of analysis for contaminants, particularly halogenated organics.

PROCEDURES FOR AND RESULTS OF LABORATORY SIMULATIONS

The spiked COMPOSITE oil was used for all laboratory simulations of physical separation measures commonly used by recyclers. The processes examined were:

1. Settling,
2. Filtration,
3. Centrifugation,
4. Clay contacting, and
5. Heating to remove water and light ends.

The simplest method of all settling proved to be of little value, most likely indicating that the four oils that were blended to prepare the COMPOSITE oil had already undergone this operation at the recyclers facility prior to their receipt by GCA. The elemental concentrations of the pretreated COMPOSITE oil (with moisture and light ends removed) and the same oil allowed to settle in a

500 ml separatory funnel for a 42-day period are shown in Table VII-2. Very little change in concentration is apparent from the data; the scatter implies that sampling or analytical problems mask any settling effects. The common elements, aluminum, calcium, and iron actually show an increase in concentration. However, little or no effect on the concentrations of lead, zinc and many other elements is shown.

Filtration

Filtration of the COMPOSITE oil was carried out with a variety of filter media, including a Gelman GA-4, 0.8 μm metricel filter and a Millipore GS 0.22 μm membrane type filter, at positive pressures up to 100 psi using a stainless steel pressure filtration funnel (Gelman Model No. 4280). Following filtration, the oil remaining on the tared filter was removed by extraction with methylene chloride and the filter was dried and reweighed.. Weight gains resulting from particulate collection were small (less than 10 percent (less than 600 μg/g of oil) of the total ash). Microscope examination of the base stock (both the COMPOSITE oil and COMPOSITE oil after dehydration and light end removal), the filtered oil, and the particulate remaining on the filter after washing with methylene chloride did not indicate any change in apparent particle size. All particles were at or below the microscope resolution limitation of about 1 μm. The results of these filtration studies are consistent with results reported by Becker and Comeford.[7] They used a scanning electron microscope to measure the particle size of particulates in waste oil passing a refractory thimble used in a test for sediment and observed a size range of 0.02 to 0.3 μm. Most particles were about 0.1 μm in diameter.

Centrifugation

Centrifugation of 100 ml of the COMPOSITE oil was conducted in a Damon IEC EXD laboratory centrifuge at about 8000 G and 150-200°F for extended periods (up to 1 hour) of time. These conditions were needed to achieve any visual signs of separation. However, the separation was significant for certain elements. Overall, the removal was about 25 percent with a 30 and 18 percent removal of lead and zinc, respectively, at a yield of 97 percent. The cause of variability in removal, as shown in Table VII-3, is probably related both to particle size and oil/water partitioning of the elements and their compounds.

Clay Contacting

One liter of the COMPOSITE oil, following pretreatment of the oil to remove moisture and light ends, was contacted with Filtrol grade 20 clay (0.12 g of clay/ml or 1 lb/gallon of oil) for 2 hours at 425°F in a stirred vessel. Filtrol-20 is an acid activated clay of about 200 mesh size designed for general purpose use in decolorizing and purifying petroleum base oils. The oil was then filtered under vacuum using a Celite filter aid supported on a fritted glass funnel. As shown in Table VII-4, removal of elements from the oil by the clay contacting operation is minimal. The increase in concentration of some elements in the filtered oil suggest that clay particles are passing through the filter or that elements are extracted from the clay.

TABLE VII-2. ELEMENTAL CONCENTRATION CHANGES DUE TO SETTLING

	Pretreated COMPOSITE oil concentration (μg/g)	Pretreated COMPOSITE oil concentration after settling (μg/g)
Aluminum	34	140
Antimony	0.6	2.2
Arsenic	10	4.2
Barium	69	80
Beryllium	0.1	0.1
Boron	9.2	0.2
Cadmium	1.4	1.0
Calcium	1100	1360
Chromium	95	100
Cobalt	1.1	0.8
Copper	36	38
Iron	280	480
Lead	1250	1260
Magnesium	240	250
Manganese	16	20
Molybdenum	3.6	4.0
Nickel	4.1	3.0
Selenium	1	1
Silicon	55	50
Silver	0.1	0.1
Sodium	260	180
Strontium	2.2	1.5
Thallium	1	2
Tin	19	6
Titanium	10	17
Vanadium	4.7	3.7
Zinc	820	800

TABLE VII-3. ELEMENTAL REMOVAL BY CENTRIFUGATION

Element	COMPOSITE oil concentration (μg/g)	Centrifuged sludge concentration (μg/g)	Percent separation[a]
Aluminum	31	480	46
Antimony	0.6	21	100
Arsenic	8.1	150	55
Barium	61	580	29
Beryllium	<0.1	2	--
Boron	6.2	80	39
Cadmium	1.3	11	25
Calcium	990	6,200	19
Chromium	7.7	150	58
Cobalt	0.8	18	68
Copper	34	160	14
Iron	210	4,300	61
Lead	1,100	11,000	30
Magnesium	210	1,100	16
Manganese	14	90	19
Molybdenum	3.2	55	52
Nickel	3.7	160	128
Selenium	<1	<7	--
Silicon	40	400	30
Silver	<0.1	<0.3	--
Sodium	260	440	5
Strontium	1.9	6.1	10
Thallium	<1	<13	--
Tin	16	500	94
Titanium	7.8	69	27
Vanadium	4.1	26	19
Zinc	730	4,330	18

[a] Percent separation $= \frac{\text{Sludge conc. x 0.03}}{\text{oil conc.}} \text{ x } 100$

TABLE VII-4. ELEMENTAL REMOVAL BY CLAY CONTACTING

Element	Pretreated COMPOSITE oil concentration (μg/g)	Clay contacted oil concentration (μg/g)	Percent separation
Aluminum	34	130	+382
Antimony	0.6	2.2	+266
Arsenic	10	4.0	-60
Barium	69	76	-9
Beryllium	<0.1	<0.1	--
Boron	9.2	8.7	-5
Cadmium	1.4	1.0	-29
Calcium	1,100	1,300	+18
Chromium	95	8.9	-6
Cobalt	1.1	0.8	-27
Copper	36	36	0
Iron	280	460	+64
Lead	1,250	1,200	-4
Magnesium	240	230	-4
Manganese	16	19	+18
Molybdenum	3.6	3.8	+6
Nickel	4.1	2.8	-32
Selenium	<1	<1	--
Silicon	55	47	-15
Silver	<0.1	<0.1	--
Sodium	260	60	-77
Strontium	2.2	12	+450
Thallium	≤1	<2	--
Tin	19	54	+184
Titanium	10	16	+60
Vanadium	4.7	3.5	26
Zinc	820	800	-2

Organic analyses were conducted on the feedstock oil, clay, the filtered oil, and the clay sludge. The effectiveness of the clay contacting was masked by the scatter of the analytical data. However, some removal of the semivolatile organics identified in the feedstock was achieved.

The percent removal, as determined by a comparison of the analysis of the product oil and the spent clay sludge with the feedstock, is shown in Table VII-5.

TABLE VII-5. REMOVAL OF ORGANICS BY CLAY CONTACTING

Compound	Percent removal based on analysis of: Product oil	Clay sludge
Phenol	0	7
Naphthalene	7	1
2,4,6 Trichlorophenol	31	15
N-Nitrosodiphenylamine	0	0
Phenanthrene/Anthracene	45	4
Pyrene	5	1
Benzo(a)pyrene	30	0
4,4'-DDE	7	2
PCBs	6	14

Dehydration and Light End Removal

The dehydration and removal of light ends from the COMPOSITE oil was carried out in a stirred round-bottom reaction flask at a pressure of 2 to 10 mm Hg. The reaction flask was fitted with an experimental train consisting of a condenser, multiple collection flasks, two liquid nitrogen traps, and the mechanical vacuum pump. The temperature of the oil within the flask was raised slowly (over a 3-hour period) from room temperature to about 210°F using an electrically heated mantle enclosing the flask. Water and some light end compound distillate appeared in the condensing system at a flask temperature of about 55°F. The transfer rate was essentially zero at the time of termination.

The yield of treated oil was about 84 weight percent with the water removed accounting for 8.8 percent of the feed and light ends (including 1.2 percent in the liquid nitrogen traps) accounting for the remaining 7.2 percent removed during this pretreatment.

The results of the inorganic analysis of the feed, product, and the water and combined organic waste streams are shown in Table VII-6. It should be noted that the disposition of the contaminants are provided in μg/g of feed. The values shown in the table must be adjusted by the relative flow rates to determine the true stream concentration values in μg/g. Concentration values in each stream are given by the value shown in the table times the ratio of the relative flow rate of the feed to the stream of interest.

Material balance recovery was in the 90 to 100 percent range for most elements. The effect of dehydration and light end removal on the elemental content of the oil is minimal. Only silicon (1.2 μg/g) and sodium (1.8 μg/g) were identified in the water fraction at levels greater than 1 μg/g or one part per million (ppm). However, somewhat higher concentrations were detected in the organic light end fraction with lead present at the 12 ppm level. The reason for the higher concentrations in the light end fraction as opposed to the aqueous phase is most likely an artifact of the experimental procedure that was employed. The elements, whether leaving the flask as vapor or entrained in droplets, would tend to deposit in the upper organic liquid portion of the collection vessel and be physically impeded from transferring into the water phase.

Results of the organic analyses are presented in Table VII-7, with values shown given per gram of feed. Almost all of the volatile organics present in the COMPOSITE oil were removed by the laboratory procedure used. The level of organic compounds identified as present in the water fraction is of the order of 670 μg/g*; the actual level is probably in excess of 1,000 μg/g. This value would require treatment prior to discharge to a POTW or to surface waters.

The material balance closure achieved for the specific organic compounds identified is highly variable. The variability in this instance appears to be a measure of analytical variability rather than the result of errors in sampling or the occurrence of chemical reactions during the pretreatment step or thereafter. As noted in the discussion of quality control in Appendix C the recoveries of organic compounds, particularly the semivolatile organics, are low, of the order of 50 percent in the oil matrix. However, given good

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*The value of 670 μg/g can be obtained by summing the positive values shown in the table (volatile components positively identified in the water phase are given as 59 μg/g) and multiplying the total by the ratio of feed flow rate (100) to the flow rate of the water phase (8.8), i.e:

$$\text{Concentration of organics} = 59 \times \frac{100}{8.8} = 670\ \mu g/g.$$

Thus, the concentration of 1,1,1 trichloroethane in the water phase is $12 \times \frac{100}{8.8}$ or about 140 μg/g . The data in Tables VII-6 and VII-7 have been presented in the units of μg/g of feed to illustrate directly the distribution of the various contaminants in the process and waste streams.

TABLE VII-6. DISPOSITION OF THE ELEMENTAL CONTAMINANTS IN PROCESS AND WASTE STREAMS FROM THE LABORATORY SIMULATION OF A DEHYDRATION AND LIGHT END REMOVAL OPERATION

	COMPOSITE oil (1)	Water (2)	Light ends (3)	Pretreated oil product (4)	Material balance (percent recovery)[a]
Relative Flow Rate (weight)	100	8.8	7.2	84	
Contaminant Weight (µg/g of feed)					
Aluminum	31	0.001	0.04	29	94
Antimony	0.6	<0.002	0.04	0.50	91
Arsenic	8.1	<0.003	<0.01	8.1	100
Barium	61	0.001	<0.01	5.8	95
Beryllium	<0.1	0.001	<0.01	<0.1	-
Boron	6.2	0.06	0.1	7.8	127
Cadmium	13	0.001	<0.01	1.2	92
Calcium	980	0.03	0.2	960	98
Chromium	7.7	<0.001	<0.01	8.0	104
Cobalt	0.8	<0.001	<0.01	0.9	113
Copper	34	<0.001	0.02	31	90
Iron	210	<0.001	0.14	236	110
Lead	1,090	<0.001	0.83	1050	96
Magnesium	210	0.002	0.01	200	95
Manganese	14	<0.001	<0.01	13	96
Molybdenum	3.2	<0.001	<0.01	3.0	94
Nickel	3.7	<0.001	<0.01	3.5	95
Selenium	1.0	<0.002	<0.06	0.8	-
Silicon	4.0	0.11	0.02	4.7	119
Silver	<0.1	<0.001	<0.01	<0.1	-
Sodium	260	0.16	0.50	220	86
Strontium	1.9	<0.001	<0.01	1.8	95
Thallium	<1	<0.003	<0.1	<0.8	-
Tin	16	0.005	0.23	16	99
Titanium	7.8	<0.001	<0.01	8.4	110
Vanadium	4.0	<0.005	<0.01	4.0	100
Zinc	730	<0.001	0.03	690	94

[a] Material balance 1 = 2 + 3 + 4 (< values not used).

TABLE VII-7. DISPOSITION OF ORGANIC CONTAMINANTS IN PROCESS AND WASTE STREAMS FROM THE LABORATORY SIMULATION OF A DEHYDRATION AND LIGHT END REMOVAL OPERATION

	COMPOSITE oil (1)	Water (2)	Light ends (3)	Pretreated oil product (4)	Material balance (percent recovery)[a]
Relative Flow Rate (weight)	100	8.8	7.2	84	
Volatiles (μg/g of feed)					
Trichlorofluoromethane	< 4	< 0.4	< 0.4	< 4	-
Trichlorotrifluoroethane	110	< 0.4	25	< 4	23
Methylene chloride	< 4	5	12	< 4	-
1,1-Dichloroethane	< 4	< 0.4	< 0.4	< 4	-
1,2-Dichloroethane	< 4	< 0.4	< 0.4	< 4	-
t-1,2-Dichloroethylene	< 4	< 0.4	< 0.4	< 4	-
Chloroform	< 8	< 0.4	16	< 4	-
1,1,1-Trichloroethane	1,500	12	1,650	<4	111
Trichloroethylene	2,000	20	1,800	<4	91
Carbon tetrachloride	<4	<0.4	<0.4	<4	-
Tetrachloroethylene	670	8	1,700	100	270
Benzene	75	<0.4	120	<8	160
Toluene	2,800	14	1,400	120	55
Ethyl benzene	570	<0.4	80	<4	14
Semivolatiles (μg/g of feed)					
Chlorobenzene	<10	<1	<1	<10	-
Phenol	11	<1	13	<10	118
Chlorophenol	<20	<2	<20	<20	-
Dichlorobenzene	80	<2	56	<20	70
Nitrobenzene	30	<1	10	<10	33
Nitrophenol	<20	<2	<2	<20	-
Naphthalene	440	<1	300	45	78
2-Chloronaphthalene	<10	<1	<1	<10	-
2,4,6-Trichlorophenol	40	<1	6	37	108
Acenaphthene	<10	<1	<1	<10	-
N-Nitrosodiphenylamine	116	<1	10	82	79
Hexachlorobenzene	<10	<1	<1	<10	-
Phenanthrene/anthracene	150	<1	6	210	144
Pyrene	60	<1	<1	24	40
Benz(a)anthracene	40	<1	<1	20	50
Benzo(a)pyrene	< 10	< 1	< 1	< 10	-
4,4'-DDE	94	<1	2	57	63
PCBs	34	<1	<1	36	106

[a] Material Balance 1 = 2 + 3 + 4 (< values not used).

reproducibility (precision) and neglecting any differences due to matrix (oil or water), the material balance approach should lead to full recovery, although at concentration levels reduced from their true values. Apparently this is not the case, and it must be inferred that the level of precision is responsible for the scatter shown in Table VII-7. To improve the precision (and accuracy) of the analytical methods, the development of other methods of sample preparation and fractionation is needed to improve recoveries and reduce interferences.

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SECTION VIII

RE-REFINING OF USED OIL--LABORATORY SIMULATIONS

Three re-refining scenarios of varying complexity were simulated in the laboratory using the COMPOSITE oil (stripped of water and light ends as described in Section VII) to determine the disposition of contaminants remaining in the pretreated oil. Two other commercial re-refining processes, the PROP process as operated by the State of North Carolina and an East Coast commercial facility, were sampled during periods of representative operation to determine, upon analysis, the disposition of contaminants present in their used oil feedstocks. The results of these sampling programs will be discussed in following sections. This section will present and discuss the results of the laboratory simulations of the three processes based on (1) solvent treatment/distillation/hydrofinishing or clay finishing, (2) distillation/hydrofinishing, and (3) acid/clay. Each process will be discussed individually and conclusions drawn with regard to the effectiveness of contaminant removal, and other aspects of the waste oil affecting production of the re-refined oil and its use. Waste streams generated by each process will be subsequently assessed in Section XII using the waste hazard index discussed in Section II, as the determinant of potential impact.

All of the laboratory simulations were run with the pretreated (water and light ends removed) COMPOSITE oil using experimental conditions suggested in the literature or by individuals associated with the used oil re-refining industry. The selection of experimental conditions as representative of typical unit operations is understandably questionable as variations can be expected in actual, often proprietary, processes. However, semiquantitative effects of such variations can be assessed, barring chemical reactions, from process principles and the simulation data. A more quantitative assessment should also be attainable using the computer simulation techniques described in Section XI.

THE SOLVENT TREATMENT/DISTILLATION/FINISHING RE-REFINING PROCESS

This process is based on work carried out at the Department of Energy's Bartlesville Energy Technology Center during the 1970s to examine innovative approaches to re-refining used oils.[1,2] The process, developed and tested at the pilot scale level, involved a series of operations to solvent treat, distill, and hydrotreat used oil to produce an automotive lubricating oil basestock. The solvent treatment step is claimed to improve process reliability and costs by virtue of its removal of contaminants which contribute to the coking and fouling tendencies of a used lubricating oil during the distillation step.[3,4] Failure to achieve commercialization can be attributed to the somewhat greater complexity of the process and the lack of a demonstration plant. It probably also reflects the uncertain future of the re-refining industry within the larger framework of the worldwide petroleum industry.

Description of the Solvent Treatment/Distillation/Finishing Re-Refining Process Laboratory Simulations

The laboratory simulations of this process were conducted as shown in Figure VIII-1. Six distinct operations, (1) solvent treatment, (2) sludge separation, (3) solvent recovery, (4) wiped film distillation, and (5) hydrofinishing or (6) clay finishing, were simulated under the conditions described below. Samples of significant product and waste streams, as indicated in the figure, were taken for analysis to determine the fate of specific contaminants present in the pretreated COMPOSITE oil feedstock.

A brief written description of each operation is provided below.

Solvent Treatment--

Solvent treatment was carried out in a mechanically stirred 5-liter flask using three parts of the solvent mix to one part of the pretreated oil. The solvent used was that suggested by DOE,[3] namely:

2 parts n-butanol,
1 part isopropanol, and
1 part methyl ethyl ketone.

One liter of the waste oil was placed in the flask and heated to 68°C prior to adding the solvent. After 30 minutes of vigorous agitation the waste oil/solvent mixture was transferred to a separatory funnel and the sludge allowed to settle over a 24-hour period. A total of 9 liters was processed for subsequent operations.

Sludge Removal--

The sludge was separated from the waste oil by draining the sludge through the valve at the bottom of the separatory funnel. No attempt was made to improve the separation by either filtration or centrifugation. The gravity separation was reasonably effective; sludge volume was 4.25 percent of the original waste oil volume.

Solvent Removal--

Solvent was removed from the waste oil/solvent mixture by distillation at reduced pressure (25 mm Hg) and modest temperatures (to 140°C). Distillation was conducted in a mechanically stirred 5-liter flask outfitted with a water cooled condenser. Solvent recovery was about 98 percent with the principal loss occurring through the vacuum system.

Wiped Film Distillation--

The solvent-free oil was distilled in a 2-inch wiped film distillation apparatus supplied by Pope Scientific Co. Distillation was conducted at a flow rate of approximately 5 ml/min at a pressure of 2 mm Hg and an outer still surface temperature of 295°-306°C. Recovery after two passes of the

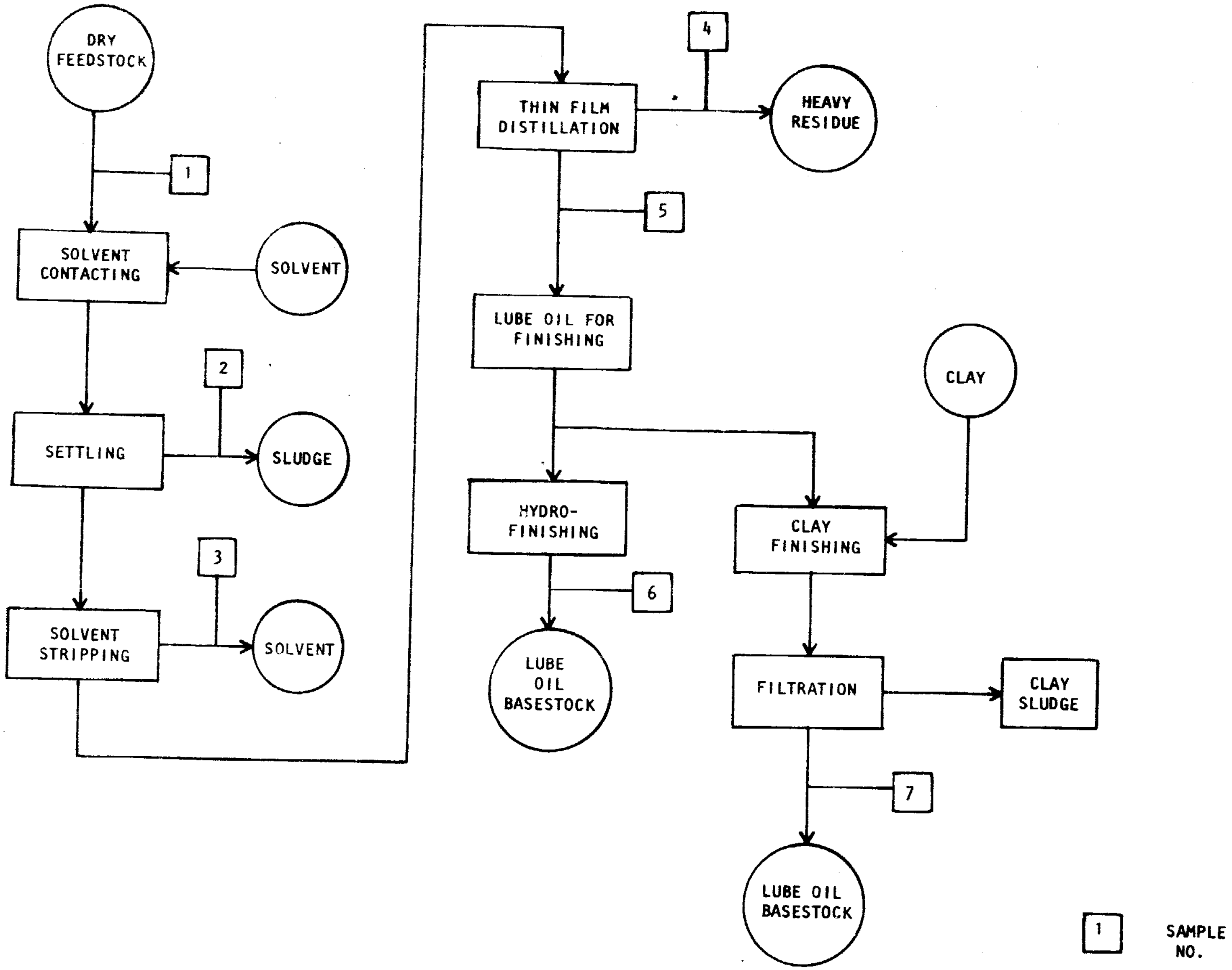

Figure VIII-1. Solvent treatment/distillation/finishing re-refining process--laboratory simulations.

undistilled portion of the oil through the still operated under identical conditions was 72 percent. Although the operating conditions were also identical to those used in the distillation/hydrofinishing process, the yield was less and some coking was noted.

Hydrofinishing--

The hydrofinishing of the oil distilled from the wiped film distillation apparatus was conducted by Hydrocarbon Research Inc., Lawrenceville, New Jersey. The hydrofinishing was carried out in a small fixed-bed unit charged with American Cyanamid's Aero HDS-2A catalyst. This catalyst is a commercial CoMo on alumina extrudate. After a 5-hour presulfiding period, representing about 5 times the excess sulfur required to sulfide all the catalyst, the distilled waste oil was fed to the unit at a rate of about 200 ml/hr, a volumetric flow rate equivalent to the volume of catalyst in the reactor. The unit was operated at a temperature of 343°C, H_2 pressure of 550 psig, and H_2 gas flow rate of 3.0 scfh for 16 hours before a sample was taken for analysis.

Clay Finishing--

Some of the distilled oil was also contacted with clay (Filtrol Grade 20 activated clay) in an agitated vessel at 232°C for 1 hour at atmospheric pressure. About 0.4 pounds of clay was used per gallon of oil. The conditions selected for this finishing step were basically those suggested in Reference 4 with the exception of time at temperature. The clay/oil mixture was vacuum filtered using a Celite filter aid supported on a glass frit. Oil recovery was about 90 percent. The product oil was low in odor although not as odor free or as light in color as the hydrotreated oil.

Results of the Solvent Treatment/Distillation/Finishing Re-Refining Process Laboratory Simulations

The results of the laboratory simulations as determined by analysis of the process waste and product streams identified in Figure VIII-1 are shown in Tables VIII-1 and VIII-2 for the elemental and organic components of the waste oil, respectively. The results have been normalized to show the distribution of constituents resulting from the processing of 1 gram of feedstock. Thus, contaminant stream concentrations in parts per million (μg/g) in the streams are equal to the values shown in the Table multiplied by the ratio of the feedstock flow rate to the stream flow rate. As an example, the value of 12 μg/g of feed shown in stream 3 for iron is equivalent to a stream concentration of about 4 μg/g.

Inorganic Analysis--

As shown in Table VIII-1 good material balance closure for the ICAP analyzed elements was achieved through the thin film distillation step. However, some elements, notably tin, nickel and iron were measured at overall levels well in excess of those introduced with the COMPOSITE oil feed.

The effectiveness of the solvent treatment operation, as determined by the overall removal of the 27 elements analyzed by ICAP, was about 35 percent. This removal is less than ash reduction values of 42-86 percent achieved by DOE in a series of tests with the same solvent system used in this

TABLE VIII-1. DISPOSITION OF ELEMENTAL CONTAMINANTS IN PROCESS AND WASTE STREAMS DURING LABORATORY SIMULATIONS OF THE SOLVENT TREATMENT/DISTILLATION/FINISHING RE-REFINING PROCESS

	Feedstock (1)	Solvent sludge (2)	Solvent (3)	Distillate residue (4)	Distillate (5)	Hydro-finished product (6)	Clay-finished product (7)	Percent recovery[a]
Relative Flow Rate (weight)	100	4.3	294	19.2	76.5	70	70	
Contaminant Weight (μg/g of feed)								
Aluminum	34	13	ND	16	4.0	1.2	0.4	97
Antimony	0.6	0.6	ND	0.6	<0.8	3.0	0.7	-
Arsenic	9.7	4.8	ND	3.3	<0.8	<0.7	<0.7	85
Barium	70	22	ND	42	<0.08	<0.07	<0.07	94
Beryllium	<0.1	0.02	ND	0.06	<0.8	<0.07	<0.7	-
Boron	9.2	1.0	ND	8.2	<0.2	0.6	0.5	100
Cadmium	1.4	0.6	ND	0.5	<0.8	<0.7	<0.7	78
Calcium	1140	300	0.6	700	3.0	1.5	0.4	88
Chromium	9.5	4.6	ND	5.2	0.1	<0.07	<0.07	104
Cobalt	1.1	0.4	ND	0.6	<0.08	<0.07	<0.07	91
Copper	36	16	ND	13	0.2	1.4	<0.07	80
Iron	280	80	12	210	26	5.1	1.2	117
Lead	1250	530	ND	420	0.3	0.3	<0.07	78
Magnesium	240	43	ND	195	1.0	0.8	<0.07	100
Manganese	16	4.0	ND	11	0.5	0.07	<0.07	94
Molybdenum	3.6	1.6	ND	1.8	<0.08	<0.07	<0.07	94
Nickel	4.1	1.3	ND	2.5	2.1	<0.15	<0.15	144
Selenium	<1.0	0.1	ND	<0.3	0.3	1.9	<0.15	-
Silicon	55	20	ND	19	6.7	5.3	<0.15	83
Silver	<0.1	<0.01	ND	<0.01	<0.8	<0.07	<0.07	-
Sodium	260	86	ND	160	2.7	2.0	1.8	96
Strontium	2.1	0.7	ND	1.2	<0.08	<0.07	<0.07	90
Thallium	<1	<0.2	ND	<0.5	<1.5	<1.5	1.5	-
Tin	19	17	ND	30	12	13	5.7	300
Titanium	10	4.1	ND	1.5	<0.08	<0.07	<0.07	66
Vanadium	4.7	1.1	ND	3.4	<0.08	<0.15	<0.15	96
Zinc	820	320	0.9	340	34	1.6	1.3	85

[a] Material balance closure for streams 1 through 5 (1 = 2 + 3 + 4 + 5).

ND = ≤0.1 μg/g

TABLE VIII-2. DISPOSITION OF ORGANIC CONTAMINANTS IN PROCESS AND WASTE STREAMS DURING LABORATORY SIMULATIONS OF THE SOLVENT TREATMENT/DISTILLATION/FINISHING RE-REFINING PROCESS

	Feedstock (1)	Solvent sludge (2)	Solvent (3)	Distillate residue (4)	Distillate (5)	Hydro-finished product (6)	Clay-finished product (7)
Relative Flow Rate (weight)	100	4.3	294	19.2	76.5	70	70
Contaminant Weight (μg/g of feed)							
Chlorobenzene	ND	ND	ND	ND	ND	ND	ND
Bis(chloromethyl)ether	ND	ND	ND	ND	ND	ND	ND
Phenol	ND*	1.5	ND*	ND*	ND*	21	ND*
Chlorophenol	ND*	ND*	ND*	ND*	ND*	ND*	ND*
Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND
Nitrobenzene	ND	ND	ND	ND	ND	ND	ND
Nitrophenol	ND*	ND*	ND*	ND*	ND*	ND*	ND*
Naphthalene	54	3.0	ND	ND	60	49	30
2-Chloronaphthalene	ND	ND	ND	ND	ND	ND	ND
2,4,6-Trichlorophenol	44	1.0	ND*	ND*	14	ND*	ND*
Acenaphthene	ND	ND	ND	ND	ND	ND	ND
N-Nitrosodiphenylamine	98	1.8	ND	ND	110	ND	ND
Hexachlorobenzene	ND	ND	ND	ND	ND	ND	ND
Phenanthrene/anthracene	260	2.7	ND	ND	34	45	80
Dibutyl phthalate	820	04	ND	ND	1,000	77	1,200
Butylbenzyl phthalate	110	ND	ND	ND	80	ND	ND
Pyrene	280	0.6	ND	ND	40	56	34
Benz(a)anthracene	24	0.6	ND	ND	30	ND	40
Triphenyl phosphate	ND	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	ND	1.7	ND	4.5	400	ND	250
4,4'-DDE[a]	68	0.5	ND	ND	40	ND	50
PCBs	43	0.6	ND	<1 μg/g	24	<1 μg/g	20

[a] DDE, added as a spike, was the only priority pollutant pesticide identified.

ND $\leq$ 10 μg/g

ND* $\leq$ 20 μg/g

study.[1] Many parameters such as temperature, agitation, and compositional factors are probable contributors to the apparent differences between the two studies.

Both clay-contacting and hydrofinishing appear to reduce the inorganic elemental content of the distilled oil. This observation suggests that more complete removal of trace elements than that achieved in this study by the earlier processing operations would be desirable to reduce catalyst poisoning and attrition during the hydrofinishing step.

Organic Analysis--

The results of the organic analysis of the various process and waste streams are presented in Table VIII-2. As shown in Appendix B, GC/ECD analysis was used for the PCB analyses; GC/MS analysis, using the NIH/EPA/MSDC mass spectral data base, was used to screen and identify the other compounds listed in the table. The table does not include the priority pollutant pesticides (with the exception of the spike compound 4,4'-DDE) which were looked for but not found in the analyses. Analyses were not conducted for the volatile organics which, with the exception of trace amounts of toluene, were removed from the COMPOSITE oil feed by the pretreatment process described in the previous section.

The results of the organic analyses are not as amenable to the construction of a material balance as are the results of the inorganic analyses. Poor material balance closure is evident for compounds such as 2,4,6-trichlorophenol and phenanthrene/anthracene. However, some observations concerning the data in Table VIII-2 are of interest. Of particular note is the relatively high concentration of benzo(a)pyrene found in the product from the wiped film distillation. It would appear that this compound was generated during the distillation operation even though a subsequent attempt to replicate this result was not successful. The possibility of formation of benzo(a)pyrene during distillation is in keeping with the coking of still surfaces observed during the particular laboratory runs in question.

Another observation of interest is the effectiveness of hydrofinishing in destroying the PCBs and nitrosoamine compounds present as spikes in the feed. In contrast, the clay-contacting operation, as simulated in the laboratory, did not result in the removal or significant decrease in the concentration of these compounds. Although some odor and color removal was noted as a result of clay-contacting, the effects were less than those observed with hydrofinishing. From the standpoint of color and odor the hydrofinished solvent treatment/distillation product was superior to the final product obtained from the other laboratory simulated processes.

DISTILLATION/HYDROFINISHING RE-REFINING PROCESS

Experimental simulations of a process sending the topped feed directly to thin film distillation (no pretreatment) followed by hydrotreating were conducted in the laboratory using the pretreated COMPOSITE oil as the feed to the distillation apparatus. This process employs thin film evaporation, often with proprietary design features, to minimize coking and degradation while producing an intermediate product which can be finished (hydrofinished or clay-contacted) to yield a high quality lubestock.[5,6]

Description of the Distillation/Hydrofinishing Re-Refining Process Laboratory Simulations

The distillation/hydrofinishing re-refining process, as shown in Figure VIII-2, was simulated in the laboratory using the COMPOSITE oil which had been pretreated to remove water and light organics as described in Section VII. Samples for analysis were taken at the locations shown in the figure. The overheads from the distillation were not analyzed since they represented only 0.2 percent of the product throughput. The equipment and conditions used are discussed below.

Thin Film Distillation--

The distillation of the pretreated COMPOSITE oil was conducted in the apparatus used for the distillation step in the solvent treatment/distillation process. The distillation in the Pope Scientific Company wiped film evaporator was conducted at 2 to 4 mm Hg pressure and 300°C at a flow rate through the 2-inch unit of about 5 ml/minute. Recovery of distillate was 79.5 percent, and coking of internal surfaces was not as pronounced as it was in the runs with the solvent-treated oil.

Hydrofinishing--

The product from the thin film distillation was hydrofinished using the small, fixed bed unit operated by Hydrocarbon Research, Inc. that was used to finish the distilled product from the solvent pretreatment process. After presulfiding of the CoMo catalyst, the distilled oil was fed to the reactor at a rate of about 200 ml/hour. The unit was operated at the same conditions used previously; i.e., a temperature of 343°C, H_2 pressure of 550 psig, and a H_2 gas flow rate of 3.0 scfh. Samples were taken at the middle and end of a 10-hour run and combined for subsequent analysis.

Results of the Distillation/Hydrofinishing Re-Refining Process Laboratory Simulations

The results of the laboratory analyses for the inorganic and organic components of the process and waste streams shown in Figure VIII-2 are presented in Tables VIII-3 and VIII-4, respectively. The quantities have been normalized to reflect the disposition of contaminants per gram of the pretreated COMPOSITE oil fed to the thin film evaporator.

Inorganic Analysis--

The results of the inorganic analysis (Table VIII-3) shows that almost all of the elements analyzed by ICAP are retained in the residue from the thin film distillation. With the exception of silicon and titanium, material balance closure is in the range of 74 to 107 percent. Boron, copper, iron, lead, manganese, sodium, tin and zinc were the only elements in the distillate product that were identified above the average detection limit of 0.1 µg/g. The good separation of product oil from elemental contamination probably reflects the excellent experimental conditions noted during the distillation, which may have reduced carryover due to physical entrainment or volatilization from hot spots on the still surface.

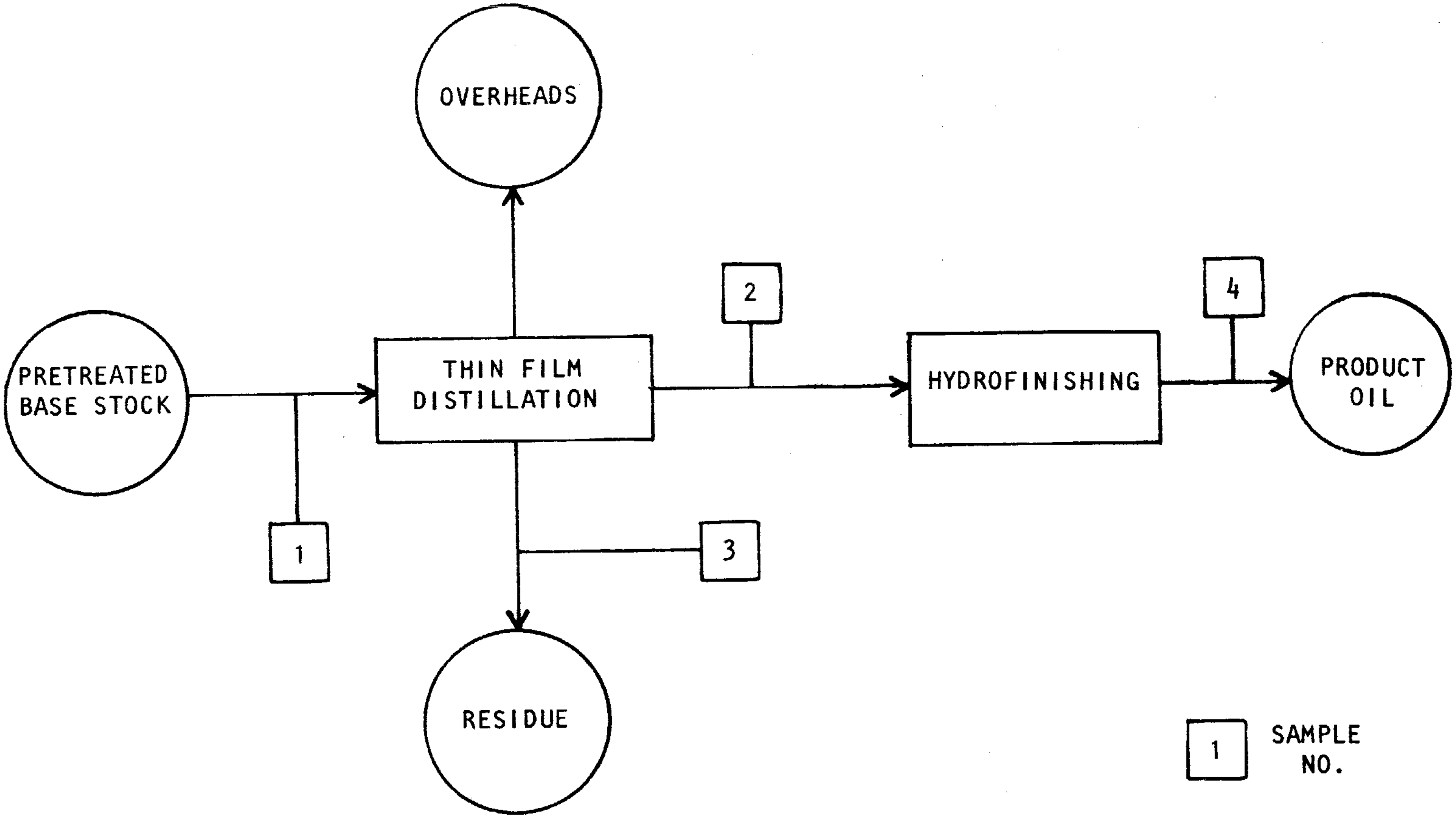

Figure VIII-2. Thin film distillation/hydrofinishing re-refining process--laboratory simulations.

TABLE VIII-3. DISPOSITION OF ELEMENTAL CONTAMINANTS IN PROCESS AND WASTE STREAMS DURING LABORATORY SIMULATIONS OF THE DISTILLATION/HYDROFINISHING RE-REFINING PROCESS

	Feedstock (1)	Distillate (2)	Distillate residue (3)	Hydrofinished product (4)	Percent closure[a]
Relative Flow Rate (weight)	100	80	20	70	
Contaminant Weight (μg/g of feed)					
Aluminum	34	<0.2	28	<0.3	82
Antimony	0.6	<0.4	0.6	<0.5	-
Arsenic	9.7	<0.6	7.2	<0.5	74
Barium	70	<0.1	67	0.15	96
Beryllium	<0.1	<0.1	0.1	<0.1	-
Boron	9.2	0.3	10	<0.5	109
Cadmium	14	0.1	1.3	<0.3	93
Calcium	1,140	<0.2	1,000	<0.3	88
Chromium	9	<0.1	7.0	<0.1	74
Cobalt	1.1	<0.1	1.1	<0.1	100
Copper	36	0.6	34	<0.3	94
Iron	280	0.1	270	2.8	97
Lead	1,250	0.8	1,150	<0.5	90
Magnesium	240	<0.4	-	<0.1	-
Manganese	16	0.1	15	<0.1	91
Molybdenum	3.6	<0.1	3.5	<0.1	97
Nickel	4.1	<0.1	4.4	<0.1	107
Selenium	<1	<0.4	-	<0.5	-
Silicon	55	<0.1	28	<0.1	50
Silver	<0.1	<0.1	-	<0.1	-
Sodium	260	0.8	250	<0.3	99
Strontium	2.1	<0.1	2.0	<0.1	95
Thallium	<1	<0.8	-	<1	-
Tin	19	0.2	17	<1	74
Titanium	10	<0.1	2.0	0.4	20
Vanadium	4.7	<0.1	42	<0.1	89
Zinc	820	0.3	760	3.4	93

[a] Material balance closure for streams 1 through 3 (< values = 0).

TABLE VIII-4. DISPOSITION OF ORGANIC CONTAMINANTS IN PROCESS AND WASTE STREAMS DURING LABORATORY SIMULATIONS OF THE DISTILLATION/HYDROFINISHING RE-REFINING PROCESS

	Feedstock	Distillate	Distillate residue	Hydrofinished product
Relative Flow Rate (weight)	100	80	20	70
Contaminant Weight (µg/g of feed)				
Chlorobenzene	ND	ND	ND	ND
Bis(chloromethyl)ether	ND	ND	ND	ND
Phenol	ND*	ND*	ND*	30
Chlorophenol	ND*	ND*	ND*	ND*
Dichlorobenzene	ND	ND	ND	ND
Nitrobenzene	ND	ND	ND	ND
Nitrophenol	ND*	ND*	ND*	ND*
Naphthalene	54	80	ND	550
2-Chloronaphthalene	ND	ND	ND	ND
2,4,6-Trichlorophenol	44	46	ND*	ND*
Acenaphthene	ND	ND	ND	ND
N-Nitrosodiphenylamine	98	90	ND	55
Hexachlorobenzene	ND	ND	ND	ND
Phenanthrene/Anthracene	260	180	0.7	275
Dibutyl phthalate	820	16	ND	ND
Butylbenzyl phthalate	110	ND	ND	ND
Pyrene	28	42	0.5	47
Benz(a)anthracene	24	9.6	0.5	6.0
Triphenyl phosphate	ND	ND	ND	ND
Benzo(a)pyrene	ND	ND	2.6	ND
4,4'-DDE	68	44	1.4	ND
PCBs	43	31	ND	ND

ND $\leq$ 10 µg/g

ND* $\leq$ 20 µg/g

Organic Analysis--

As noted in the discussion of the results of the previous process the results of the organic analyses of the process and waste streams are not amenable to the development of a material balance. Generally, however, as shown in Table VIII-4, the semivolatile organics present in the feedstock are contained within the product stream. This was true also in the case of the solvent pretreated oil process. In contrast to the solvent treatment process the compound benzo(a)pyrene, although present at the 13 ppm level in the distillate residue, did not appear in the distillate product stream. Conditions which led to the formation of the compound during the previous distillation simulation, if such was the case, apparently did not occur to any extent during this distillation simulation. Although, benzo(a)pyrene was also not detected in the product of a subsequent distillation, its formation during the distillation process, particularly during periods when coking is occurring, appears to be a distinct possibility. The hydrofinishing operation provided a product which was odor free, although somewhat darker than the comparable solvent treatment/distillation product. Chlorinated compounds appear to be completely destroyed by the hydrofinishing operation. However, the detection of naphthalene at high levels in the hydrofinished product raises the possibility that cracking or other alterations can occur during hydrofinishing.

ACID/CLAY RE-REFINING PROCESSES

The acid/clay process was for many years the most widely used re-refining process in the United States. Its use has been drastically reduced because of cost and the difficulty of disposal of the acid/clay waste products. However, the process, when properly operated, can produce a high quality oil. Concentrated sulfuric acid is capable of removing most lube additives and other contaminants such as resinous and asphaltic substances, oxygen compounds, nitrogen bases and sulfur compounds. Metals such as lead and barium are partially removed as insoluble sulfates in the sludge formed by contact with the sulfuric acid.[7]

Following acid contacting, the oil is clay-contacted to improve color and odor and to neutralize the residual acid. Polar and high molecular weight materials are selectively adsorbed by the clay. Processing conditions vary greatly from plant to plant but all processes face a difficult and expensive task in disposing of the acid sludge. Disposal of the spent clay is also difficult and expensive. These environmental factors plus the marginal effectiveness of acid treatment in treating used oils with high level additive packages seems to be leading to the elimination of this process as a viable re-refining option.

Description of the Acid/Clay Re-Refining Process Laboratory Simulations

The laboratory simulations conducted are shown schematically in Figure VIII-3. The process and waste streams sampled for analysis are also shown.

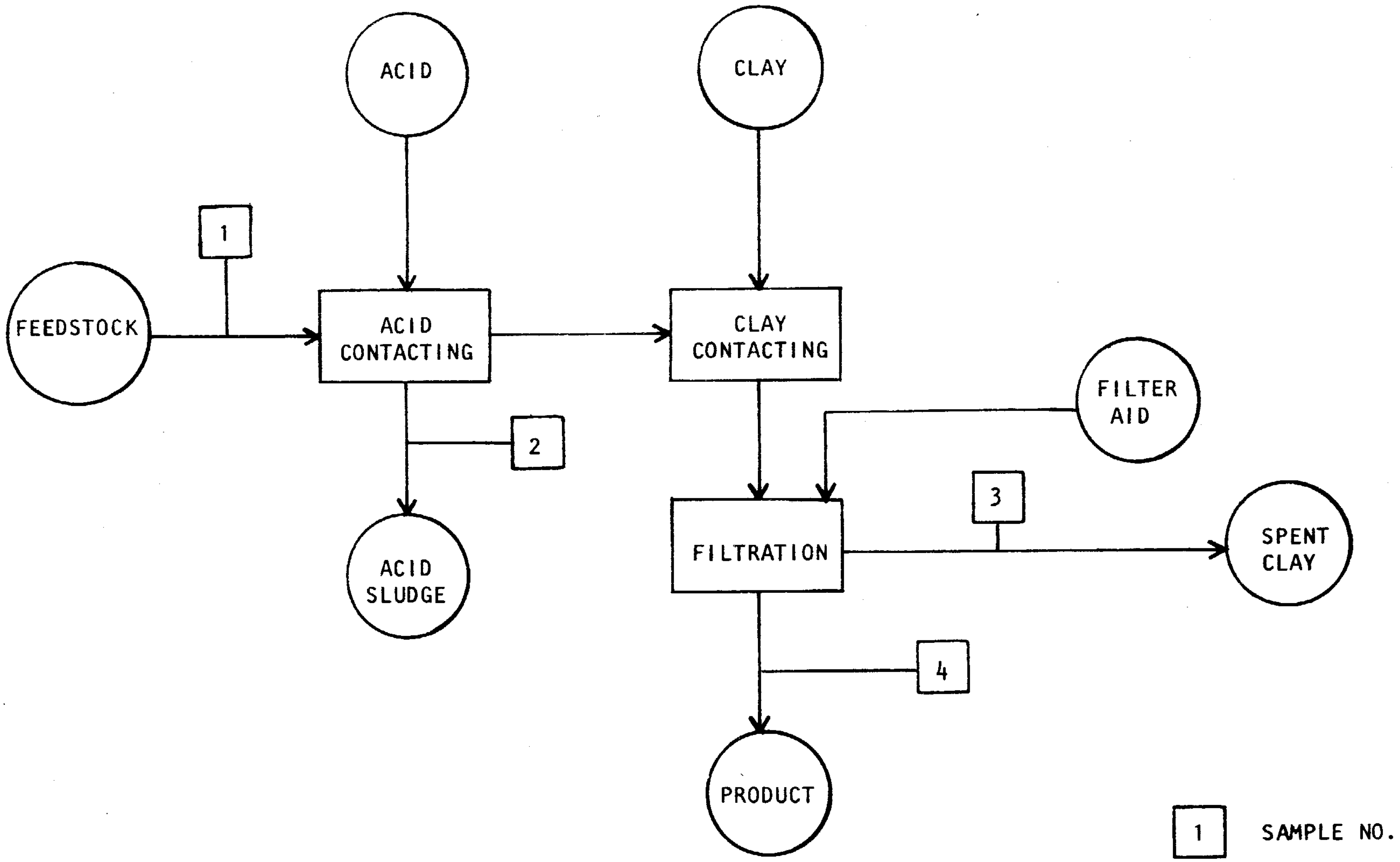

Figure VIII-3. Acid/clay re-refining process--laboratory simulations.

Acid Contacting--

The pretreated COMPOSITE oil was mixed with 5 volume percent of 93 percent sulfuric acid and the mixture was vigorously agitated in a flask for one hour at a temperature of 100°F. After this period the oil/acid mixture was then transferred to a separatory funnel and allowed to settle for a 24 hour period. The sludge was then drained from the bottom of the funnel. This process was repeated a second time. The yield of the pretreated oil after separation from the second contacting was 80 percent.

Clay Contacting--

The partially processed oil from the acid contacting operation was mixed with Filtrol Grade 20 clay adsorbent. Ninety grams of clay were used for each 1000 ml of the oil (0.75 lb/gallon of oil). The oil/clay mixture was heated to 425°F at an absolute pressure of 5-10 mm Hg for three hours. The clay contacting process yielded about 2 volume percent of additional overhead. Despite the use of a diatomaceous filter aid, a great deal of difficulty was experienced in filtering the clay/oil/filter aid mixture. Efforts were terminated with 65 percent of the oil fed to the acid/clay contacting process recovered as product.

Results of the Acid/Clay Re-Refining Process Laboratory Simulations

The results of the acid/clay laboratory simulations are provided in Tables VIII-5 and VIII-6 for the elemental and organic analyses, respectively. Acid contacting resulted in an overall 70 percent removal of the inorganic elements. The reductions in the lead and zinc content of the acid contacted oil were 70 and 77 percent, respectively. The material balance closure for the elements analyzed was reasonable for all but a few elements e.g., aluminum, strontium, tin and titanium. The high values for these elements can be attributed to contributions from the acid/clay reactants.

Results of the organic analyses indicate that most of the semivolatile organics are maintained within the product stream. Although some reduction in concentration levels have resulted from the acid/clay treatments the reduction is not pronounced for the compounds analyzed. The acid contacting step appears to have removed the n-nitrosodiphenylamine added as a spike to the oil. The two phthalate compounds present in the feed also appear to have been destroyed in the acid contacting step. Reduction of most compounds shown as positively identified would not be expected. Most are resistant to sulfuric acid attack and not preferentially adsorbed by the clay.

GENERAL CONCLUSIONS--LABORATORY SIMULATIONS OF RE-REFINING PROCESSES

The laboratory simulation of the three processes yielded products that are lighter in color than the feedstock; odor is also appreciably reduced. For the conditions employed in the laboratory, the solvent treatment/distillation process was the most effective in reducing both color and odor followed by the distillation/hydrofinishing process and the acid/clay process in that order. It is recognized that all these processes under proper conditions can yield a satisfactory lube oil basestock product.

TABLE VIII-5. DISPOSITION OF ELEMENTAL CONTAMINANTS IN PROCESS AND WASTE STREAMS DURING LABORATORY SIMULATIONS OF AN ACID/CLAY RE-REFINING PROCESS

	Feedstock (1)	Acid sludge (2)	Clay sludge (3)	Clay-contacted product (4)	Material balance (percent closure[a])
Relative Flow Rate (weight)	100	20	15	65	
Contaminant Weight (μg/g of feed)					
Aluminum	34	28	12	12	152
Antimony	0.6	0.9	<0.1	0.8	-
Arsenic	9.7	5.4	<0.2	2.0	76
Barium	70	41	1.5	12	80
Beryllium	<0.1	0.07	<0.01	<0.1	-
Boron	9.2	9.8	<0.01	0.2	108
Cadmium	1.4	1.1	<0.01	<0.1	79
Calcium	1,140	650	20	130	70
Chromium	9.5	75	<0.01	0.4	84
Cobalt	1.1	8.9	<0.01	<0.1	82
Copper	36	41	0.04	0.2	113
Iron	280	225	11	51	103
Lead	1,250	880	30	240	92
Magnesium	240	190	11	56	107
Manganese	16	13	0.2	1.3	88
Molybdenum	3.6	3.4	<0.01	<0.1	94
Nickel	4.1	4.5	<0.01	<0.2	110
Selenium	<1	<0.2	<0.1	<0.5	-
Silicon	55	12	9.5	13	65
Silver	<0.1	0.06	<0.01	<0.1	-
Sodium	260	160	2.3	15	68
Strontium	2.1	1.4	0.4	2.0	180
Thallium	<1	<0.4	<0.1	<1	-
Tin	19	43	1.1	1.2	238
Titanium	10	3.8	1.7	7.5	130
Vanadium	4.7	4.2	0.4	0.2	94
Zinc	820	630	3.0	9.0	78

[a] Material balance closure for streams 1 through 4 (< values = 0).

TABLE VIII-6. DISPOSITION OF ORGANIC CONTAMINANTS IN PROCESS AND WASTE STREAMS DURING LABORATORY SIMULATIONS OF AN ACID/CLAY RE-REFINING PROCESS

	Feedstock (1)	Acid sludge (2)	Clay sludge (3)	Product (4)
Relative Flow Rate (weight)	100	20	15	65
Contaminant Weight (μg/g of feed)				
Chlorobenzene	ND	ND	ND	ND
Bis(chloromethyl)ether	ND	ND	ND	ND
Phenol	ND*	ND*	1.2	ND*
Chlorophenol	ND*	ND*	ND*	ND*
Dichlorobenzene	ND	ND	ND	ND
Nitrobenzene	ND	ND	ND	ND
Nitrophenol	ND*	ND*	ND*	ND*
Naphthalene	54	9.0	6.0	3.3
2-Chloronaphthalene	ND	ND	ND	ND
2,4,6-Trichlorophenol	44	14	8.3	3.6
Acenaphthene	ND	ND	ND	ND
N-Nitrosodiphenylamine	98	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND
Phenanthrene/Anthracene	260	28	10	8.5
Dibutyl phthalate	820	ND	ND	ND
Butylbenzyl phthalate	110	ND	ND	ND
Pyrene	28	ND	0.4	5.0
Benz(a)anthracene	24	ND	0.5	ND
Triphenylphosphate	ND	1.8	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND
4,4'-DDE	68	2.6	2.6	ND
PCBs	43	3.4	10	2.7

ND $\leq$ 10 μg/g

ND* $\leq$ 20 μg/g

As will be discussed in Section XII all three processes produce wastes that are hazardous under the definitions contained in RCRA. These include the solvent sludge, distillate residue, and the clay sludge from the solvent treatment process; the distillate residue from the distillation/hydrofinishing process, and the acid waste and the clay sludge from the acid/clay processes. Although other waste streams, such as gas vents and condensate streams, can exist within these processes and their variations, they generally will not be as difficult to manage as the aforementioned streams.

Although the acid waste from the acid/clay process is probably the most difficult and expensive to treat, all of the identified waste streams involve similar treatment problems resulting from the high concentrations of metals and organics in the wastes. In terms of weight of waste, the ranking of the three processes in increasing order of waste produced would be the distillation/hydrofinishing process, solvent treatment (with hydrofinishing), and the acid clay process. A ranking of waste streams with regard to their potential hazard can be found in Section XII.

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SECTION IX

SAMPLING AND ANALYSIS OF THE NORTH CAROLINA PROP FACILITY IN GARNER, NC

The North Carolina oil re-refining facility in Garner, NC uses the Phillips Re-refined Oil Process (PROP) to produce a lubricating oil base stock from waste crankcase oil. The plant has the capacity to process 2 million gal/yr of waste oil, and is operated by the State of North Carolina. The waste oil is collected mainly from state vehicles.

The Phillips Re-refined Oil Process is shown schematically in Figure IX-1 along with identification numbers for the streams sampled during January and February of 1982. Waste oil entering the process is demetallized by treating with diammonium phosphate and diatomaceous earth. Diammonium phosphate (DAP) reacts with metals in the oil to form metal phosphates which form a precipitate insoluble in oil. The DAP contacting step is conducted at temperatures above the boiling point of water; thus, most of the water in the oil is removed as overheads in this step. After DAP treating, the oil is contacted with diatomaceous earth, which binds the metal phosphate precipitate, and filtered to remove the diatomaceous earth and the metals.

After demetallization and water removal, the oil is contacted separately with clay and charcoal to remove any remaining metals and is then catalytically hydrofinished. The clay, charcoal, and catalyst are periodically changed, and spent bed materials are landfilled.

A fuel fraction is removed from the oil in a flash drum following the hydrotreater. In addition, light hydrocarbons removed from the oil during dewatering are separated from water in an oil/water separator and sold for fuel.

RESULTS OF THE ANALYSES FOR THE PROP PROCESS AND WASTE STREAMS

The results of the analyses of key process streams are presented in Tables IX-1 and IX-2, respectively, for the inorganic and organic contaminants. Stream flow rates given in Table IX-1 are rough estimates based on operating experience at the North Carolina PROP facility. Because the contaminant concentrations in oil treating materials (diammonium phosphate, diatomaceous earth, and clay) are not known, material balances could not be determined for the elements in the waste oil and thus are not presented in Table IX-1.

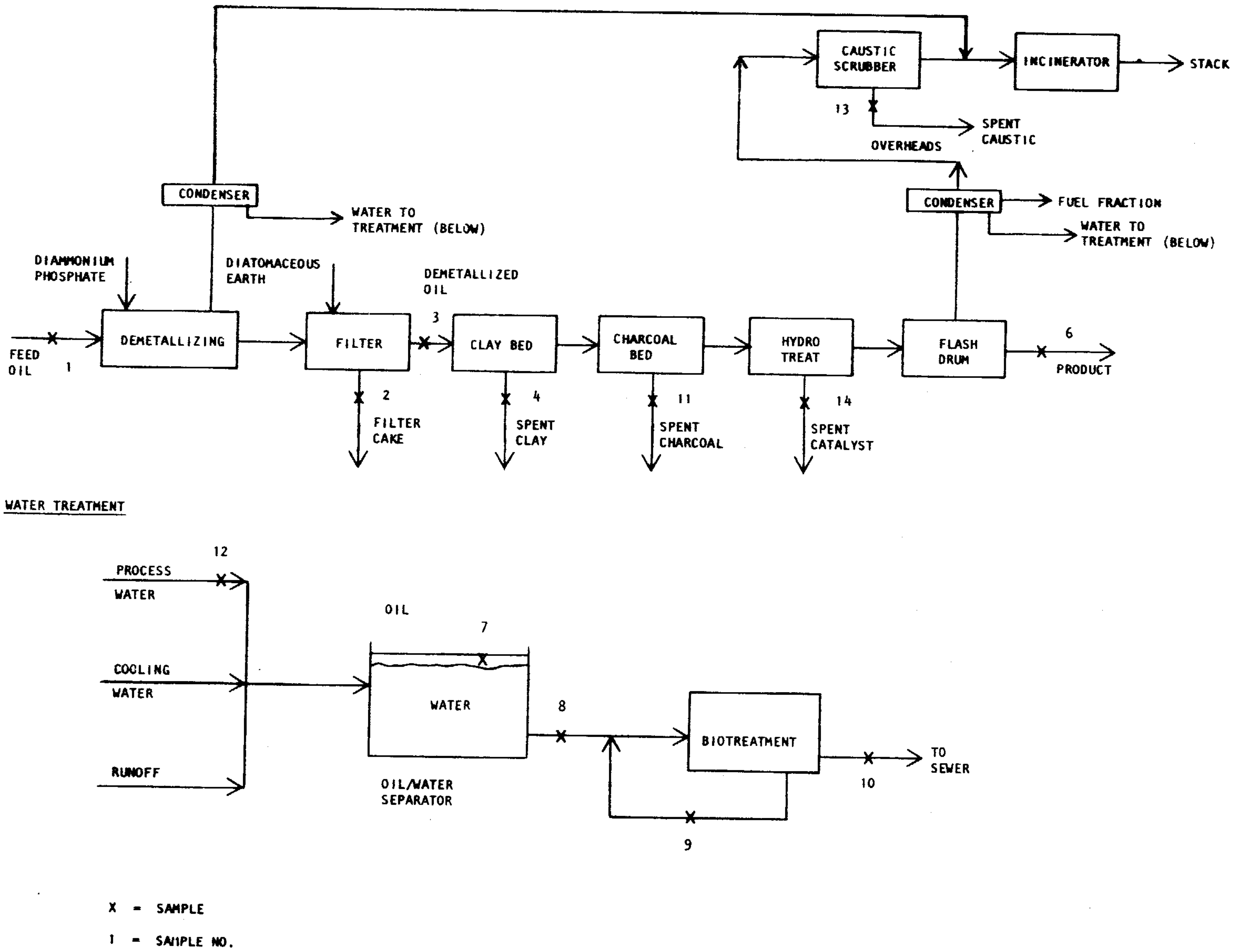


Figure IX-1. Schematic of North Carolina PROP facility.

TABLE IX-1. DISPOSITION OF ELEMENTAL CONTAMINANTS IN PROCESS AND WASTE STREAMS FROM THE NORTH CAROLINA PROP FACILITY

	Feedstock (1)	Filter cake (2)	Demetallized oil (3)	Spent clay (4)	Fuel fraction (5)	Product oil (6)
Relative Flow Rate (weight)	100	11	90	1.4	5	85
Contaminant Weight (μg/g of feed)						
Aluminum	8.3	37	<0.2	260	<0.01	<0.1
Antimony	<0.3	0.07	1.0	<0.1	<0.02	<0.3
Arsenic	1.7	9.2	1.6	1.8	<0.03	<0.5
Barium	150	130	2.2	2.6	<0.01	0.06
Beryllium	<0.04	0.07	<0.01	0.07	<0.01	<0.01
Boron	6.6	8.1	2.8	1.8	0.02	0.09
Cadmium	0.8	0.4	0.05	0.3	<0.01	<0.02
Calcium	610	420	14	130	0.08	1.5
Chromium	3.4	3.1	<0.06	1.0	<0.01	<0.06
Cobalt	0.2	2.2	<0.06	0.1	<0.01	<0.06
Copper	13	4.6	2.3	6.7	0.03	<0.03
Iron	110	250	5.2	180	0.1	2.6
Lead	2,060	1,300	180	250	0.03	3.5
Magnesium	270	-	1.3	-	<0.02	0.2
Manganese	13	13	0.04	5.9	<0.01	0.08
Molybdenum	1.4	0.5	0.3	0.04	<0.01	<0.03
Nickel	0.6	0.4	<0.1	0.3	<0.01	<0.09
Selenium	<0.4	<1	<0.4	<0.1	<0.02	<0.3
Silicon	22	<0.2	<0.1	0.8	<0.01	<0.09
Silver	<0.04	<0.1	<0.02	<0.01	<0.01	<0.02
Sodium	59	370	89	12	<0.01	<0.2
Strontium	0.1	0.2	<0.02	0.2	<0.01	<0.02
Thallium	<1.7	<2	<0.8	<0.2	<0.04	<0.7
Tin	2.2	2.0	2.1	0.2	<0.03	<0.7
Titanium	2.2	4.8	0.02	3.4	<0.01	<0.02
Vanadium	<0.2	3.5	<0.1	0.6	<0.01	<0.09
Zinc	630	400	3.3	13	0.01	0.3

TABLE IX-2. DISPOSITION OF ORGANIC CONTAMINANTS IN PROCESS AND WASTE STREAMS FROM THE NORTH CAROLINA PROP FACILITY

	Feedstock (1)	Fuel fraction (5)	Demetallized oil (3)	Product oil (6)
Relative Flow Rate (weight)	100	5	90	85
Contaminant Weight (μg/g of feed)				
Volatiles				
Trichlorofluoromethane	<20	<1	<19	<17
Trichlorotrifluoroethane	<20	<1	<19	<17
Methylene chloride	<20	<1	<19	<17
1,1-Dichloroethane	<20	<1	<19	<17
1,2-Dichloroethane	<20	<1	<19	<17
t-1,2-Dichloroethylene	<20	<1	<19	<17
Chloroform	<20	<1	<19	<17
1,1,1-Trichloroethane	<20	<1	<19	<17
Trichloroethylene	<20	<1	<19	<17
Carbon tetrachloride	<20	<1	<19	<17
Tetrachloroethylene	<20	<1	<19	<17
Benzene	90	32	<19	<16
Toluene	670	75	260	160
Ethylbenzene	160	45	150	70
Semivolatiles				
Chlorobenzene	<20	<2	<19	<17
Phenol	<10	5	<10	<10
Chlorophenol	<10	<1	<10	<10
Dichlorobenzene	<10	<1	<10	<10
Nitrobenzene	<10	<1	<10	<10
Nitrophenol	<10	<1	<10	<10
Naphthalene	280	30	210	95
2-Chloronaphthalene	<10	<1	<10	<10
2,4,6-Trichlorophenol	<10	<1	<10	<10
Acenaphthene	<10	<1	<10	<10
N-nitrosodiphenylamine	<10	<1	<10	<10
Hexachlorobenzene	<10	<1	<10	<10
Phenanthrene/anthracene	130	5	110	71
Pyrene	20	2	15	15
Benz(a)anthracene	12	<1	<10	5
Benzo(a)pyrene	<10	<1	16	6
4,4'-DDE	<20	<2	<19	<17
PCBs	<1	<0.1	<1	<1

Although the demetallizing step is reasonably effective, the lead content of the oil from the demetallizer is relatively high (~200 μg/g). Much of the lead, however, appears to have been removed by clay treatment, with high levels of lead found in the spent clay. The lead content of the final product was less than 5 μg/g. The elemental content of the fuel fraction was negligible with only iron at 2 μg/g found at levels exceeding 1 μg/g. Use of this fraction as a process fuel appears to be environmentally acceptable.

The organic data shown in Table IX-2 indicate the waste oil feedstock contains only trace amounts of chlorinated solvents. Only a few volatile components were identified in the feedstock. Some of these volatiles, notably toluene, were not totally removed by the process, and this compound is present in the product oil at a 200 μg/g level. Other compounds present in both feedstock and product are naphthalene and POM compounds including benz(a)pyrene at modest levels (~10 μg/g).

CONCLUSIONS AND RECOMMENDATIONS

The data presented in Tables IX-1 and IX-2 are not sufficient of themselves to formulate a clear picture of the significance of the various steps in the PROP process. Although the solid waste streams, including the filter sludge from the demetallizer, the spent clay, and most likely the spent charcoal, contain high levels of metal contamination, these streams are currently approved for landfill. Catalyst is treated as a hazardous waste.

The environmental impact that can be attributed to the organic contaminants is not as apparent.

SECTION X

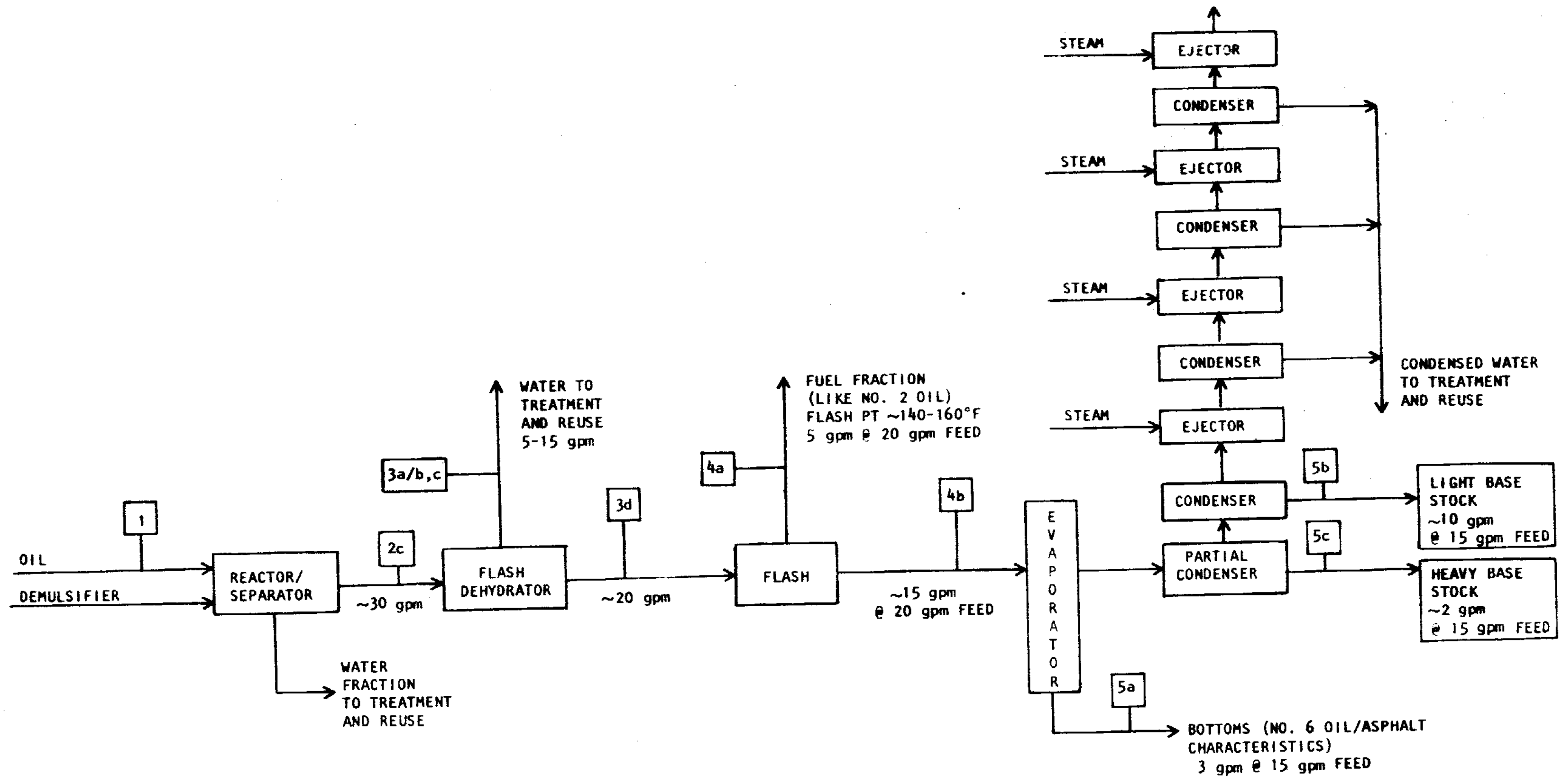
SAMPLING AND ANALYSIS AND COMPUTER SIMULATION OF A PRETREATMENT/DISTILLATION/CLAY TREATMENT PROCESS

A sampling and analysis program and computer simulations were conducted for a plant using a pretreatment/distillation/clay treatment process to produce a lubricating oil base stock from waste oil. The facility typically processes about 45 barrels of waste oil per hour.

The process is shown schematically in Figure X-1 along with identification numbers for streams sampled in the fall of 1982. Waste oil entering the process is pretreated with a proprietary demulsifier which causes partial separation of oil and water. The water phase is decanted and the pretreated oil is fed to a series of two flash drums which remove water and light ends. Product oil from the second flash drum is fed to a thin film evaporator which vaporizes the lube stock, leaving oil bottoms. Oil removed overhead from the evaporator is collected in a series of two condensers, the first of which collects heavy lube stock, while the second condenses the remaining lube stock. Overheads from the second condenser are condensed in a series of six steam ejectors and water condensers which serve to maintain the vacuum in the thin film evaporator and its associated oil condensers. Light and heavy lube stock from the two oil condensers are blended to meet buyer specifications and are treated with clay. The clay treatment used is not shown in Figure X-1.

This operation is a fully-automated, continuous system. This continuous system is possible because of the unique configuration and assemblage of the various unit operations. However, to handle industrial oils selectively and put them in a form amenable to subsequent continuous processing, a batch pretreatment step is utilized. Additionally, the process involves the innovative use of a Luwa Thin Film Evaporator in a partial condensation mode. The partial condensation aspect of the distillation step and the three-stage vacuum ejector used in the stripping step allow for production of a wide variety of different products.

Historically, the most significant disadvantage associated with any type of high-temperature vacuum distillation attempts was the continual fouling which caused substantial downtime and costly clean-outs. The use of the Luwa Thin Film Evaporator is expected to minimize the problems commonly associated with high temperature, vacuum distillation by significantly reducing fouling



PRETREATMENT

BATCH

OIL IS MIXED W/A DEMULSIFIER, THEN ALLOWED TO SETTLE. WATER AND OIL ARE THEN DRAWN OFF.

DEHYDRATION

ISOTHERMAL FLASH
T = 300°F ± 50°F
P = 1 ATM

STRIPPING

ISOTHERMAL FLASH
T = 375-450°F
P = 25-50 mm Hg
Product Specs:
I.B.P. = 450°F @ 25-50 mm Hg

DISTILLATION

THIN FILM EVAPORATOR
FILM IS 2 mm THICK
T = 600-700°F (MAINTAINED BY DOWTHERM JACKET)
ΔT = 10-30°F (BOTTOM TO TOP)
P = 1-10 mm Hg (usu. 5 mm Hg)

PARTIAL CONDENSER
T = 450-600°F
P = SAME AS EVAPORATOR

TOTAL CONDENSER
T = 85°F
P = SAME AS EVAPORATOR

☐ SAMPLE I.D.

Figure X-1. Schematic of re-refining facility.

and minimizing downtime. The low hold-up in the Luwa Evaporator limits the amount of time the oil is subjected to high temperatures while the agitation imparted by the rotor reduces "hot-spots" that could allow degradation and coking. The process is the first commercial-scale application of the Luwa unit in the re-refining industry.

RESULTS OF LABORATORY ANALYSES

The results of the laboratory analyses of the samples collected at the re-refining facility in the Fall of 1982 are shown in Tables X-1 and X-2 for the elemental and organic components, respectively. The values shown are given in µg/g of process or waste stream, representing actual stream concentrations, as opposed to the material balance oriented flow units (µg/g of feed) used in previous sections.

The inorganic elemental contents of the feedstock, although relatively low in lead and zinc, are consistent with a used crankcase oil. Eventually, the preponderance of the elements in the used oil feedstock end up in the bottoms from the Luwa unit. The elemental content of the aqueous phase from the dehydration step is within EP toxicity limits. Concentrations are generally reduced further by the wastewater treatment system shown schematically in Figure X-2.

Material balance calculations for the elements were made across the dehydration unit, the fuel stripper, and the vacuum distillation unit. Overall, the results, as shown in Table X-3, are not as good as those obtained for the laboratory simulations conducted in this program. Recoveries across the dehydration unit appear reasonable. However, recoveries across the fuel stripper and the distillation unit are highly variable and lower in general than those across the dehydrator. The lower recoveries found across the fuel stripping and distillation system may be due partially to the relative stream flow rates shown in Table X-1 and used in the material balance calculations. For example, an increase in the flow rate of stream 4b would increase the recoveries across the fuel stripper. However, any increase in stream 4b (the input to the distillation unit) would have to be matched by a corresponding increase in the bottoms stream from the still if the already low recoveries across the distillation unit are to be maintained.

The clay treatment step was not included in the material balance calculations. However, as shown in Table X-1, the already low-elemental content of the distilled light lube is further reduced by clay contacting.

Material balance calculations were also made for the organic components shown in Table X-4. The recoveries of the volatile organic components across the dehydration unit were variable. Losses to air may account for the tendency to low recoveries, although such losses are small according to facility data. Volatiles remaining after the dehydration step were almost completely removed from the main process stream leaving the fuel stripping unit (see stream 4b in Table X-2).

TABLE X-1. RESULTS OF ELEMENTAL ANALYSIS OF FEED, WASTE AND PROCESS STREAMS FROM RE-REFINING FACILITY (μg/g)

		Dehydration				Vacuum distillation					
	Feedstock 1	Organic phase 3a/b	Aqueous phase 3c	Product 3d	Fuel cut 4a	Feed 4b	Bottoms 5a	Light lube[a] 5b	Heavy lube[a] 5c	Spent clay 6a	Light product[a] 8
Relative flow rates (weight)	100	3	17	80	14	66	13	45	8	6	<3
Elements											
Aluminum	650	100	0.8	680	32	470	670	0.8	2.4	2.08%	1.4
Antimony	1.1	0.4	0.02	1.0	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Arsenic	4.5	0.4	0.03	5.5	0.7	3.7	8.3	0.7	0.7	0.4	0.7
Barium	84	12	0.2	95	7.0	100	14	0.03	0.3	140	0.07
Beryllium	0.3	0.06	0.001	0.3	0.02	0.1	0.3	0.02	0.02	211	0.02
Boron	11	0.4	1.5	8.9	3.3	6.3	13	1.0	1.3	27	0.3
Cadmium	1.0	0.1	0.001	1.2	0.1	1.8	5.7	0.02	0.02	0.5	0.02
Calcium	1,030	24	22	890	83	1,290	3,480	0.8	4.2	7,730	0.7
Chromium	18	3.0	0.004	20	1.7	16	35	0.4	0.1	18	0.07
Cobalt	1.2	0.09	0.005	1.0	0.07	0.5	1.4	0.07	0.07	1.5	0.07
Copper	130	20	0.1	130	9.3	150	265	4.7	2.6	14	0.9
Iron	1,300	220	3.5	1,260	120	1,080	1,600	30	6.8	7,120	1.7
Lead	350	56	1.5	500	57	930	2,090	2.8	7.4	0.4	2.7
Magnesium	240	9.4	3.9	220	20	330	900	0.4	0.8	9,450	0.4
Manganese	27	0.8	0.4	32	1.5	24	43	0.07	0.1	90	0.02
Molybdenum	12	1.8	0.004	14	0.8	11	26	0.04	0.04	0.04	0.04
Nickel	25	1.7	0.08	17	2.1	10	16	0.5	1.3	6.9	0.4
Selenium	0.4	0.4	0.02	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Silicon	200	0.1	1.7	200	36	5.2	8.6	10	7.0	150	4.7
Silver	0.02	0.02	0.001	0.02	0.02	0.02	0.02	0.02	0.2	0.02	0.02
Sodium	450	22	13	610	33	420	590	5.1	7.9	400	4.2
Strontium	3.4	0.3	0.02	3.7	0.2	4.1	8.7	0.02	0.02	44	0.02
Thallium	0.9	0.8	0.04	0.9	0.9	0.8	0.8	0.9	0.9	0.8	0.9
Tin	16	2.9	0.03	18	2.0	23	34	0.7	1.3	4.1	0.7
Titanium	20	0.9	0.001	28	2.3	26	53	0.02	0.2	200	0.2
Vanadium	7.5	1.0	0.005	5.5	0.5	5.9	6.2	0.1	0.1	20	0.1
Zinc	340	19	4.4	400	47	880	2,960	0.5	4.6	140	0.5

[a] Clay treated product.

TABLE X-2. ORGANIC COMPOUNDS IN FEED, WASTE AND PROCESS STREAMS FROM RE-REFINING FACILITY (μg/g)

		Dehydration				Vacuum distillation					
	Feedstock 1	Organic phase 3a/b	Aqueous phase 3c	Product 3d	Fuel cut 4a	Feed 4b	Bottoms 5a	Light lube[a] 5b	Heavy lube[a] 5c	Spent clay 6a	Light product[a] 8
Relative flow rates (weight)	100	3	17	80	14	66	13	45	8.5	6	43
Volatile Organics											
Trichlorotrifluoroethanes	1,400	13,000	370	<20	<30	<30	NA	NA	NA	NA	NA
Dibromoethanes	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Dibromoethenes	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Cyclopentane, methyl	<30	1,900	<20	<20	<30	<30	NA	NA	NA	NA	NA
Cyclohexane, methyl	280	4,900	<20	90	<30	<30	NA	NA	NA	NA	NA
Chloromethane	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Dichlorodifluoromethane	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Bromomethane	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Vinyl chloride	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Chloroethane	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Methylene chloride	<30	2,400	<20	<20	<30	<30	NA	NA	NA	NA	NA
Acrolein	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Acrylonitrile	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Trichlorofluoromethane	<30	3,100	<20	<20	<30	<30	NA	NA	NA	NA	NA
1,1-Dichloroethylene	<30	280	<20	<20	<30	<30	NA	NA	NA	NA	NA
1,1-dichloroethane	<30	360	<20	<20	<30	<30	NA	NA	NA	NA	NA
Trans-1,2-dichloroethylene	<30	400	<20	<20	<30	<30	NA	NA	NA	NA	NA
Chloroform	<30	<90	<20	<20	<30	<30	NA	NA	NA	NA	NA
1,2-Dichloroethane	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
1,1,1-Trichloroethane	1,700	50,000	610	200	<30	<30	NA	NA	NA	NA	NA
Carbon tetrachloride	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Bromodichloromethane	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Bis-chloromethyl ether	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
1,2-Dichloropropane	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Trans-1,3-dichloropropene	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Trichloroethylene	790	20,000	230	160	110	<90	NA	NA	NA	NA	NA
Dibromochloromethane	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Cis-1,3-dichloropropene	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA
1,1,2-Trichloroethane	<30	<20	<20	<20	<30	<30	NA	NA	NA	NA	NA

(continued)

TABLE X-2 (continued)

		Dehydration				Vacuum distillation					
	Feedstock 1	Organic phase 3a/b	Aqueous phase 3c	Product 3d	Fuel cut 4a	Feed 4b	Bottoms 5a	Light lube[a] 5b	Heavy lube[a] 5c	Spent clay 6a	Light product[a] 8
Volatile Organics (cont.)											
Benzene	< 100	1,600	<20	<90	<90	<30	NA	NA	NA	NA	NA
2-Chloroethylvinyl ether	< 30	< 20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Bromoform	< 30	< 20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Tetrachloroethene	690	8,200	110	140	<30	<30	NA	NA	NA	NA	NA
1,1,2,2-Tetrachloroethane	< 30	< 20	<20	<20	<30	<30	NA	NA	NA	NA	NA
Toluene	1,400	26,000	1,300	340	290	< 90	NA	NA	NA	NA	NA
Chlorobenzene	<30	<20	<20	<20	< 30	< 30	NA	NA	NA	NA	NA
Ethylbenzene	440	19,000	<20	30	130	<30	NA	NA	NA	NA	NA
Dimethylbenzenes	1,400	18,000	270	600	550	<30	NA	NA	NA	NA	NA
Alkylbenzenes (C_9H_{12})	<30	21,000	<30	3,600	< 30	<30	NA	NA	NA	NA	NA
Semivolatile Organics											
Phenol	46	<5	<0.02	26	110	<5	< 4	12	< 5	< 1	12
Chlorophenol isomers	<6	<5	<0.02	<5	<4	<5	< 4	<5	< 5	< 1	< 5
Dichlorobenzene isomers	15	<5	0.2	9	<4	<5	< 4	<5	< 5	< 1	< 5
Nitrobenzene	<6	<5	<0.02	<5	<4	<5	< 4	<5	< 5	< 1	< 5
2-Nitrophenol	<6	<5	<0.02	<5	<4	<5	< 4	<5	< 5	< 1	< 5
Naphthalene	270	1,400	0.7	280	470	31	< 4	27	< 5	< 1	< 5
2-Chloronaphthalene	<6	<5	<0.02	< 5	<4	<5	< 4	<5	< 5	< 1	< 5
2,4,6-Trichlorophenol	<6	8	<0.02	< 5	<4	<5	< 4	<5	< 5	< 1	< 5
Acenaphthene	9	<5	<0.02	< 5	98	<5	< 4	13	< 5	< 1	< 5
N-Nitrosodiphenylamine	<6	<5	<0.02	< 5	140	<5	< 4	<5	< 5	< 1	8
Hexachlorobenzene	<6	<5	<0.02	< 5	<4	<5	< 4	<5	< 5	< 1	< 5
Phenanthrene/Anthracene	150	40	0.03	150	670	46	< 4	200	22	< 1	40
Dibutylphthalate	<6	<5	<0.02	< 5	10	<5	< 4	<5	< 5	< 1	< 5
Butylbenzylphthalate	<6	<5	<0.02	< 5	<4	<5	< 4	29	< 5	< 1	< 5
Bis(2-ethylhexyl) phthalate	32	7	0.1	93	115	25	< 4	93	69	< 1	< 5
Pyrene	20	<5	<0.02	25	100	18	< 4	48	23	5	32
Benz(a)anthracene	18	<5	<0.02	19	83	31	< 4	91	100	4	36
Triphenyl phosphate	<6	<5	<0.02	< 5	<5	<5	< 4	<5	< 5	8	< 5
Benzo(a)pyrene	<6	<5	<0.02	< 5	<5	<5	< 4	16	65	2	15
4,4'-DDE	<6	<5	<0.02	< 5	<5	<5	< 4	<5	< 5	< 1	< 5
PCBs	18	<11	<10	<21	<8	<19	<11	<11	< 11	< 8	< 14

[a] Clay treated product.
NA = Not Analyzed (analyses not conducted for volatile components).

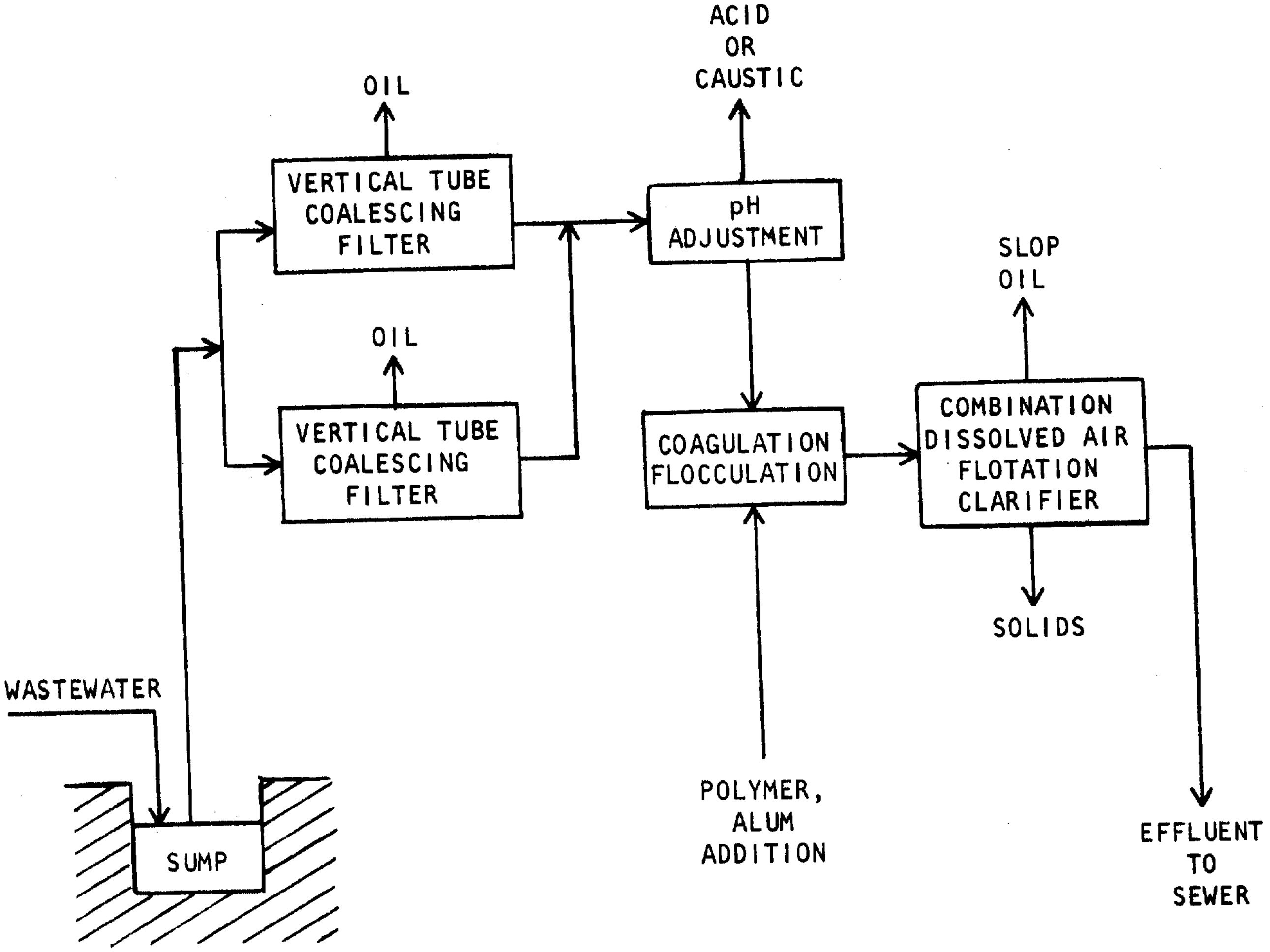


Figure X-2. Schematic of aqueous treatment system.

TABLE X-3. MATERIAL BALANCE FOR ELEMENTS

Element ICAP/Analysis	Percent recovery across system components		
	Dehydration unit[a]	Fuel cut[b]	Vacuum distillation[c]
Aluminum	84	58	28
Antimony	72	-	-
Arsenic	98	54	44
Barium	91	88	<10
Beryllium	80	-	-
Boron	68	63	55
Cadmium	96	125	64
Calcium	70	121	53
Chromium	89	68	44
Cobalt	67	-	-
Copper	80	96	37
Iron	78	72	31
Lead	115	153	45
Magnesium	74	125	54
Manganese	95	63	35
Molybdenum	93	68	47
Nickel	55	51	36
Selenium	-	-	-
Silicon	80	<10	177
Silver	-	-	-
Sodium	110	57	29
Strontium	87	94	-
Thallium	-	-	-
Tin	90	107	32
Titanium	112	78	40
Vanadium	59	89	21
Zinc	94	182	61

[a] 1 = 3a/b + 3c + 3d

[b] 3c = 4a + 4b

[c] 4b = 5a + 5b + 5c

Note: See Table X-1 for Stream ID Nos.

TABLE X-4. MATERIAL BALANCE FOR ORGANICS

Compounds	Percent recovery across system components		
	Dehydration unit[a]	Fuel cut[b]	Vacuum distillation[c]
Trichlorotrifluoroethanes	53	-	-
1,1,1-trichloroethane	104	-	-
Trichloroethylene	97	-	-
Tetrachloroethene	55	-	-
Toluene	91	-	-
Ethylbenzene	135	-	-
Phenol	45	74	-
Naphthalene	99	40	54
Phenanthrene/anthracene	81	103	302
Pyrene	100	130	197
Benz(a)anthracene	84	276	240
Benzo(a)pyrene	-	-	375[d]

[a] 1 = 3a/b + 3c + 3d

[b] 3c = 4a + 4b

[c] 4b = 5a + 5b + 5c

[d] Based on an inlet concentration in 4b of 5 μg/g

Note: See Table X-2 for Stream ID Nos.

Material balances for the semivolatile organics were reasonably good across the dehydration unit. Thereafter, the recoveries (except that for naphthalene) exhibit a general increase across the subsequent system components, i.e., the fuel stripper and the distillation unit. Recoveries of the PNA compounds actually showed overall increases ranging from 100 to 200 percent or more. The significance of these data are questionable, both because of the limited data and the accuracy of the analytical test procedures used for these compounds. However, formation of these compounds in the high temperature environment is a possibility that appears to justify further study. In any event, the PNA compounds listed in Tables X-2 and X-4 are largely contained in the main process streams, although some are lost in the fuel cut. Further reduction through clay contacting also appears to take place as shown by concentrations of these compounds in streams 5b and 8 in Table X-2.

COMPUTER SIMULATION OF THE COMMERCIAL PROCESS

Computer simulations were conducted for unit operations in the process to see how well theoretical equilibrium calculations can predict the fate of oil contaminants. The simulations were carried out using the PROCESS® program developed by Simulation Sciences, Inc.* Use of the program was arranged through McDonnell Douglas Automation Co.** and Control Data Corp.,+ licensees of Simulation Sciences. The PROCESS® program allows simulation of most chemical reactions and separation processes for which the degree of completion is determined by thermodynamic equilibrium. Thus, it was possible to simulate the flash drums, the evaporator, and the condensers in the process. The clay treatment step could not be simulated because the reactions between the clay and oil contaminants are controlled by mass transfer and kinetics in addition to equilibrium. In addition, the contaminants are not well enough characterized nor are the reactions in which they participate well enough understood to allow simulation by the techniques used. Insufficient information was available to simulate the demulsifier pretreatment step, or to determine whether the step can be simulated using the PROCESS® software.

For vapor-liquid separation operations, such as the steps simulated for the commercial process, the PROCESS® program makes iterative multicomponent vapor-liquid equilibrium calculations to determine the compositions of product streams. For the petroleum fractions which make up the major portion of waste oil, and for most of the contaminants detected in waste oil, the thermodynamic properties data required to make equilibrium calculations are available in the

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*Simulation Sciences, Inc.
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PROCESS® component properties data library. In the cases of chlorinated biphenyls and trichlorophenol, for which data were not available in the PROCESS® library, thermodynamic properties data were taken from published literature,[1-3], or calculated using techniques provided in Perry's Handbook of Chemical Engineering.[4] The Braun K-10 and Chao-Seader methods were selected from the methods available in the program software to calculate vapor-liquid equilibrium constants from thermodynamic properties data.

The operating parameters used for the simulations were based on the conditions typically used at the plant. The water removal flash drum simulation was conducted at 121°C and atmospheric pressure, and the light ends removal simulation operation was simulated at 213°C and 35 mmHg. The thin film evaporator used at the plant is a distillation column with one tray and a small temperature drop from top to bottom. Thus, it could be simulated as a flash drum. The temperature and pressure used for the simulation were 343°C and 7 mmHg. The pressure in the two condensers following the evaporator is approximately the same as that in the evaporator. The temperatures used in the simulation of these units were 282°C, for the first condenser, and 29°C, for the second condenser. Table X-5 summarizes the operating parameters used in the simulation, and compares them to the conditions typically used at the plant. As the table shows, the conditions used in the simulation are within the range of conditions used at the facility.

Table X-6 compares the unit operation product flows predicted by the computer simulation with those typically encountered at the facility. The flows of product streams predicted by the simulation were close to those encountered at the plant. The boiling range used for the feedstock in the simulation was based on analyses of waste oils conducted by GCA and does not provide a quantitative measure of the less volatile components. Table X-7 shows the boiling curve for the feedstock used in the simulation, as well as the boiling curves predicted by the simulation for the product streams.

Table X-8 traces the fate of oil contaminants through the process as predicted by the unit operation simulations. Values shown are μg/g of feed. The contaminant concentrations used for the simulation feedstock were based on the results of analyses conducted by GCA on the plant feedstock and on other waste oils. For the simulation, the concentration of each chlorinated biphenyl was increased to approximately the total chlorinated biphenyl concentration detected in the feedstock analysis. In addition, the benzo(a)pyrene concentration used in the simulation is higher than the typical concentration of this compound in waste oil. Higher concentrations were used for these compounds in order to insure against rounding errors.

As Table X-8 shows, volatile compounds are largely removed in the dehydration and fuel removal steps. Benzo(a)pyrene is divided approximately evenly between the light and heavy lube stocks, while chlorinated phenol and biphenyls are found in the light lube stock.

The fate of metals in the re-refining process could not be simulated for a number of reasons. First, although data are available on the concentrations of a number of metals in waste oil, data generally are not available on the compound forms of metals in waste oil. For metals added to lube oil to alter

TABLE X-5. OPERATING PARAMETERS USED IN THE COMPUTER SIMULATION COMPARED TO THE RANGE USED AT THE PLANT

Unit operation	Simulation specifications T(°C)	Simulation specifications P(mmHg)	Typical plant operating conditions T(°C)	Typical plant operating conditions P(mmHg)
Dehydration	121	760	121-177	760
Light ends removal	212	35	191-232	25-50
Thin film evaporator	343	7	316-371	1-10
Partial condenser	282	7	232-316	1-10
Total condenser	29	7	~29	1-10

TABLE X-6. COMPARISON OF UNIT OPERATION PRODUCT FLOWRATES PREDICTED BY THE SIMULATION WITH THOSE TYPICALLY ENCOUNTERED AT THE PLANT

Unit operation	Product stream	Product stream rate (percent of unit feed) Plant experience	Product stream rate (percent of unit feed) Simulation results
Dehydration	Water	20-50	22.4
	Dry oil	50-80	77.6
Light ends removal	Light ends	~25	20.3
	Stripped oil	~75	79.7
Thin film evaporator	Bottoms	~20	17.5
	Overheads (oil)	~80	82.5
Partial condenser	Heavy lube stock	~15	13.0
	Overheads (light lube)	~85	87.0
Total condenser	Light lube stock	100	100
	Overhead	0	0

TABLE X-7. BOILING CURVES USED FOR THE COMPUTER SIMULATION FEEDSTOCK AND PREDICTED FOR THE PRODUCT STREAMS (TBP AT ATMOSPHERIC PRESSURE)

Fraction vaporized (percent)	Temperature (°C)						
	Feed oil	Water stream organics	Light ends	Stripped oil	Light lube stock	Heavy lube stock	Bottoms
0	134	74	142	199	192	372	402
5	162	137	147	330	316	413	515
10	180	141	158	365	352	431	571
30	359	159	182	408	400	489	641
50	412	172	218	435	419	526	654
70	453	185	243	483	439	572	663
90	638	217	330	651	480	651	
95	663	221	383	663	503	663	
100		252	424	663	539		
End point	663					663	663

TABLE X-8. COMPUTER SIMULATION PREDICTION OF THE FATE OF CONTAMINANTS IN THE RE-REFINING PROCESS

	Feedstock (pretreated oil)	Overhead from dehydration	Dry oil	Light ends	Stripped oil	Light lube oil	Heavy lube oil	Bottoms
Relative flow (weight)	100	22.4	77.6	13.1	64.5	46.2	6.91	11.3
Water content (wt percent)	16.3	72.7	5.15	30.5	--	--	--	--
Contaminant content (μg/g of feed)								
Phenanthrene	147	0.16	146	34	113	112	0.42	0.12
Tetrachloroethene	671	532	139	137	1.9	1.9	--	--
Naphthalene	264	40	225	202	22	22	0.007	0.003
Anthracene	147	0.14	146	31	115	114	0.46	0.13
1,1,1-Trichloroethane	1,650	1,530	125	124	0.8	0.8	--	--
Trichloroethylene	772	695	77	76	0.6	61	--	--
Toluene	1,370	1,140	227	224	2.7	2.7	--	--
Ethylbenzene	429	307	123	120	2.3	2.3	--	--
Benzo(a)pyrene	33	--	33	0.013	33	19.4	11.4	2.1
Pyrene	40	0.003	40	1.2	38	37	0.8	0.17
Benz(a)anthracene	24	--	24	0.85	24	23	0.44	0.095
Chlorobiphenyl	25	0.61	24	17	6.9	6.9	0.005	0.002
Dichlorobiphenyl	29	0.064	29	9.5	19.6	19.5	0.05	0.015
Trichlorobiphenyl	34	0.1	34	13.5	20	20	0.04	0.013
Tetrachlorobiphenyl	38	0.06	38	10.5	2,750	27.4	0.09	0.027

its properties, the compound form is known at the time of addition; however, the compound form may change as the oil ages, or during reprocessing. In addition, for metals present in the form of organometallic compounds, insufficient data are available to evaluate the thermodynamic properties necessary for simulation. For metals in the form of inorganic salts, the impact of interaction with oil on their degree of vaporization cannot be predicted.

With the exception of tetra-alkyl lead, which may be present in waste oil as a result of its use in gasoline, most organometallic compounds which would be expected to be present in waste oil are higher boiling than the bulk of the oil. Thus, little volatilization of metals would be expected to occur in the dehydration and fuel removal steps. Tetra-alkyl lead could be vaporized in both of these steps. Vaporization of other organometallics and also metallic chlorides would occur in the evaporator, resulting in the presence of metals in the light and heavy lube stocks. Metal oxides would be expected to leave the process in the evaporator bottoms.

COMPARISON BETWEEN SAMPLING AND ANALYSIS PROGRAM AND LABORATORY SIMULATION RESULTS

Correlations between the results of the laboratory simulation program and the computer simulation are difficult to discern from a comparison of Tables X-2 and X-8. To assist in the comparison the results are presented in Table X-9 which shows the percent of each contaminant present in the major process stream.

The results indicate reasonable agreement between the sampling and analysis program and the computer simulation, considering the uncertainties of the chemical analysis. It is interesting to note that the PNA concentrations measured downstream of the distillation unit show a definite increase. This occurrence has been noted on other occasions throughout this program and appears to indicate that some chemical rearrangements are taking place during the high temperature distillations.

Computer simulations can be useful in following the flow of contaminants through a re-refining process in which chemical interactions are not significant. The simulations would be particularly useful in projecting the disposition of species not detected in the feed stream during a sampling and analysis program but which may be expected to be present in some feed batches. Such species include PCBs and other potential oil contaminants. Simulation would also be useful where simultaneous sampling of feed and product streams is not possible. More sophisticated simulations than the one used here can also find application in designing a system to ensure that vapor-liquid separation are consistent with the delivery of satisfactory fuel oil and lubricating oil products.

TABLE X-9. COMPARISON OF DISPOSITION OF ORGANICS IN PROCESS STREAMS[a]

Contaminant	Oil from dehydration	Oil from fuel stripping	Oil from vacuum distillation		
			Bottoms	Light lube	Heavy lube
Phenanthrene	80(100)	20(77)	0(<1)	60(76)	1(<1)
Tetrachloroethene	16(21)	2(<1)	0(0)	0(0)	0(0)
Naphthalene	83(85)	8(8)	0(0)	5(8)	0(0)
Anthracene	80(100)	20(78)	0(<1)	60(76)	1(<1)
1,1,1-trichloroethane	9(8)	<1(<1)	0(0)	0(0)	0(0)
Trichloroethylene	16(10)	<1(<1)	0(0)	0(0)	0(0)
Toluene	19(17)	4(<1)	0(0)	0(0)	0(0)
Ethylbenzene	5(29)	<1(<1)	0(0)	0(0)	0(0)
Benzo(a)pyrene	-(100)	-(100)	0(6)	>120(60)[b]	>92(35)[b]
Pyrene	100(100)	60(97)	0(<1)	108(94)	10(3)
Benz(a)anthracene	85(100)	100(97)	0(<1)	227(94)	47(2)

[a] Values in table are percent of contaminant in oil feed found in process streams as determined by laboratory experiments and (by computer simulations).

[b] Based on feedstock concentration of <6 μg/g.

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SECTION XI

COMPUTER SIMULATIONS OF RE-REFINING OPERATIONS

PROCEDURES AND RESULTS

Computer simulations of oil re-refining unit operations were used to aid in the determination of the fate of contaminants in waste oil in the solvent treatment/distillation/finishing, distillation/hydrofinishing, and acid/clay processes. These processes are shown in Figures XI-1 through XI-3, respectively.

The solvent treatment/distillation/finishing process begins with dehydration and removal of fuel fractions. The waste oil is then contacted with a solvent, which selectively dissolves the lubricating oil. The oil solvent extract is separated from the solvent sludge and distilled to recover the solvent. The solvent treated oil is then fractionated into the desired lubricating oil stocks which are further upgraded by hydrotreating or clay contacting.

The distillation/hydrofinishing re-refining process also begins with removal of water and fuel fractions. The waste oil is then separated into a fuel cut, a lubricating oil stock, and a heavy residue by vacuum distillation. The lubricating oil stock is hydrotreated, and then fractionated by another vacuum distillation step.

The acid/clay process allows for the greatest variation in design parameters. The oil is dehydrated and stripped of fuel fractions, then mixed with sulfuric acid. The acid draws out most of the contaminants to form an acid sludge which is separated from the oil by centrifuging. The oil is contacted with clay to remove additional contaminants. The cleaned oil can then be fractioned into different oil stocks by vacuum distillation.

Flash drums, stripping columns, and fractionation columns were simulated for these three processes using the Simulation Sciences PROCESS® program. This program and the technique used to obtain the necessary thermodynamic property inputs are discussed in Section X. Because of the difficulties in fully describing the chemical reactions occurring in the acid treatment, clay treatment, hydrofinishing, and solvent extraction operations, these steps could not be simulated by computer techniques.

For the flash, stripping, and fractionation operations used in the three processes described above, a variety of different operating pressures and temperatures have been proposed or used. In order to simplify the simulations, distillation and flash operations were simulated using the same operating conditions for the three processes.

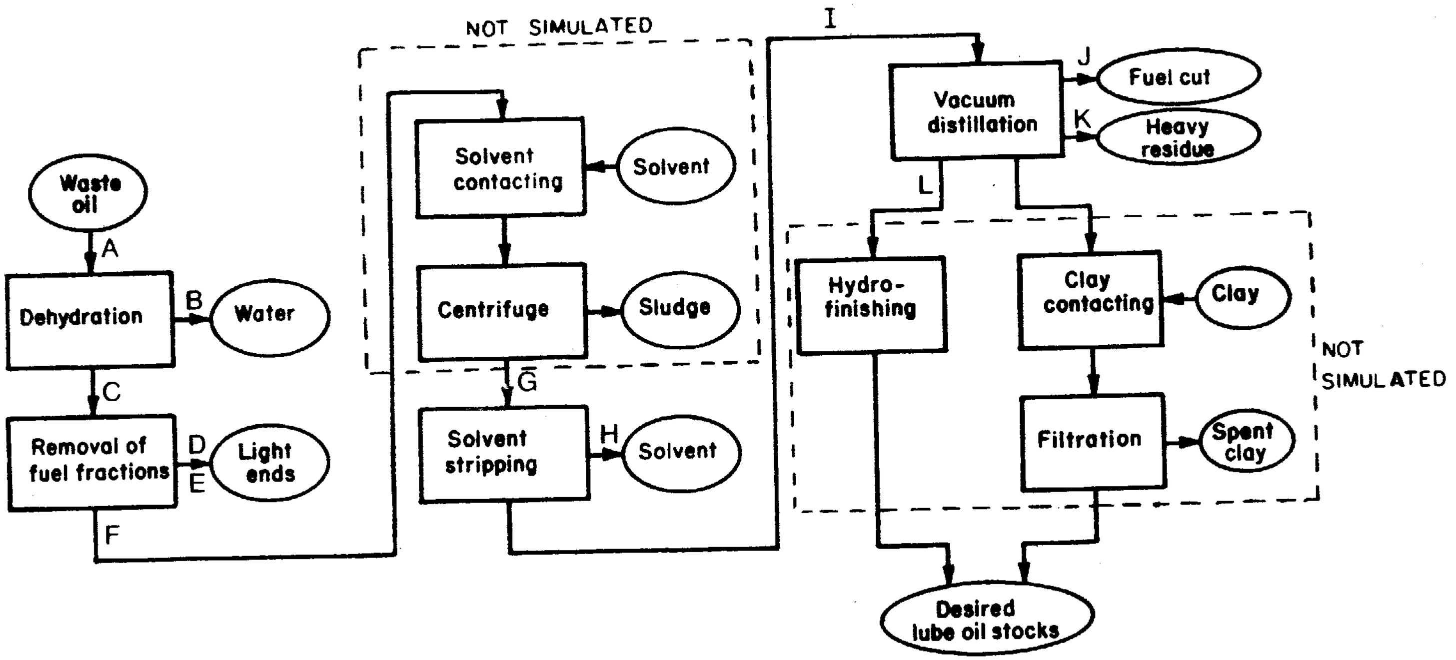


Figure XI-1. Streams from the solvent treatment/distillation/finishing re-refining process.

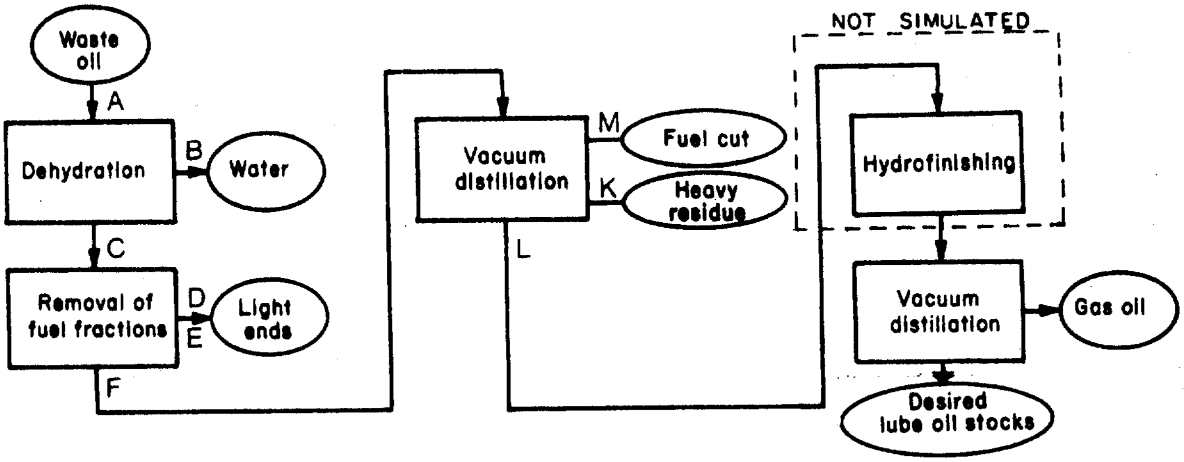


Figure XI-2. Streams from the distillation/hydrofinishing re-refining process.

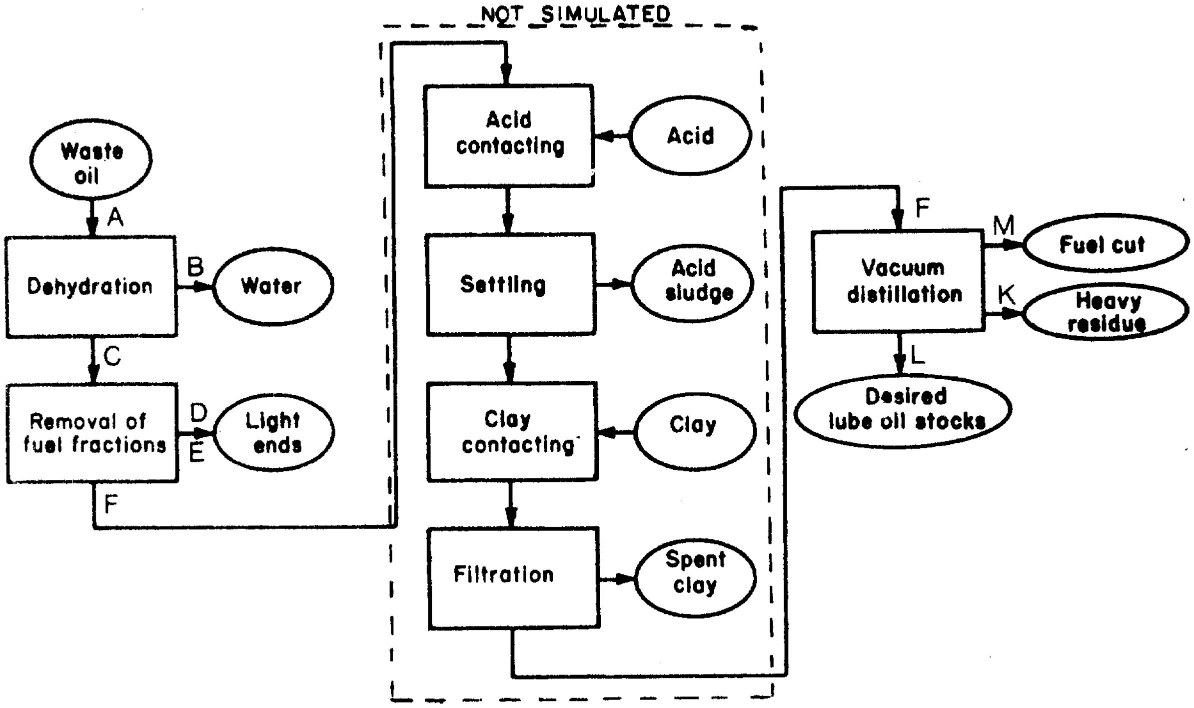


Figure XI-3. Streams from the acid/clay re-refining process.

The flash drum simulation, used for water removal in all three process simulations, was operated isothermally at a temperature of 228°F and an internal pressure of 20 psia (see Table XI-1). The heat required to separate 98.6 percent of the incoming water from the resultant product oil stream was 23,000 Btu/bbl waste oil feed. Flash columns are also used in the simulations to heat, cool, or change the pressure of a stream between two unit operations.

TABLE XI-1. OPERATING PARAMETERS FOR WATER REMOVAL

Reboiler heating duty 0.0230 MMBtu/bbl feed	
Feed is at 228°F and 20 psia	
<u>Products</u>	
Overhead (vapor)	326 ft^3/bbl feed (0.048 bbl/bbl feed)
Bottoms	0.952 bbl/bbl feed

Fuel fractions in the waste oil feed stream have a boiling point range of 290-650°F. They comprised approximately 8.8 percent of the feed. Fuel fraction removal was accomplished in a seven tray distillation column. The feed entered on the third tray at 228°F and 20 psia. Temperature and pressure profiles of the column can be found in Table XI-2. This column removed 98.7 percent of the fuel fractions found in the oil entering the column. A small fraction of the fuel had already been removed in the water removal flash operation.

In the simulation of the solvent treatment process, an additional column was needed to remove the solvent from the oil. This was accomplished with an eight tray distillation column. The feed entered on tray 4 at 220°F and 19.0 psia. The temperature and pressure profile for the column is presented in Table XI-3. The solvent-to-oil ratio was about 3/1. The column stripped 95 percent of the solvent from the oil/solvent mixture entering the column, a value appreciably lower than that which was achieved in the laboratory simulation. The overhead stream from this column contained only solvent.

The last unit operation in the three processes is a vacuum distillation column used for the final separation of lube oil from the heavy and light ends. The fractioning column has twelve trays with the feed oil entering on the sixth tray. The feed stream enters at 326°F and 19.2 psia. Temperature and pressure profiles of the column can be found in Table XI-4. Light ends were removed as an overhead stream and heavy ends were removed as a bottoms product. The lubricating oil was removed as a liquid side stream from tray 5. The reflux ratio for this column was 5.7 and a maximum temperature constraint of 650°F was imposed on the column to minimize the cracking of hydrocarbons. The column recovered 71.6 percent of the lube oil entering the column.

TABLE XI-2. OPERATING PARAMETERS FOR FUEL REMOVAL COLUMN

Number of trays	7
Location of feed tray	3
Condenser cooling duty	-0.0202 MMBtu/bbl feed
Reboiler heating duty	0.0820 MMBtu/bbl feed

Feed stream is at 180°F and 19.0 psia

Product Flowrates

Overhead (vapor)	0.00595 ft^3/bbl feed (0.0018 bbl/bbl feed)
Overhead (liquid)	0.137 bbl/bbl feed
Bottoms (liquid)	0.861 bbl/bbl feed

Tray Profiles

Tray	Temperature °F	Pressure psia
1	112	0.37
2	355	0.57
3	418	0.60
4	461	0.63
5	483	0.66
6	508	0.69
7	551	0.72

TABLE XI-3. OPERATING PARAMETERS FOR SOLVENT REMOVAL COLUMN

Number of trays	8
Location of feed tray	4
Condenser cooling duty	-0.0800 MMBtu/bbl feed
Reboiler heating duty	0.0853 MMBtu/bbl feed

Feed stream is at 220°F and 19.0 psia

<u>Product Flowrates</u>

Overhead (liquid)	0.724 bbl/bbl feed
Bottoms (liquid)	0.276 bbl/bbl feed

<u>Tray Profiles</u>

Tray	Temperature °F	Pressure psia
1	223	19.20
2	238	19.17
3	245	19.18
4	249	19.18
5	258	19.19
6	262	19.19
7	265	19.20
8	326	19.20

TABLE XI-4. OPERATING PARAMETERS FOR FRACTIONATING COLUMN

Number of trays	12
Location of feed tray	6
Condenser cooling duty	0.125 MMBtu/bbl feed
Reboiler heating duty	0.149 MMBtu/bbl feed

Feed is at 326°F and 19.2 psia

Product Flowrates

Overhead (liquid)	0.205 bbl/bbl feed
Sidedraw (liquid)	0.716 bbl/bbl feed
Bottoms (liquid)	0.079 bbl/bbl feed

Tray Profiles

Tray	Temperature °F	Pressure psia
1	76	0.48
2	367	0.48
3	463	0.44
4	481	0.39
5	511	0.34
6	565	0.29
7	626	0.26
8	644	0.23
9	648	0.19
10	648	0.16
11	647	0.13
12	647	0.10

The computer simulations of the three processes effectively demonstrated the fate of the contaminants which were input with the feed waste oil. The properties of the product lube oil are summarized in Table XI-5. The concentrations of the 19 spike compounds used in the computer simulations for all of the process streams are found in Table XI-6. The locations of the streams in each of the three processes are indicated in the process flow diagrams (Figures XI-1 to XI-3). Polychlorinated biphenyl concentrations in the waste oil were very low. To assure an accurate trace of these compounds, the feed concentrations of four separate PCBs were increased from 2.5 ppm to 25 ppm.

TABLE XI-5. PROPERTIES OF PRODUCT LUBE OIL

Temperature (°F)	Viscosity (cp)	Density (lbs/gal)
100	42.2	7.46
210	8.96	7.18

COMPARISON OF LABORATORY SIMULATION AND COMPUTER SIMULATION RESULTS

Comparisons between the results of the laboratory simulation program and the computer simulations are presented in Tables XI-7 and XI-8 for the solvent treatment/distillation/finishing process and the vacuum distillation process step of the distillation/hydrofinishing process. The results indicate reasonable agreement between the two techniques in the case of PCBs. Results for dibutyl phthalate are in agreement for the solvent treatment/distillation process but not for the distillation/hydrofinishing process. This disagreement may be the result of the contamination of laboratory samples with phthalate esters from laboratory equipment. Phthalate esters are used as plasticizers in flexible plastic vessels and tubing, and are commonly noted as contaminants.

In the laboratory simulation of the solvent treatment/distillation/finishing process, there was a definite increase in the concentration of B(a)P downstream of the vacuum distillation unit. These results suggest the formation of B(a)P and probably other PNAs in the vacuum distillation unit. Because the computer simulation program used does not take into account chemical reactions, it can not be used to predict the fate of PNAs or other unstable or reactive compounds. However, the computer simulation technique is useful in predicting the fate of stable compounds such as PCBs and other chlorinated species.

TABLE XI-6. COMPONENT CONCENTRATIONS IN COMPUTER SIMULATED PROCESS STREAMS

	A	B	C	D/E	F	G	H	I	J	K	L	M
Relative flow (weight)	100	5.24	94.8	12.4	82.4	319	224	94.9	18.1	7.99	68.8	5.56
Contaminant content (µg/g of feed)												
Benzene	112	66.5	45.5	45.5	0	0	0	0	0	0	0	0
Tetrachloroethylene	64.7	21.5	43.2	43.2	0	0	0	0	0	0	0	0
Naphthalene	384	7.23	377	377	0	0	0	0	0	0	0	0
Anthracene	194	0.01	194	93.6	101	101	0	101	94.5	0	6.49	94.0
Dichlorodifluoroethylene	28.9	26.6	2.29	2.29	0	0	0	0	0	0	0	0
Trichlorofluoroethylene	647	539	108	108	0	0	0	0	0	0	0	0
Trichlorotrifluoroethane	241	182	59.2	59.2	0	0	0	0	0	0	0	0
1,1,2-Trichloroethane	41.8	15.7	26.1	26.1	0	0	0	0	0	0	0	0
Trichloroethylene	119	65.5	53.3	53.3	0	0	0	0	0	0	0	0
Toluene	541	215	326	326	0	0	0	0	0	0	0	0
Ethylbenzene	29.8	7.18	22.6	22.6	0	0	0	0	0	0	0	0
o-Xylene	225	44.5	181	181	0	0	0	0	0	0	0	0
Dibutylphthalate	271	0.02	271	144	127	127		127	120	0	7.50	119
Butylbenzene	1030	66.0	967	967	0	0	0	0	0	0	0	0
Benzo(a)pyrene	13.9	0	13.9	0	13.9	13.9	0	13.9	0	1.11	12.8	0
Chlorobiphenyl	24.9	0.06	24.8	24.8	0	0	0	0	0	0	0	0
Dichlorobiphenyl	24.9	0.01	24.9	23.5	1.32	1.32	0	1.32	1.30	0	0.03	1.28
Trichlorobiphenyl	24.9	0.01	24.9	24.6	0.26	0.26	0	0.26	0.25	0	0	0.26
Tetrachlorobiphenyl	24.9	0.01	24.9	20.8	4.14	4.14	0	4.14	3.98	0	0.14	3.89

TABLE XI-7. COMPARISON OF DISPOSITION OF ORGANICS IN SOLVENT TREATMENT/DISTILLATION/FINISHING PROCESS AS PREDICTED BY BENCH SCALE AND COMPUTER SIMULATIONS[a]

Contaminant	Dry feedstock (1/F)[b]	Solvent (3/H)[b]	Vacuum distillation products Residue (4/K)[b]	 Distillate (5/L,J)[b]
Anthracene	100 (100)	ND (0)	ND (0)	13 (100)
Dibutylphthalate	100 (100)	ND (0)	ND (0)	122 (100)
Benzo(a)pyrene	ND (100)	ND (0)	75[c] (7.9)	6670[c] (92.1)
PCBs	100 (100)	ND (0)	ND (0)	55.8 (100)

[a] Values presented are the weights of contaminants in process streams as percentages of the weights in the dry feedstock as predicted by bench scale simulation and (by computer simulation).

[b] Stream numbers refer to Figure VIII-1 and Table VIII-2; and letters refer to Figure XI-1 and Table XI-6.

[c] Based on a dry feedstock concentration of 6 μg/g.

ND = Not found above detection limits.

TABLE XI-8. COMPARISON OF THE DISPOSITION OF ORGANICS IN VACUUM DISTILLATION AS PREDICTED BY BENCH SCALE AND COMPUTER SIMULATIONS[a]

Contaminant	Dry feedstock (1/F)[b]	Vacuum distillation products: Residue (3/K)[b]	Vacuum distillation products: Distillate (2/L,M)[b]
Anthracene	100 (100)	ND (0)	69 (93)
Dibutyl phthalate	100 (100)	ND (0)	0.2 (94)
B(a)P	ND (100)	ND (7.9)	43[c] (92.1)
PCBs	ND (100)	ND (0)	73 (100)

[a] Values presented are the weights of contaminants in process streams as percentages of the weights in the dry feedstock as predicted by bench scale simulation and (by computer simulation).

[b] Stream numbers refer to Figure VIII-2 and Table VIII-4; and letters refer to Figure XI-2 and Table XI-6.

[c] Based on a dry feedstock concentration of 6 μg/g.

ND = Not found above detection limits.

SECTION XII

FATE AND POTENTIAL IMPACT OF CONTAMINANTS

The results of the laboratory and computer simulations of re-refining processes and laboratory studies of other recycling scenarios have been discussed in previous sections of this report. This discussion will consolidate the assessment of the data resulting from this study, and serve as a guide to developing conclusions and recommendation for future actions.

FATE OF CONTAMINANTS

As a prelude to assessing the potential impact of the contaminants and disposal and recycling scenarios, a matrix table has been prepared (see Table XII-1). This table presents, for each recycling scenario and its major waste streams, the concentration of each contaminant (11 contaminants were selected as indicators of the environmental potential of each stream on the basis of their environmental impacts and concentrations); a weighted relative hazard factor for each contaminant; an overall relative hazard factor for each waste stream obtained by summing the hazard factors for each contaminant; the estimated potential flow rate (equivalent gallons (weight) per year); and the product of the flow rate and the summacion of the weighted hazard factors for the 11 contaminants. The product provides a figure of merit termed the potential weighted discharge severity. The higher the weighted discharge severity the greater the potential impact. Information in this table will assist in developing the conclusions and recommendations for the disposal and recycling scenarios in the following section.

It should be noted that the concentrations, overall weighted hazard factors, and flow rates which determine the weighted discharge severity of each waste stream are based on limited data and, in many cases, a number of assumptions relating to health and ecological effects and processing and disposal procedures, e.g., the oil content of a filter cake or sludge and its means of disposal. Whenever possible, data generated in this study have been used to determine concentration and flow rate values because of their mutual interdependence. Because of this interdependence, the product of the concentration and its flow rate will tend to remain constant over a wide range of process conditions for many waste streams. As an example, the product of the elemental concentration in a distillate residue and the volume of this residue remains constant provided that no trace elements are lost to the overhead, a condition generally met in this study.

TABLE XII-1. MATRIX OF PROCESS AND WASTE STREAMS AND WEIGHTED RELATIVE HAZARDS (HEALTH AND ECOLOGY) OF CONTAMINANTS AND STREAMS

Stream	Concentration/(Weighted Relative Hazard)[a]											H_s Stream Weighted Relative Hazard	Q Flow Rate (gallons/year)	H_s x Q Potential Weighted Discharge Severity
	Ba	Cd	Cr	Pb	Zn	Chlorinated Hydrocarbons	Toluene	Phenol	B(a)A	B(a)P	PCBs			
Relative Hazard Index, Air	25,000	2,500	25,000	7,500	2.5×10^5	1×10^7	2.3×10^5	11×10^6	2,250	1	50	—	—	—
Relative Hazard Index Water, Oil, Solid Wastes	5×10^5	2,000	50,000	10,000	20,000	2×10^5	2×10^5	1,000	1.3×10^5	60	1	—	—	—
Waste Oil	70 (<1)	1 (1)	10 (<1)	1,100 (110)	800 (40)	1,700 (9)	3,100 (16)	25 (25)	15 (<1)	5 (83)	2 (2,000)	2,293	$1,200 \times 10^6$	$2,750 \times 10^9$
Re-Refined Oil	160 (<1)	0 (0)	0 (0)	0 (0)	400 (20)	0 (0)	0 (0)	10 (10)	5 (<1)	3 (50)	0 (0)	80	100×10^6	8×10^9
Virgin Oil	160 (<1)	0 (0)	0 (0)	0 (0)	400 (20)	0 (0)	0 (0)	10 (10)	0.1 (<1)	0.05 (<1)	0 (0)	30	$2,860 \times 10^6$	90×10^9
Sewer Disposal												<1	1×10^{12}	—
Water Soluble	<1 (–)	<1 (–)	<1 (–)	<1 (–)	<1 (–)	<1 (–)	<1 (–)	<1 (–)	<1 (–)	<1 (–)	0 (0)			
Oil Phase	70 (<1)	1 (1)	10 (<1)	1,100 (110)	800 (40)	0 (0)	0 (0)	0 (0)	15 (<1)	5 (83)	2 (2,000)	2234	20×10^6	45×10^9
Road Oiling												10	0.7×10^6	0.007×10^9
Water Soluble	<1 (–)	<1 (–)	<1 (–)	<1 (–)	0 (0)	0 (0)	0 (0)	10 (10)	0 (0)	0 (0)	0 (0)	2	60×10^6	120×10^6
Oil Phase[b]	70 (<1)	1 (1)	10 (<1)	1,100 (<1)	800 (<1)	0 (0)	0 (0)	0 (0)	15 (<1)	5 (<1)	2 (2)	--	10×10^6	—
Air Emissions	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	NE	NE	0 (0)	0 (0)	0 (0)	0 (0)			
Combustion ($\mu g/m^3$)												15	5×10^{10}	750×10^9
Atomizing Unit	3,800 (2)	60 (<1)	450 (<1)	100,000 (13)	60,000 (<1)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	30	5×10^{10}	$1,500 \times 10^9$
Vaporizing Unit	90 (<1)	3 (<1)	50 (<1)	580 (<1)	250 (<1)	0 (0)	0 (0)	0 (0)	30 (0)	30 (0)	0 (0)	6	5×10^{10}	300×10^9
Commercial Facility	300 (<1)	40 (<1)	95 (<1)	43,000 (6)	35,000 (<1)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)			

(continued)

TABLE XII-1 (continued)

Stream	Concentration/(Weighted Relative Hazard)[a]											H_s Stream Weighted Relative Hazard	Q Flow Rate (gallons/year)	H_s x Q Potential Weighted Discharge Severity
	As	Cd	Cr	Pb	Zn	Chlorinated Hydrocarbons	Toluene	Phenol	B(a)A	B(a)P	PCBs			
Physical Treatment														
Sedimentation (water phase)	230 (<1)	37 (19)	10 (<1)	550 (55)	1,300 (65)	200 (<1)	600 (3)	150 (150)	0 (0)	0 (0)	0 (0)	292	60×10^{6}	18×10^{9}
Filtration/Centrifugation Sludge[b]	800 (<1)	12 (<1)	120 (<1)	1,300 (2)	10,000 (<1)	1,550 (<1)	2,850 (<1)	23 (<1)	14 (<1)	4 (<1)	2 (2)	4	20×10^{6}	80×10^{6}
Clay Contacting Sludge[b]	7 (<1)	<1 (-)	1 (<1)	100 (<1)	75 (<1)	0 (0)	0 (0)	55 (<1)	33 (<1)	11 (<1)	4 (4)	4	100×10^{6}	400×10^{6}
Dehydration/Light End Removal														
Water Phase	<1 (-)	<1 (-)	<1 (-)	<1 (-)	<1 (-)	600 (3)	150 (<1)	<1 (-)	0 (0)	0 (0)	0 (0)	3	70×10^{6}	0.21×10^{9}
Organic Phase[c]	<1 (-)	<1 (-)	<1 (-)	12 (1)	<1 (-)	70,000 (350)	20,000 (100)	180 (180)	0 (0)	0 (0)	0 (0)	631	55×10^{6}	35×10^{9}
Solvent Treatment/ Distillation Re-Refining														
Solvent Sludge[b]	500 (<1)	15 (<1)	100 (<1)	12,500 (2)	8,000 (<1)	0 (0)	0 (0)	<1 (-)	15 (<1)	40 (<1)	15 (15)	17	5×10^{6}	85×10^{6}
Distillate Residue[b]	210 (<1)	3 (<1)	30 (<1)	2,100 (<1)	1,700 (<1)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	<1	20×10^{6}	$<20 \times 10^{6}$
Clay Sludge[b]	100 (<1)	<1 (-)	2 (<1)	<1 (-)	25 (<1)	0 (0)	0 (0)	210 (<1)	1 (<1)	80 (2)	10 (10)	12	6×10^{6}	72×10^{6}
Distillation/Hydro-Finishing Re-Refining														
Distillate Residue[b]	340 (1)	7 (4)	35 (<1)	6,000 (<1)	4,000 (<1)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	<1	20×10^{6}	$<20 \times 10^{6}$
Acid/Clay Re-Refining														
Acid Sludge[b]	200 (<1)	6 (3)	40 (<1)	4,500 (<1)	3,200 (<1)	0 (0)	0 (0)	5 (5)	10 (<1)	3 (<1)	2 (2)	2	20×10^{6}	40×10^{6}
Clay Sludge[b]	600 (<1)	<1 (-)	15 (<1)	300 (<1)	30 (<1)	0 (0)	0 (0)	8 (<1)	3 (<1)	40 (<1)	70 (70)	70	15×10^{6}	$1,050 \times 10^{6}$

(continued)

TABLE XII-1 (continued)

Stream	Concentration/(Weighted Relative Hazard)[a]											H_s Stream Weighted Relative Hazard	Q Flow Rate (gallons/year)	H_s x Q Potential Weighted Discharge Severity
	Ba	Cd	Cr	Pb	Zn	Chlorinated Hydrocarbons	Toluene	Phenol	B(a)A	B(a)P	PCBs			
PROP														
DAP Sludge[b]	1,200 (<1)	3 (<1)	30 (<1)	12,000 (2)	4,000 (<1)	0 (0)	0 (0)	15 (<1)	10 (<1)	3 (<1)	1 (1)	3	11 x 10^6	33 x 10^6
Clay Sludge[b]	200 (<1)	20 (<1)	75 (<1)	17,600 (2)	900 (<1)	0 (0)	0 (0)	1,000 (1)	300 (<1)	100 (<1)	40 (40)	43	2 x 10^6	86 x 10^6
Commercial Facility														
Water from Flash Dehydrator	<1 (-)	<1 (-)	<1 (-)	2 (<1)	5 (<1)	1,000 (5)	1.300 (7)	0 (0)	0 (0)	0 (0)	0 (0)	12	17 x 10^6	0.2 x 10^9
Organics from Flash Dehydrator[c]	12 (<1)	1 (<1)	3 (<1)	56 (6)	20 (1)	100,000 (500)	26,000 (139)	<5 (-)	<5 (-)	<5 (-)	<11 (-)	646	3 x 10^6	2 x 10^9
Distillate Residue[b]	14 (<1)	6 (3)	35 (<1)	2,100 (<1)	2,960 (<1)	0 (0)	0 (0)	0 (0)	<1 (-)	20 (1)	<1 (-)	1	13 x 10^6	13 x 10^6
Spent Clay[b]	140 (<1)	<1 (-)	20 (<1)	<1 (-)	140 (<1)	0 (0)	0 (0)	<1 (-)	4 (<1)	2 (<1)	<8 (-)	8	6 x 10^6	48 x 10^6

[a] Concentration values shown are in $\mu g/m^3$ for air, mg/l for water, and μg/g for oil and solid waste; weighted relative hazard determined by dividing concentration value in appropriate units ($\mu g/m^3$ for air, μg/l for water, μg/kg for oil, and μg/g for solid waste discharges) by relative hazard index for contaminant and media.

[b] Solid waste discharge.

[c] Burned as fuel by recyclers or users.

- = Not determined for less than values

NE = Not estimated; see Section V for discussion of ongoing activity.

The designation of the relative hazard index value for contaminants in air, water, and solid waste is a major uncertainty in establishing the final discharge severity value for each waste stream. These values are continually being evaluated and revised. Also because of the wide range of numerical values associated with these contaminants, a few contaminants, e.g., PCBs (health), PNAs (health) and lead (ecology), tend to dominate the relative weighted severity discharge of each stream. It should be noted that the individual contaminant hazard factors, as used in this study, have also been normalized for convenience, as discussed in Section II. This normalization will affect the absolute value of the stream discharge factor but does not affect relative stream rankings. However, no consideration is given within this rating system for local conditions which may obviate potential hazards. Other factors which can contribute to deficiencies in the rating system include the availability and application of treatment technologies and effects such as biodegradation which may appreciably reduce the effect of discharge in scenarios such as road oiling.

Brief discussions of the data and assumptions used to arrive at the values shown in Table XII-1 are presented below. The selection of the relative hazardous index factors and the general rationale to this approach have been provided in Section II of this report.

Sewer Disposal

The total annual discharge was assumed to be 20 x 10^6 gallons per year, a value greater than the value of 7 x 10^6 gallons per year reportedly discharged into sewers. The contaminant concentrations used were those determined for the average oil. The rating system negates the impact of the water-soluble components due to the high dilution factor.

Road Oiling

All values were derived from the program data with flows and concentrations based on results of the laboratory simulations. Air emissions, which are the subject of an ongoing EPA program, were not estimated.

Combustion

Data obtained from the tests of the commercial facility and the space heater test studies were used to determine the values in the table. The flow rate was set equal for all units to provide a measure of relative impact. However, on a real time basis, the flow rate at the commercial facility will be 25 to 80 times greater than that of an individual space heater. Moreover, the rating procedure makes no provision for reduction in the severity of emissions from the much higher stack of the commercial facility. A ranking of the potential impact of specific contaminant emissions was presented earlier in Section VI, based on an assessment scheme which does consider the effects of size and stack height.

Physical Treatment

Sedimentation--

Concentration values for the elements were taken from data in Reference 1. These concentration values are appreciably greater than those determined in this study for the partitioning of elements in the water phase (see Section IV - Sewer Scenario). The flow rate assumes that all waste oil collected annually (775×10^6 gallons) is a source of a water-phase waste stream, due to the presence of free water at a concentration of 8 percent in the oil.

Filtration/Centrifugation--

The concentration values given in the table are based upon a 35 percent separation of metals present in the oil at a concentration of 0.7 percent. The weight of metals and oil contained in the filter media and cake or in the centrifuged residue was assumed to be 3 percent of the total oil treated. The flow rate was calculated based on this type of discharge, assuming all collected oil was subjected to this treatment.

Clay Contacting--

The concentration values are based on a 30 percent removal of organic contaminants (original composition equivalent to that in the composite oil) and no removal of elemental contamination. A value of 1 pound of clay per gallon of oil and a small 1 percent loss of oil in the clay cake were used in establishing the overall flow rate, assuming all oil collected is clay contacted.

Water and Light End Removal--

The data obtained in this study were used to establish concentrations of contaminants in both the water and organic phases shown in the table. Flow rates assume all oil collected is distilled to remove 8.8 percent water and 7.2 percent organics.

Re-Refining

Solvent Treatment/Distillation/Finishing--

The values in the table were derived from the laboratory simulations. Clay requirement for the finishing operation was assumed to be 0.4 pounds of clay per gallon of oil, with the oil loss fixed in proportion to that lost in the clay contacting pretreatment process. Thirty percent removal of organic contaminants in the distillate from the still was assumed as a result of the clay contacting step. The flow rates for all waste streams were extrapolated from laboratory data, assuming 100×10^6 gallons per year of pretreated oil were re-refined by the process. The same overall re-refining flow rate was used for all re-refining processes.

Distillation/Hydrofinishing--

All data were taken from the results of the laboratory simulations. A residual weight of 20 percent of the initial pretreated feed weight was assumed.

Acid/Clay--

The concentration values used were those obtained in the laboratory simulations. The acid volume was 5 percent of the oil volume treated; clay loading was 0.75 pounds per gallon of oil.

PROP--

Because of the lack of laboratory analytical data, several assumptions were made with regard to the organic concentrations in the two waste streams listed in Table XII-1. These include complete removal of volatiles in the demetallizing operation, and 50 percent removal of the organic contaminants with the filtered clay sludge.

Commercial Facility--

The data obtained from the sampling and analysis program were used to formulate the concentration and flow data shown in the table for this process. The computer simulation program was useful in confirming disposition of organics in the waste streams.

POTENTIAL IMPACT OF CONTAMINANTS IN WASTE STREAMS

To simplify the assessment of the environmental impact of the waste streams shown in Table XII-1, an additional table (Table XII-2) has been prepared showing the relative ranking of these streams for air, water, and land discharge. The table lists the relative rankings and associated weighted discharge severity factors for two conditions. The first condition depicts the results as shown in Table XII-1 using stream relative hazard factors derived from all 11 contaminants listed in the table. The second condition presents results derived from only 10 pollutants (minus the contribution of the PCBs). The elimination of the PCBs from the ranking system has a pronounced effect on the relative rankings of the solid waste streams. The ranking system with PCBs considered serves to identify those processes which employ clay as the primary means of removing organics such as PCBs which, because of their thermodynamic properties, tend otherwise to remain with the body of lube oil constituents.

The organic-phase stream generated in light end removal operations was not considered in Table XII-2. In actual practice, these streams are generally effectively discharged to air through their use as a fuel supplement. This was the only case in which the application of control measures (i.e., combustion) was considered in assessing the relative stream rankings. Other factors which contribute to potential hazard and/or processing difficulties are either not incorporated into this rating system or are masked by the assumption of worst case conditions. For example, the acid sludge ranking is achieved without penalties associated with the acidity of the waste stream and the transformation of many metals from insoluble oxides to water-soluble sulfates.

TABLE XII-2. RELATIVE RANKING OF WASTE STREAMS BY WEIGHTED DISCHARGE SEVERITIES

Waste stream	Ranking with 11 pollutants		Ranking with 10 pollutants (minus PCBs)	
	Ranking	Weighted discharge severity	Ranking	Weighted discharge severity
Air				
Vaporizing unit	1	1500×10^9	1	1500×10^9
Atomizing unit	2	750×10^9	2	750×10^9
Commercial facility	3	300×10^9	3	300×10^9
Water				
Sewer disposal	1	45×10^9	2	5×10^9
Sedimentation - water discharge	2	18×10^9	1	18×10^9
Dehydration - water phase	3	0.2×10^9	3	0.2×10^9
Land				
Acid clay process - clay sludge	1	1050×10^6	11	$<15 \times 10^6$
Physical treatment - clay contacting	2	400×10^6	6	$<100 \times 10^6$
Road oiling	3	120×10^6	7	$<60 \times 10^6$
PROP process - clay sludge	4	86×10^6	5	6×10^6
Solvent treatment process - solvent sludge	5	85×10^6	4	10×10^6
Physical treatment - filtration	6	80×10^6	1	40×10^6
Solvent treatment process - clay sludge	7	72×10^6	3	12×10^6
Acid/clay process - acid sludge	8	40×10^6	8/9/10	$<20 \times 10^6$
PROP process - DAP sludge	9	33×10^6	2	22×10^6
Commercial process - clay sludge	10	$<48 \times 10^6$	13	$<6 \times 10^6$
Distillation/hydrofinishing process - distillate residue	11/12	$<20 \times 10^6$	8/9/10	$<20 \times 10^6$
Solvent treatment process - distillate residue	11/12	$<20 \times 10^6$	8/9/10	$<20 \times 10^6$
Commercial process - distillate residue	13	$<13 \times 10^6$	12	$<13 \times 10^6$

It should be noted that the absolute values of the discharge severity should not be used across the media of air, water and land as relative indicators of hazard. Normalization has led to the introduction of a modifier which is different for all three media. The values in the table should be adjusted upward (50X for air, 200X for water, and 10X for land to account for this normalization). Further, the exact significance of the adjusted values is questionable when applied across different media.

REFERENCES

1. Williams, B. R. Automotive Crankcase Drainings Used for Fuel. In: NBS Special Publication 488, National Bureau of Standards, Gaithersburg, MD, August 1977.

SECTION XIII

CONCLUSIONS AND RECOMMENDATIONS

The major objectives of this study were, first: to establish the identity and range of concentrations of contaminants in used oils and, second: to determine the fate and potential impact of these pollutants during disposal and recycling. Conclusions and recommendations relevant to the above objectives are presented below.

CONCLUSIONS

Several conclusions regarding specific pollutants in used oil and their disposition during disposal and recycling can be drawn from the results of this study. These conclusions are presented below.

- Used oil contains a myriad of pollutants at the part per million level, including a number of EPA priority and RCRA pollutants.
- Organochlorine solvents are frequent contaminants in waste oils. All but 2 of the 24 representative oils tested contained one or more of these compounds. The absence of these materials in virgin oils suggests that these contaminants are introduced during collection and storage. The chlorinated aliphatics, such as trichloroethylene and tetrachloroethylene for instance, are degreasing agents commonly used for cleaning machinery and engine parts.
- Lead contents of used oil decreased almost tenfold over the past 10 years as shown by a comparison of the average value measured in this study with those determined in earlier studies.
- The barium content of used oil has also decreased in recent years. An average value of about 60 μg/g was found in this study compared to an average of about 300 μg/g found by DOE in a study of 30 used oils published in 1977. Only one oil in the DOE study had a barium content less than this study's average.
- Some PNAs, such as pyrene, benzo(a)pyrene, and benz(a)anthracene, are present in used oil at ppm levels. While it is generally agreed that the concentrations of PNAs naturally present in lubricating virgin oils (at a reported level of 0.03 to 0.28 ppm) are increased as a result of use, the available data base is not extensive. PNA concentrations in used oil are comparable to those found in fuel oils.

- The data here establish that PCBs are not normally found in used oils. However, their measured presence, at levels ranging from 7 to 65 μg/g in 4 of the 24 representative oils tested, suggests that deliberate contamination of used oils does occur.

- The results of the analyses of the representative oils indicate that, of the contaminants normally found in used oil and identified in this study, B(a)P and lead are the most significant from a health standpoint. Other PNAs may be significant, and metals such as aluminum and zinc are of concern because of ecological effects.

- In general, the assessment of the potential environmental impact of waste streams associated with the used oil recycling scenarios, as determined in this program and summarized in Section XII, appears to be a reasonable first order approximation. Data gaps, for the most part, are associated with a lack of understanding of the nature of the contaminants in waste oil and the associated mobility of these contaminants upon entering the environment.

- Road oiling should be regulated to reduce impacts associated with discharges of elemental and organic contaminants to soil and water. The significance of air emissions of contaminants such as chlorinated solvents was not evaluated in this program. EPA is now evaluating such emissions (see Section VI).

- Physical treatments to produce a specification fuel do not significantly reduce the metals content of the oil (a 25 percent reduction was achieved with difficulty in this program). Dehydration by distillation is effective in reducing the water and volatile organic contents of used oils but does not reduce trace element or PCB and PNA concentrations.

- The effectiveness of clay contacting as a means of significantly reducing the concentrations of specific organic compounds, such as the PNAs and PCBs identified in this study, was not demonstrated in laboratory simulations.

- Catalytic hydrofinishing appears to be the most effective means of PCB destruction if those compounds are present in the used oil feedstock prior to re-refining operations. The higher boiling PCBs, if not destroyed by hydrofinishing, will remain largely with the lube oil fractions during re-refining.

- Re-refining processes can produce a product similar in most respects to virgin lube oils. A possible distinguishing chemical feature is the increased concentration of PNAs such as benz(a)anthracene and benzo(a)pyrene in the used oil. These contaminants are largely contained within the lube oil fraction during re-refining, as observed in this study, and may possibly be created under certain conditions during high temperature distillation operations.

- Computer simulations of certain re-refining operations such as dehydration and vacuum distillation can be used to predict the fate of certain compounds, provided their thermodynamic properties are known and chemical modifications do not occur.

RECOMMENDATIONS

The following recommendations are intended to identify suggested areas of activity not undertaken or successfully resolved in this study. They identify both data gaps and shortcomings in existing analytical protocols for characterizing waste oils.

- A methods development program should be undertaken to improve the recoveries and detection limits of the analytical procedure for semivolatile organics in oils. Fractionation procedures should be emphasized. This is a major undertaking that will be feasible only if a predefined list of components of interest can be established.
- Better resolution of the differences in the contaminant levels of virgin and used oils is needed, particularly for organic constituents such as chlorinated hydrocarbons and PNAs. A sampling and analysis program that utilizes direct collection from generators is recommended as a means of avoiding uncertainties associated with possible contamination during collection and storage of used oils.
- The additive package and the physical/chemical states of its components need better definition. Although changes in the elemental content of the typical lubricating oil additive package over time can be inferred from the results of this study, little can be said about the nature of the additives and their breakdown products for both elemental and organic constituents.
- Analytical activities are needed to confirm or deny the presence of contaminants such as nitrosoamines and chromium VI in waste oil. Work will be required, at least in the case of chromium VI, to develop analytical methods.
- The characteristics and significance of the water-soluble chlorine components in waste oils should be established. Effective pretreatments, more effective modeling, and, possibly, use as an indicator of chlorine contamination are potential benefits.
- There is a definite requirement for the development of a simple analytical technique for chlorine content determination, preferably one that can be applied in the field.

The following recommendations for future activities are presented as a means of more effectively assessing the fate of contaminants in used oils and their environmental impacts during recycling. They supplement those recommendations above, which were largely directed at developing techniques for better characterizing the physical and chemical form of known (and suspected) contaminants of significance.

- Partitioning coefficients of contaminants between aqueous and organic fractions should be developed. As noted previously, the laboratory simulations conducted in this study showed only a limited degree of water solubility of major hazardous contaminants found in waste oil. This finding was in contrast to some literature sources which reported appreciably higher contaminant levels (at least of metal contaminants) resulting from the commingling of water and oil. Computer simulations should also be considered.

- The fate of contaminants in used oils applied to road surfaces is not well defined. It is recommended that additional laboratory simulation studies be devised and conducted under carefully defined conditions with well characterized soils, rainfall, and oils to study pollutant transport, particularly that attributable to solubility. Experiments using artificially generated rainfall in a contaminant free environment or percolation type studies should be considered, possibly using traceable amounts of known contaminants similar to those found in used oil.

- Although EPA has undertaken several programs to establish the fate of wastes or contaminants burned in small combustion systems, the results of the combustion activities undertaken in this program, particularly with the vaporizing space heater, indicate that further attention should be given to this class of combustion unit. The question of whether or not vaporizing units are significant sources of PNA emissions should be resolved for the benefit of both manufacturers and users of such equipment. The fate of chlorine during combustion is another area of uncertainty which should be resolved.

- Because the effectiveness of clay contacting was not demonstrated in this study, there is a need for additional data concerning the effectiveness of clay contacting over the range of conditions practiced industrially. The removal of key organic species of interest, including those present as additives, could be determined in a series of parametric experiments.

- Questions have been raised in this program with regard to PNA formation during distillation. A number of experimental routes, including systematic checks of existing units or further laboratory or pilot studies under controlled conditions, should be considered to determine the cause, frequency, and extent of such chemical transformations.

APPENDIX A

FIELD SAMPLING AND ANALYSIS

The SASS train, Figure A-1, is a high volume (6 scfm at 400°F) sampling system for collection of particulates, volatile organics, and volatile metals, usually from a point of average flue gas velocity in the duct. Particulates in the flue gas are size classified into the four ranges below by three cyclones and a 142 mm filter.

1. $\geq$ 10 μm
2. 3 μm to 10 μm
3. 1 μm to 3 μm
4. <1 μm (filter stage)

The gas phase organic materials are collected in an organic sorbent trap maintained at 68°F. The sorbent, XAD-2, is a porous polymer resin capable of adsorbing a broad range of organic species. Volatile inorganic species are collected downstream of the organic sorbent module in a series of four impingers containing absorbing solutions of 30 percent hydrogen peroxide and 0.2M ammonium presulfate plus 0.02M silver nitrate.

The precleaning of all sampling equipment, as well as the collection and recovery of samples, were conducted in strict accordance with the Level 1 procedures outlined in EPA/IERL-RTP Procedures Manual: "Emissions Assessment of Conventional Stationary Combustion Systems: Methods and Procedures Manual for Sampling and Analysis, EPA-600/7-79-029w, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, NC, January 1979."

A RAC Staksamplr™ train, Figure A-2, modified to allow for the collection of volatile organic species, was used to conduct the Method 5 tests by extracting an isokinetic sample of flue gas from traverse points in the ducting. The organic species of interest are collected in a condenser-adsorbent trap assembly placed in line at the exit from the particulate filter. The adsorbent trap contained XAD-2 resin and, as in the case of the sorbent trap of the SASS train, was maintained at a temperature of 68°F throughout the sampling period. The particulate and organic samples associated with this train were recovered using procedures similar to those specified in the EPA-IERL Level 1 Environmental Assessments.

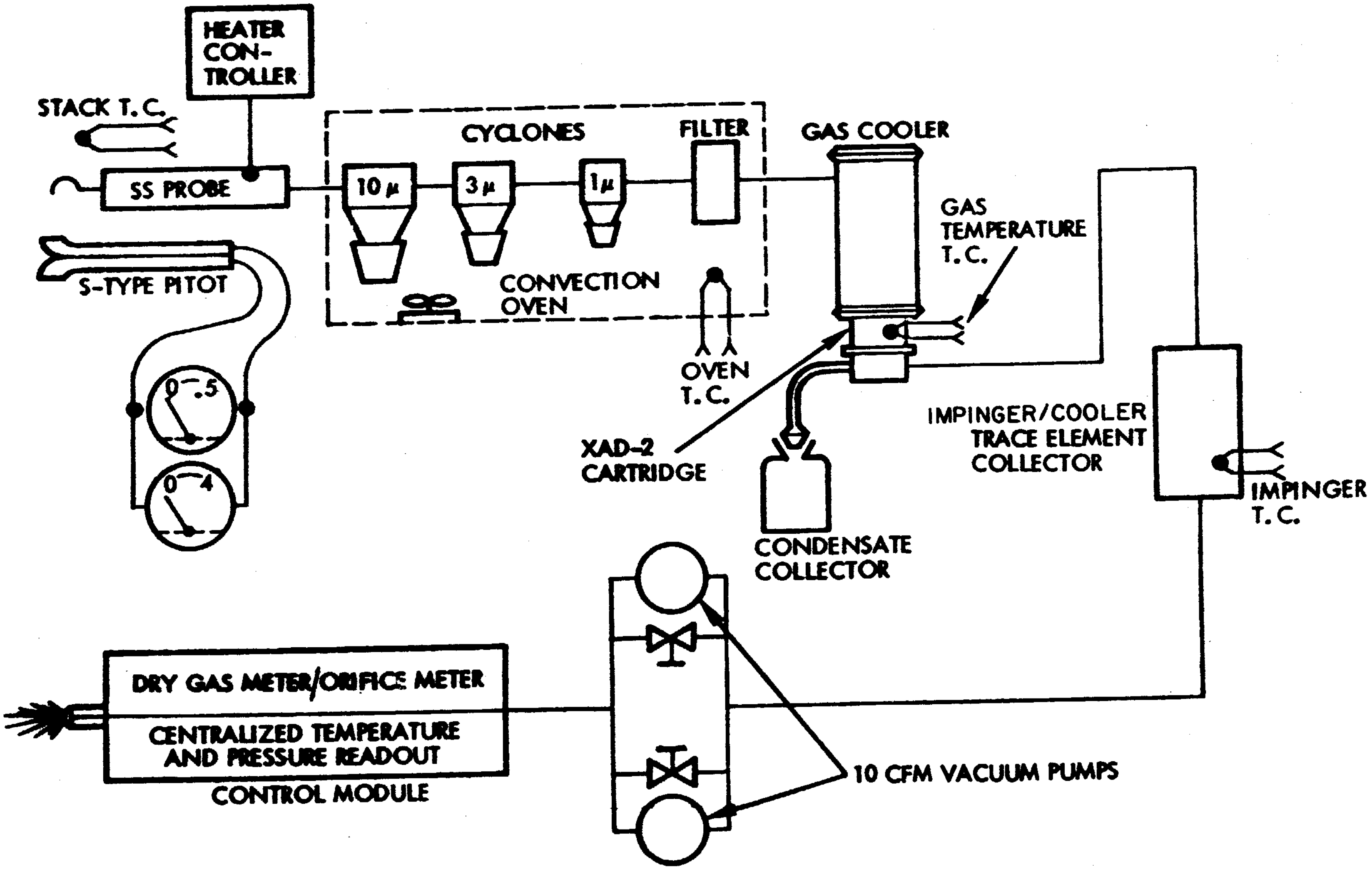
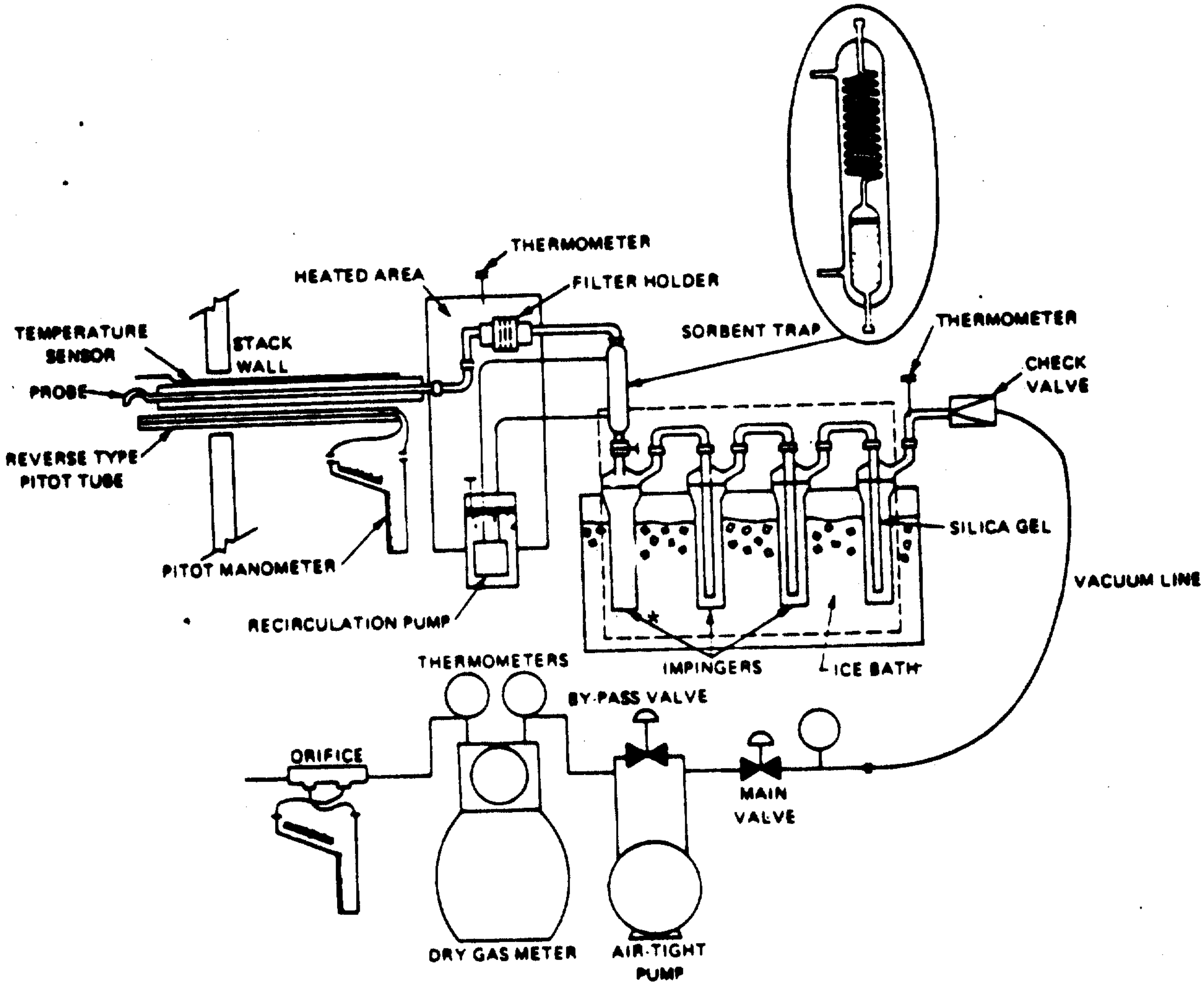


Figure A-1. SASS schematic.



*First impinger which serves as condensate trap has a very short stem that does not extend into the condensate.

Figure A-2. Modified Method 5 train.

APPENDIX B

LABORATORY ANALYSIS

LABORATORY ANALYSIS

Laboratory analyses for organic and inorganic constituents were conducted at the GCA Laboratory in Bedford, MA, for all major process and waste streams associated with the recycling scenarios including both the fuel feed and flue gas samples from the combustion scenarios. Generalized schematics of the characterizations performed for combustion studies are shown in Figures B-1 and B-2. Selected physical properties of the representative oils were determined either in-house or by appropriate subcontractors. The analytical protocols used during this program are provided in the following pages. These analytical methods are specific to the instrumentation, reagents and procedural modifications routinely used in the GCA/Technology Division Analytical Laboratories.

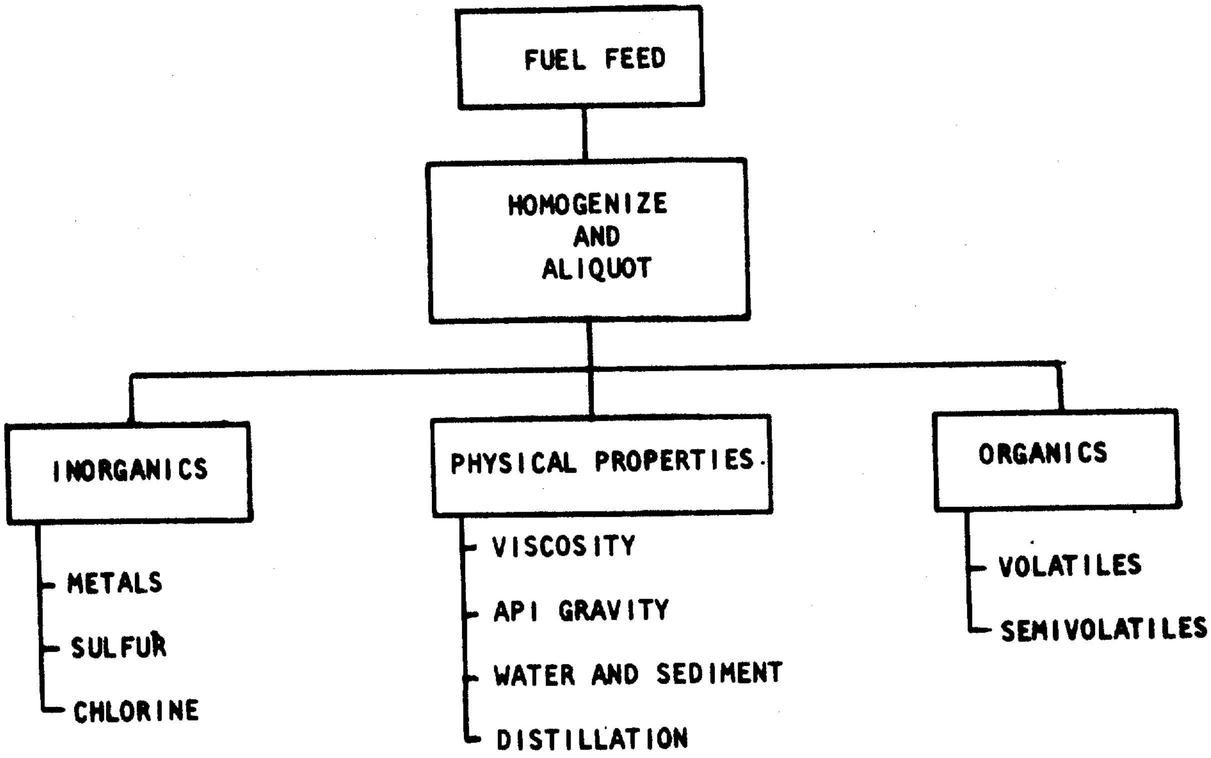


Figure B-1. Oil and fuel feed characterization.

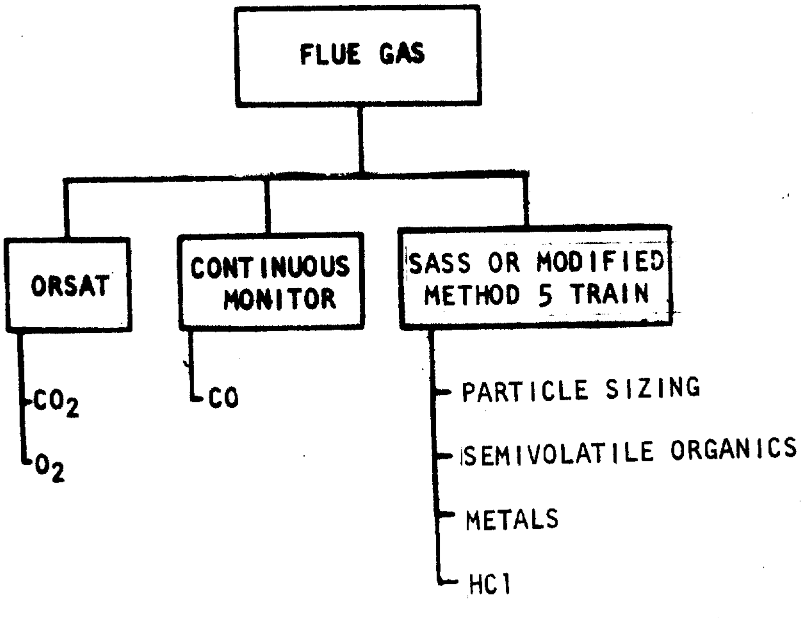


Figure B-2. Flue gas characterization.

INORGANIC ANALYSIS PROCEDURES

The procedures used for the determination of metals in oils and particulate and of total chlorine and sulfur in oils are described in the following pages. Major procedures addressed and their page locations are as tabulated below.

Procedure	Page
Dry ashing procedure for the determination of metals in petroleum products	B-4
HNO_3-HF digestion of particulate samples	B-5
General ICAP method for trace element analysis	B-6
Sulfur in petroleum products	B-13
Chlorine in petroleum products	B-17

DRY ASHING PROCEDURE FOR THE DETERMINATION OF METALS IN PETROLEUM PRODUCTS

SCOPE AND APPLICATION

This procedure may be used to prepare petroleum products for trace element analysis by AA or ICAP.

SUMMARY OF METHOD

A 2-5 g portion of oil is ashed and the residue is taken up in nitric and hydrochloric acids. The resulting sample can then be analyzed by AA or ICAP for trace element content.

REAGENTS

1. Baker "Instra-Analyzed" HNO_3 and HCl

APPARATUS

1. Muffle furnace
2. IR lamps
3. Platinum Crucibles, 15-ml capacity

PROCEDURE

1. Place 2-5 g of oil in a platinum crucible.
2. Place the sample under an IR lamp with the lamp at its highest position. Lower the lamp position gradually, do not allow the sample to boil. Leave the lamp at its lowest position until the sample appears ashed.
3. To complete ashing, place the sample in the muffle furnace and slowly increase the temperature (every half hour) from 100-600°C.
4. When the sample appears completely ashed, wash the ash into a 150 ml beaker using 2-3 ml 1:1 HNO_3. Wash the platinum crucible with several portions of 1:1 HNO_3 and add the washings to the beaker. Continue this until approximately 10 ml of 1:1 HNO_3 has been added to the beaker. Rinse the crucible with several portions of deionized water and add the rinsings to the beaker. Add 2 ml of concentrated HCl and heat the sample gently for 15 minutes. Cool, transfer to a 100 ml volumetric flask and dilute to volume. The sample may now be analyzed by AA or ICAP.

HNO_3-HF DIGESTION OF PARTICULATE SAMPLES

SCOPE AND APPLICATION

This procedure may be used to prepare loose particulate or particulate collected on a filter for trace element analysis by AA or ICAP.

SUMMARY OF METHOD

The particulate is digested using HNO_3 and HF. The resulting solutions are analyzed by AA or ICAP for trace element content.

APPARATUS

1. Beakers, 150 ml Pyrex and 250 ml Teflon
2. Hot Plates
3. Millipore filters, 0.45μ and filtering apparatus
4. Volumetric flasks, 25 ml
5. Nalgene Bottles, 60 ml

PROCEDURE

1. Place a cut filter portion or weighed portion of particulate in a 150 ml beaker.
2. Add 40 ml of 3M HNO_3 and heat on a low setting for 30 minutes.
3. Decant off the acid solution into a second beaker. Add 40 mls of water to the first beaker and heat on a low setting for 30 minutes.
4. Combine the extracts and filter through a 0.45μ Millipore filter. Save both filter and filtrate.
5. Place the filtrate on a hot plate and reduce the volume to less than 20 mls. Transfer to a 25 ml volumetric flask and dilute to volume with 3M HNO_3.
6. Transfer the filter used in Step 4 to a 250 ml Teflon beaker. Add 10 ml concentrated HNO_3 and 2 ml HF. Heat at a low setting to wet salts. If the sample is not totally digested, repeat using additional HNO_3 and HF.
7. Transfer the digest to a 25 ml volumetric flask, washing the beaker well with deionized water. Dilute to volume and transfer to a Nalgene container.
8. The aliquots are analyzed separately by AA or ICAP and the results are added to produce a single value.

GENERAL ICAP METHOD FOR TRACE ELEMENT ANALYSIS

SCOPE AND APPLICATION

This method is designed to detect and quantify 27 elements in water and wastewater using Inductively Coupled Plasma. The elements detected by this procedure are shown in Table B-1.

TABLE B-1. DETECTION LIMITS AND WAVELENGTHS FOR ICP ANALYSIS

Element	Wavelength (nm)	Detection limit (μg/l)
Ag	328.0	1.0
Al	308.2	9.0
As	197.2	32
B	249.6 (second order)	4.0
Ba	493.4	0.6
Be	234.8	0.4
Ca	317.9	10
Cd	228.8 (second order)	0.8
Co	228.6	3.0
Cr	205.5 (second order)	2.6
Cu	324.7	1.6
Fe	259.9	3.4
Mg	279.0	20
Mn	257.6	0.4
Mo	202.0	2.2
Na	589.0	10
Ni	231.6 (second order)	4.8
Pb	220.3	16
Sb	206.8	15
Se	196.0 (second order)	22
Si	251.6	5.0
Sn	189.9	30
Sr	421.5	1.0
Ti	334.9	1.2
Tl	190.8 (second order)	41
V	292.4	5.4
Zn	213.8	0.8

INTERFERENCES

A variety of interferences may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

- Spectral interferences
- Physical interferences
- Chemical interferences.

It is recommended that whenever a new or unusual sample matrix is encountered, the following tests should be performed:

- Serial Dilution--If the analyte concentration is at least a factor of 10 above the instrumental detection limit after dilution, an analysis of a dilution should agree within 5 percent of the original determination. If the values do not agree within 5 percent, a chemical or physical interference should be suspected.
- Spike Addition--The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit should be recovered to within 90 to 110 percent. If not, a matrix effect should be suspected. The use of the method of standard addition will usually compensate for matrix effects. However, this technique does not detect coincident spectral overlap. If this is suspected, use of computerized compensation or comparison with an alternate method is recommended.
- Comparison with Alternate Method of Analysis--Comparison with another analytical technique, such as Atomic Absorption Spectrophotometry may be helpful in detecting interferences.

REAGENTS

1. Acids--All acids should be either J.T. Baker Ultrex or Instra-Analyzed grade.
   a. Acetic acid
   b. Hydrochloric acid, concentrated and (1+1). Prepare (1+1) HCl by adding 500 ml concentrated HCl to 400 ml deionized water and diluting to 1 liter.
   c. Nitric acid, concentrated and (1+1). Prepare (1+1) nitric acid by adding 500 ml concentrated HNO_3 to 400 ml deionized water and diluting to 1 liter.
2. Stock standard solutions, 1,000 µg/ml
   a. Aluminum--Dissolve 1.000 g of aluminum metal in an acid mixture of 4 ml of (1+1) HCl and 1 ml of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 ml of (1+1) HCl and dilute to 1,000 ml with deionized water.

b. Antimony--Dissolve 2.669 g K(SbO) $C_4H_4O_6$ in deionized water, add 10 ml (1+1) HCl and dilute to 1,000 ml with deionized water.

c. Arsenic--Dissolve 1.320 g of As_2O_3 in 100 ml of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 ml conc. HNO_3 and dilute to 1,000 ml with deionized water.

d. Barium--Dissolve 1.516 g $BaCl_2$ (dried at 250°C for 2 hrs) in 10 ml deionized water with 1 ml (1+1) HCl. Add 10.0 ml (1+1) HCl and dilute to 1,000 ml with deionized water.

e. Beryllium--Dissolve 1.000 g of beryllium metal in a minimum volume of (1+1) HCl. Dilute to 1 liter with 1 percent (v/v) HCl.

f. Boron Solution--Do not dry. Dissolve 5.716g anhydrous H_3BO_3 in deionized water and dilute to 1,000 ml. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

g. Cadmium--Dissolve 1.142 g CdO in a minimum volume of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized water.

h. Calcium--Suspend 2.498 g $CaCO_3$, which was dried at 180°C for 1 hr before weighing, in deionized water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized water.

i. Chromium--Dissolve 3.735g of potassium chromate in 1 liter of deionized water.

j. Cobalt--Dissolve 1.000 g of cobalt metal in a minimum volume of (1+1) HNO_3. Add 10.0 ml (1+1) HCl and dilute to 1,000 ml with deionized water.

k. Copper--Dissolve 1.252 g CuO in a minimum volume of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized water.

l. Iron--Dissolve 1.430 g Fe_2O_3 in a warm mixture of 20 ml (1+1) HCl and 2 ml of conc. HNO_3. Cool, add an additional 5 ml of conc. HNO_3 and dilute to 1,000 ml with deionized water.

m. Lead--Dissolve 1.599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HCl and 2 ml of conc. HNO_3 and dilute to 1,000 ml with deionized water.

n. Magnesium--Dissolve 1.658 g MgO in a minimum volume of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized water.

o. Manganese--Dissolve 1.000 g of manganese metal in a mixture of 10 ml conc. HCl and 1 ml conc. HNO_3, and dilute to 1,000 ml with deionized water.

p. Molybdenum--Dissolve 2.043 g $(NH_4)_2MoO_4$ in deionized water and dilute to 1,000 ml.

q. Nickel--Dissolve 1.000 g of nickel metal in 10 ml hot conc. HNO_3, cool and dilute to 1,000 ml with deionized water.

r. Selenium--Do not dry. Dissolve 1.727 g H_2SeO_3 (actual assay 94.6%) in deionized water and dilute to 1,000 ml.

s. Silicon--Fuse 2.139 g of silicon dioxide with 8 g of sodium hydroxide until a clear melt is obtained. Cool, dissolve the cake in 100 ml of 1:3 hydrochloric acid and make up to 1 liter.

t. Silver--Dissolve 1.575 g $AgNO_3$ in 100 ml of deionized water and 10 ml conc. HNO_3. Dilute to 1,000 ml with deionized water.

u. Sodium--Dissolve 2.542 g NaCl in deionized water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized water.

v. Strontium--Dissolve 1.685g $SrCO_3$ in 10 ml 1:1 HNO_3 and dilute to 1 liter with deionized water.

w. Thallium--Dissolve 1.303 g $TlNO_3$ in deionized water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized water.

x. Tin--Dissolve 1.000g of tin in 100 ml HCl (warm to 60° if necessary). Cool and dilute to 1 liter with (1+9) HCl.

y. Titanium--Dissolve 1.000g of titanium metal in 100 ml of (1+1) HCl. Cool and dilute to 1 liter with (1+1) HCL.

z. Vanadium--Dissolve 2.297 g NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized water.

aa. Zinc--Dissolve 1.245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized water.

3. Mixed Calibration Standard Solutions--Prepare by combining appropriate volumes of the stock solutions in volumetric flasks. The final acid concentration should be 2 percent HNO_3. Prepare mixed standard V in a polyethylene flask. Mixed calibration standards are prepared fresh daily.

The following mixed calibration standards are normally prepared:

- Mixed Calibration Standard I--Blank, 2% HNO_3
- Mixed Calibration Standard II--Fe, Al, Ba, Ni, Cr, Ti
- Mixed Calibration Standard III--Mg, Cu, Sb, As, Co, Pb, Mo, Se, Si, Tl, Be
- Mixed Calibration Standard IV--Ca, Cd, Ag
- Mixed Calibration Standard V--V, Sn, Sr, Mn, Zn, Na, B

APPARATUS

1. Jarrell-Ash Model 855 Atom Comp ICP
2. Liquid Argon
3. Beakers
4. Pipets
5. Volumetric flasks
6. Hot plates
7. Watch glasses

QUALITY CONTROL REQUIREMENTS

Each group of 20 or fewer samples carried through the preparation and analysis procedures must include a blank, a spiked sample prepared from an EPA trace metals concentrate, and a duplicate.

After calibrating the instrument, analyze an EPA trace elements concentrate to verify the preparation of the mixed calibration standards. Enter the reported values in the instrument logbook.

Procedure

1. Set up the instrument as specified in the Jarrell-Ash operating manual. Allow 30 minutes for warm-up prior to calibration.

2. Program the sample matrix into the computer.

3. Profile and calibrate the instrument using the mixed calibration standards. Flush the system with the calibration blank between each standard.

4. Analyze an EPA trace metals concentrate. The values obtained should be within 5 percent of the expected value. Enter the values in the instrument logbook.

5. Analyze the samples. Flush the system with the calibration blank between each sample.

6. If the method of standard addition is required, use the following procedure:

   Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$c_x = \frac{S_B V_s c_s}{(S_A - S_B) V_x}$$

   where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughtly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

   1. The analytical curve must be linear.
   2. The chemical form of the analyte added must respond the same as the analyte in the sample.
   3. The interference effect must be constant over the working range of concern.
   4. The signal must be corrected for any additive interference.

CALCULATIONS

1. Sample values are reported directly as concentration in ppm. All values should be blank corrected using the appropriate reagent blank.

2. If dilution was required, correct the sample values by the appropriate factor.

3. Data should be reported in μg/ml using up to three significant figures.

REFERENCE

1. "Inductively Coupled Plasma--Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes", Method 200.7, U.S. Environmental Protection Agency, Cincinnati, Ohio.

SULFUR IN PETROLEUM PRODUCTS

SCOPE AND APPLICATION

This method covers the determination of sulfur in petroleum products including lubricating oils containing additives; it is applicable to any petroleum product sufficiently low in volatility that it can be weighed accurately in an open sample boat.

SUMMARY OF METHOD

The sample is oxidized by combustion in a bomb containing oxygen under pressure. The sulfur, as sulfate in the bomb washings, is determined by ion chromatography.

SAMPLE COLLECTION AND PRESERVATION

No special precautions required.

INTERFERENCES

No known interferences at this time.

REAGENTS

1. Oxygen, free of combustible material and sulfur compounds, available at a pressure of 40 atmospheres.

2. Sodium Carbonate Solution--Dissolve 50 g of anhydrous Na_2CO_3 in deionized water and dilute to 1 liter.

3. 1000 µg/ml Sulfate Solution--Dissolve 1.479 g of dried (105°C) Na_2SO_4 in deionized water and dilute to 1 liter.

4. Working Standard Solutions--Prepare, as a minimum, the following working conditions by dilution of the stock standard with deionized water: 5, 10 and 30 µg/ml.

5. Air--compressed.

6. Standard Eluent (0.003 $\underline{M}$ $NaHCO_3 \cdot$ 0.024 $\underline{M}$ Na_2CO_3)--Prepare by dissolving 1.0080 g $NaHCO_3$ and 1.0176 g Na_2CO_3 in deionized water and dilute to 4 liters.

7. Regeneration Solution (1N H_2SO_4)--Dilute 111 ml concentrated sulfuric acid to 4 liters with deionized water.

APPARATUS

1. Parr Bomb
2. Platinum sample cup
3. Platinum firing wire
4. White nylon or cotton sewing thread
5. Ignition circuit capable of supplying sufficient current to ignite the nylon or cotton thread without melting the wire.
6. Beakers (600 ml and 50 ml) and speedy vaps
7. Volumetric flasks, 100 ml
8. Hot plates
9. Dionex Ion Chromatograph
10. Plastic Syringe, 5-ml capacity
11. Millipore syringe filter unit 0.22 μm
12. Recorder

QUALITY CONTROL REQUIREMENTS

1. A method blank and an appropriate laboratory control sample such as NBS SRM 1619 must be analyzed with each group of samples.

PROCEDURE

1. Preparation of bomb and sample:

   Cut a piece of firing wire approximately 100 mm in length. Coil the middle section (~20 mm) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Insert a nylon or cotton thread into the coil, of such length that one end extends into the sample cup. Place 10 ml Na_2CO_3 solution in the bomb and by means of a rubber policeman wet the interior surface of the bomb, including the head, as thoroughly as possible. Weigh 0.8 g to 1.0 g sample into the sample cup.

2. Addition of oxygen:

   Place the sample cup in position and arrange the thread so that one end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen slowly (to avoid blowing the oil from the cup) until pressure is reached as indicated in the table below:

Bomb Capacity (ml)	Min. Gage Pressure atm.	Max. Gage Pressure atm.
300-350	38	40
350-400	35	37
400-450	30	32
450-500	27	29

3. Combustion:
   Immerse the bomb in a cold water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion of at least 10 min. Release the pressure at a slow uniform rate such that the operation requires not less than 1 minute. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination.

4. Collection of Sulfur Solution:
   Rinse the interior of the bomb, the oil cup and the inner surface of the bomb cover with a fine jet of deionized water. Collect the washings in a 600-ml beaker which has a mark to indicate 75 ml. Remove any precipitate in the bomb by means of a rubber policeman. Wash the base of the terminals until the washings are neutral to a suitable indicator. Add 10 ml of saturated bromine water to the washings in the beaker. (The volume of the washings is normally in excess of 300 ml). Place the sample cup in a 50 ml beaker. Add 5 ml of saturated bromine water, 2 ml of HCl and enough distilled water to cover the cup. Heat the contents of the beaker to just below its boiling point for 3 or 4 minutes and add to the beaker containing the bomb washings. Wash the sample cup and the 50-ml beaker thoroughly with deionized water. Remove any precipitate in the cup by means of a rubber policeman. Add the washings from the cup and the 50-ml beaker, and the precipitate, if any, to the bomb washings in the 600-ml beaker. Evaporate the combined washings to approximately 75 mls. Cool and dilute to volume in a 100 ml volumetric flask.

IC ANALYSIS

1. Set up the instrument according to the operator's manual.

2. Inject appropriate standards and record the peak heights. Analyze an EPA quality control sample to verify instrument calibration; the reported value should be within 5 percent of the expected value. Enter the results in the instrument logbook.

3. Inject the samples and record the peak heights. Make the necessary dilutions or adjustmnt of the μMHO scale on the instrument to bring the sample into the linear range.

4. Calculate the regression data for the standards, enter the peak height value for each sample and record the calculated ppm value.

5. Calculate %S in the following manner:

$$\%S = \frac{\mu g/ml\ SO_4^{=}\ (\text{from curve}) \times \text{Dilution} \times \text{sample volume (ml)} \times 0.334}{\text{Sample weight (g)} \times 10{,}000}$$

REFERENCE

1. Standard Test Method for Sulfur in Petroleum Products (General Bomb Method) ANSI/ASTM D 129-64.

CHLORINE IN PETROLEUM PRODUCTS

SCOPE AND APPLICATON

This method covers the determination of chlorine in lubricating oils and greases, including new and used lubricating oils and greases containing additives, and in additive concentrates.

SUMMARY OF METHOD

The sample is oxidized by combustion in a bomb containing oxygen under pressure. The chlorine compounds thus liberated are absorbed in a sodium carbonate solution and the amount of chloride present is determined by Ion Chromatography.

SAMPLE COLLECTION AND PRESERVATION

Limit headspace of sample containers to preclude volatilization.

INTERFERENCES

No known interferences at this time.

REAGENTS

1. Oxygen--free of combustible material and halogen compounds, available at a pressure of 40 atmospheres.
2. Sodium Carbonate Solution--Dissolve 50 g of anhydrous Na_2CO_3 in deionized water and dilute to one liter.
3. 1000 µg/ml Chloride Standard--Dissolve 1.6484 g NaCl in deionized water and dilute to one liter.
4. Working Standard Solutions--Usually the following standards are prepared using deionized water for dilutions: 0.5 µg/ml, 1.0 µg/ml, 3.0 µg/ml.
5. Air--Compressed.
6. Standard Eluent (0.003 $\underline{M}$ $NaHCO_3 \cdot$ 0.0024 $\underline{M}$ Na_2CO_3)--Prepare by dissolving 1.0080 g $NaHCO_3$ and 1.0176 g Na_2CO_3 in deionized water and dilute to 4 liters.
7. Regeneration Solution (1N H_2SO_4)--Dilute 111 ml concentrated sulfuric acid to 4 liters with deionized water.

APPARATUS

1. Parr Bomb
2. Stainless steel sample cup
3. Stainless steel firing wire
4. Nylon or white cotton sewing thread
5. Ignition circuit, capable of supplying sufficient current to ignite the nylon or cotton thread without melting the wire.
6. Beakers--600 ml pyrex
7. Speedy-vaps to fit 600 ml beakers
8. Volumetric flasks--100 ml
9. Hot plates
10. Dionex Ion Chromatograph
11. Plastic syringe, 5 ml capacity
12. Millipore syringe filter unit, 0.22 μm
13. Recorder

QUALITY CONTROL REQUIREMENTS

1. Spiked samples and a reagent blank should be analyzed with each group of samples.

PROCEDURE

1. Preparation of bomb and sample:

   Cut a piece of firing wire approximately 100 mm in length. Coil the middle section (~20 mm) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Insert a nylon or cotton thread into the coil, of such length that one end extends into the sample cup. Place 10 ml Na_2CO_3 solution in the bomb and by means of a rubber policeman wet the interior surface of the bomb, including the head, as thoroughly as possible. Weigh 0.8 g to 1.0 g sample into the sample cup.

2. Addition of oxygen:

   Place the sample cup in position and arrange the thread so that one end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen slowly (to avoid blowing the oil from the cup) until pressure is reached as indicated in the table below:

Bomb Capacity (ml)	Min. Gage Pressure atm.	Max. Gage Pressure atm.
300-350	38	40
350-400	35	37
400-450	30	32
450-500	27	29

3. Combustion:

   Immerse the bomb in a cold water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion of at least 10 min. Release the pressure at a slow uniform rate such that the operation requires not less than one minute. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination.

4. Collection of chloride sample:

   Using deionized water, rinse the interior of the bomb, the sample cup, and the inner surface of the bomb cover into a 600 ml beaker. Scrub the interior of the bomb and the inner surface of the bomb cover with a rubber policeman. Wash the base of the terminals into the beaker. Cover the beaker with a speedy vap and gently reduce volume to 75 ml or less. Remove from the hot plate and cool to room temperature. Transfer the contents of the beaker into a 100 ml volumetric flask. Rinse the beaker several times, transferring rinses to the volumetric flask. Dilute to volume.

IC ANALYSIS

1. Set up the instrument according to the operator's manual.

2. Inject appropriate standards and record the peak heights.

3. Inject the samples and record the peak heights. Make the necessary dilutions or adjustment of the μMHO scale on the instrument to bring the sample into the linear range.

4. Calculate the linear regression data for the standards, enter the peak height value for each sample and record the calculated ppm value.

5. Calculate % Cl--using the following equation:

$$\text{Wt\% Cl} = \frac{\text{Sample ppm (from curve) x Dilution x Sample volume (ml)}}{\text{Sample Weight (g) x 10,000}}$$

REFERENCE

1. Standard Test Method for Chlorine in New and Used Petroleum Products (Bomb Method) ANSI/ASTM D 808-63.

ORGANIC ANALYSIS PROCEDURES

The procedures used for the determination of volatile and semivolatile organic compounds and PCBs in oil are described in the following pages. Major procedures addressed and their page locations are as tabulated below.

Procedure	Page
Volatile organics: tetraglyme extraction with modified Method 624 analysis	B-21
Volatile organics (Federal Register Method 624)	B-24
Semivolatile organics	B-31
Base/neutrals, acids and pesticides (Federal Register Method 625)	B-34
PCBs in oil	B-44
Pesticides and PCBs (Federal Register Method 608)	B-45

VOLATILE ORGANICS: TETRAGLYME EXTRACTION WITH MODIFIED METHOD 624 ANALYSIS

SCOPE AND APPLICATION

This method is designed to prepare a variety of nonaqueous samples for analysis for volatile organic compounds. It is applicable to oils, sludges, and solid wastes. It allows the detection and quantitation of organic compounds amenable to analysis by the purge and trap method as outlined in Method 624.

SUMMARY OF METHOD

A 1 gram portion of sample is extracted with 20 ml of tetraglyme. After phase equilibration, the tetraglyme layer is withdrawn, placed in a screw-cap vial with a minimum of headspace, and stored at 4°C for subsequent analysis. At the time of analysis, an aliquot of the extract is spiked into 25 ml of deionized water and Method 624 protocol are followed for the determination of volatile organics.

SAMPLE COLLECTION AND PRESERVATION

Samples collected for volatile organics analysis should be placed in 40 ml glass vials equipped with a septum-lined screw cap (same as in 624).

1. Fill the sample vial as completely as possible. Nonfluid samples should be packed into the vial with a minimum of headspace; fluid samples should be collected so no air bubbles remain in the vial.
2. Seal the vial.
3. Collect a duplicate sample.
4. Store the sample at 4°C until the time of extraction.

INTERFERENCES

1. See Method 624.
2. Daily analysis of method blanks--Analyze a sample of deionized water taken from the Inorganic Wet lab and spiked with 100 µl of tetraglyme from the same batch as that used for sample extraction.
3. After each analysis, rinse the purge tube with deionized water. Bake the trap for a minimum of 20 min. to ensure adequate desorption of high molecular weight purgeables. Nonaqueous samples typically contain more high-molecular weight material than do water samples, and the possibility of system contamination must be recognized.

4. Sample analysis time should be a minimum of 40 minutes to allow elution of higher boiling purgeables. Each chromatogram should be checked for possible chromatographic carryover; should this be suspected, the trap and oven should be baked out for 30 minutes before sample analysis continues.

REAGENTS

1. See Method 624.

2. Tetraglyme--cleaned by placing in a rotovap under aspirator suction for a minimum of 30 minutes. Tetraglyme cleaned in this fashion should be analyzed prior to use for extraction. A 100 µl aliquot spiked into 25 ml of deionized water should not interfere with detection of the internal standards used in Method 624 or cause baseline elevation greater than 30 percent the peak height of the highest internal standard used for analysis.

3. Calibration standards--standards used for Method 624 analysis are spiked with 100 µl tetraglyme prior to calibration curve analyses.

PROCEDURE

Tetraglyme Extraction

1. Weigh 1 gram portion of sample into a precleaned 40 ml glass screw cap vial.

2. Cover the sample immediately with 20 ml of tetraglyme measured with a delivery pipette.

3. Replace the vial cap and shake the vial until the layers mix or emulsify (no longer than 1 minute). If the sample is solid or highly viscous, sonication should be performed with the sonicator probe for 30 seconds at a setting of 5 and a 25 percent pulsed duty cycle.

4. Allow the tetraglyme/sample mixture to equilibrate until the layers are clearly separated. The appropriate time will vary with sample type; oil samples should be stored at 4°C overnight in contact with the tetraglyme while extracts from solids will require less time. Some samples may completely mix with the tetraglyme to form a solution.

5. Withdraw the tetraglyme layer and place in a precleaned screw cap glass vial. Allow a minimum of headspace. Store at 4°C.

Method 624 Analysis

1. The volume of tetraglyme extract appropriate for Method 624 analysis within the established calibration curve will vary with the level of volatile content of the original sample. If this is known to an approximation, the volume of tetraglyme extract to be used for

analysis may be calculated by the following equation. This equation is based upon the assumption that tetraglyme added to 25 ml water will give most accurate quantitation if the resultant solution is in the middle range of the calibration curve, or about 100 µg/l, for organic volatiles.

Volume of tetraglyme to use (ml) =

$$\frac{100\ \mu g/l \times 0.025\ \text{liter} \times 20\ \text{ml tetraglyme extract}}{\text{Sample wt (g) extracted} \times \text{sample contaminant levels } (\mu g/g)}$$

2. For samples of unknown content, a nominal 10 µl aliquot is measured with a 25 µl syringe and spiked into 25 ml of deionized water.

3. Analysis is conducted by purge and trap protocol as outlined in Method 624.

4. The total ion chromatogram is reviewed after analysis to determine whether maximum detection for the sample has been achieved without instrument saturation. This is done by monitoring the abundance of the base peak for major organic volatile components. The mass spectrometer is saturated when the count for the base peak of a compound exceeds 32767 for a single scan. If the maximum counts for the base peaks of the compounds detected as major components are less than 3000, detection limits may be reduced by an order of magnitude or greater. Reanalysis using 100 1 or greater portions of the tetraglyme extract may be conducted without instrument saturation occurring.

   If instrument saturation occurs during the analysis of the 10 µl tetraglyme aliquot, base peak counts for a single scan will exceed 32767. If this is noted, reanalysis should be conducted on a 1 µl aliquot of the extract.

Sample Quantitation

1. Determine the level of organic components in the water solution using the established calibration curve.

2. Calculate the level of sample content by the following equation:

Sample concentration (µg/g) =

$$\frac{\text{Water conc. } (\mu g/l) \times 0.025\ \text{liter} \times 20\ \text{ml tetraglyme}}{\text{Vol. of tetraglyme extract spiked into water} \times \text{wt of sample extracted (g)}}$$

VOLATILE ORGANICS

(FEDERAL REGISTER METHOD 624)

1.0 SCOPE AND APPLICATION

This method is designed to detect and quantify volatile organic compounds which are amenable to the purge and trap method; the compounds routinely determined by this procedure are shown in Table B-2. This method has been approved for NPDES monitoring.

2.0 SUMMARY OF METHOD

A 25-ml sample is purged with a stream of helium. The volatile organics present in the sample are transferred to the vapor phase and trapped on a sorbent column. After purging is completed, the sorbent column is heated and backflushed with helium to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components which are detected by a mass spectrometer.

3.0 SAMPLE COLLECTION AND PRESERVATION

Grab samples are collected in 40-ml glass vials equipped with a septum and screw cap. Prior to use, the vials, caps and septa must be soap- and water-washed, rinsed with deionized water and dried at 105°C for 1 hour. The following procedure is used for sample collection and storage.

3.1 Fill the sample vial completely, do not allow any air bubbles to pass through the sample.

3.2 Seal the vial; check that no air bubbles have been trapped in the sample.

3.3 Collect a duplicate sample.

3.4 Store sample at 4°C until the time of analysis; analysis must be performed within 14 days of sample collection.

4.0 INTERFERENCES

A variety of interfering substances may be present in more complex samples such as industrial effluents. The most common problem associated with this analysis is contamination; the following steps should be taken to detect contamination introduced in sample handling or analysis.

4.1 Analysis of field biased blanks--Deionized water carried through the sampling, storage and analysis procedures.

4.2 Daily analysis of method blanks--Analyze a sample of deionized water at the start of each analysis session, this detects contamination introduced by the purge gas or the plumbing ahead of the trap.

4.3 After analysis of a high level sample, a blank of deionized water should be analyzed to ensure that contamination of subsequent samples by carry-over does not occur.

5.0 REAGENTS

5.1 Organic-free deionized water--Water from the Continental deionized water system should be used. To avoid possible contamination by methylene chloride, obtain the water from the tap in the Inorganic Wet Lab.

5.2 Sorbent Trap Materials

a. 2,6-Diphenylene oxide polymer - 60/80 mesh Tenax, chromatographic grade.

b. Methyl silicone packing - 3 percent OV-1 on 60/80 mesh Chromosorb W.

c. Silica gel, Davison Chemical, 35/60 mesh, grade 15.

5.3 Calibration Standards

5.3.1 Stock solutions - 2 mg/ml: With the exception of the gases, the stock standard solutions may be either purchased from Supelco or prepared from the pure compound. Stock solutions for the gases (bromomethane, chloroethane, chloromethane and vinyl chloride) are always purchased. If stock solutions are prepared from the pure compound the following procedure is used:

a. Place 9.8 ml of methanol in a 10 ml ground glass stoppered volumetric flask.

b. Allow flask to stand unstoppered for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

c. Using a 100 µl syringe, add 2 to 3 drops of the standard material to the flask. Be certain that the drops fall directly into the alcohol without contacting the neck of the flask. Reweigh the flask.

4. Store stock standards at 4°C; prepare fresh standards every 2 weeks.

5.3.2 Working Standard Solutions

a. Prepare 100 ml of each of the following working standard solutions by dilution of the stock solutions: 5, 10, 50, 100, 150 µg/l.

5.4 Internal Standard Solution

5.4.1 The internal standard spiking solution is prepared by dilution of the Supelco standard which contains the three internal standards, bromochloromethane, 2-bromo-1-chloropropane and 1,4-dichlorobutane, at a concentration of 20 mg/ml. Alternately, this solution may be prepared from the stock standards.

5.4.2 Add 1 ml of the Supelco solution to 90 ml of deionized water in a 100 ml volumetric flask.

5.4.3 Dilute to volume and invert to mix. The concentration of this solution is 0.20 mg/ml. Each sample is spiked with 2.5 µl of this solution.

5.4.4 Prepare a fresh internal standard solution monthly.

5.5 UHP Helium--used as purge gas and GC carrier gas.

6.0 APPARATUS

6.1 Hewlett-Packard 5985 GC/MS.

6.2 Purge and Trap Device - Tekmar LSC 3.

6.3 GC Column - 1 Percent SP-1000 on Carbopack B, 8 ft x 2 mm ID column.

6.4 Syringe - glass, 25-ml hypodermic with Luer-Lok tip.

6.5 Microsyringes - 10, 25, 100 µl.

6.6 Volumetric glassware for preparation of standards.

7.0 QUALITY CONTROL REQUIREMENTS

7.1 A method blank of deionized water must be analyzed daily.

7.2 The volatiles laboratory control sample (LCS) must be analyzed daily. The reported value for each of the parameters should be entered in the instrument logbook. If the reported values for any of the components of the LCS are outside the established control limits (±2S), corrective action should be taken prior to running samples.

8.0 CALIBRATION AND TUNING

8.1 A five-point calibration curve is used, a new calibration curve is prepared every 2 weeks. Run each of the five working standard solutions as outlined in the procedures section. The information regarding response ratio versus area ratio for each standard is stored in the computer and used to calculate sample concentration.

8.2 Calculate the response factor (RF) for each compound using the following equation:

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where A_s = Area of the primary characteristic ion for the compound to be measured.

A_{is} = Area of the primary characteristic ion of the internal standard.

C_{is} = Concentration of the internal standard.

C_s = Concentration of the compound to be measured.

8.3 The instrument should be tuned daily according to the following procedures:

8.3.1 Allow column oven and trap to heat to their maximum temperatures (220°C and 180°C, respectively).

8.3.2 Tune the instrument with DFTPA using the following criteria:

Mass	Ion Abundance Criteria
69	100%
131	28-35% of mass 69
219	22-28% of mass 69

The ion abundance values for mass 131 and mass 219 should differ by 4 to 8 percent.

8.3.3 After allowing the column and trap to cool, analyze the Laboratory Control Sample.

9.0 PROCEDURE

9.1 Remove standards and samples from cold storage at least 1 hour prior to analysis and allow to warm to room temperature.

9.2 Adjust the helium flow rate to 40 ml/minute. Attach the trap inlet to the purging device and set the device to the purge mode. Open the syringe valve located on the purging device sample introduction needle.

9.3 Remove the plunger from a 25-ml syringe; open the sample or standard bottle and pour the sample or standard into the syringe barrel until it overflows. Replace the syringe plunger and adjust the sample volume to 25-ml. Replace the cap on the sample bottle and return to cold storage.

9.4 Remove the Luer tip of the 25-ml syringe and add 2.5 µl of the internal standard solution; replace the Luer-Lok.

9.5 Inject the sample into the purging chamber.

9.6 Purge with helium to transfer the volatile components to the trap. Adjust helium flow rate to 40 ml/min. Set the purging device to purge and purge the sample for 10.0 ± 0.1 minutes at ambient temperature.

9.7 After 10 minutes of purging adjust the device to the desorb mode and begin GC/MS analysis and data acquisition using the following conditions:

GC Conditions

GC Column	1% SP-1000 on Carbopack B, 8 ft x 2 mm ID column.
Temperature Program	Isothermal at 60°C for 4 min, then 10°/min to 220°C and held at that temperature for 15 min.
Injector Temperature	225°C
Carrier Flow	UHP helium, 30 ml/min.

Purge and Trap Conditions

Desorption Temperature	180°C
Desorption Time	4 min
Oven Temperature	200°C

MS Conditions

Emission	300 µa
Electron Energy	70 eV
Scan Rate	133.3 amu/sec
Mass Interval	41-350 amu

10.0 QUALITATIVE AND QUANTITATIVE DETERMINATION

10.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and at least two other characteristic ions. The following criteria must be met for a qualitative identification:

10.1.1 The characteristic ions of each compound of interest must maximize in the same scan or within one scan of each other.

10.1.2 The retention time must fall within ±60 seconds of the retention time of the authentic compound.

10.1.3 The relative peak heights of the characteristic ions in the EICPs must fall within ±20 percent of the relative intensities of these ions in a reference mass spectrum. The reference mass spectrum may be that of a standard or from a reference library.

10.1.4 Table B-2 shows the compounds routinely reported and the primary ion used to quantify each.

10.1.5 Quantitative determination of each compound is done using the internal standard method. Calculate the concentration of each compound according to the following equation:

$$\text{Concentration: } \mu g/l = \frac{(A_s)(C_{is})}{(A_{is})(RF)}$$

where A_s = Area of the primary characteristic ion of the compound to be measured.

C_{is} = Concentration of the internal standard in µg/l in the samples.

A_{is} = Area of the primary characteristic ion of the internal standard.

RF = Response factor of the compound being quantified.

These calculations are normally performed by the HP 5985 computer.

11.0 REFERENCE

11.1 Method 624, Federal Register, Monday, December 3, 1979, 40 CFR Part 136.

TABLE B-2. REPORTED COMPOUNDS AND THEIR CHARACTERISTIC IONS

Compound	Primary Ion
chloromethane	50
dichlorodifluoromethane	85
bromomethane	94
vinyl chloride	62
chloroethane	64
methylene chloride	84
trichlorofluoromethane	101
1,1-dichloroethylene	96
1,1-dichloroethane	63
trans-1,2-dichloroethylene	96
chloroform	83
1,2-dichloroethane	98
1,1,1-trichloroethane	97
carbon tetrachloride	117
bromodichloromethane	83
bis-chloromethyl ether	79
1,2-dichloropropane	63
trans-1,3-dichloropropene	75
trichloroethylene	130
dibromochloromethane	129
cis-1,3-dichloropropene	75
1,1,2-trichloroethane	83
benzene	78
2-chloroethylvinyl ether	106
bromoform	173
1,1,2,2-tetrachloroethene	166
1,1,2,2-tetrachloroethane	83
toluene	91
chlorobenzene	112
ethylbenzene	91
acrolein	56
acrylonitrile	53

SEMIVOLATILE ORGANICS

The following procedures relate to the determination of polynuclear aromatic hydrocarbons, nitrosoamines and related semivolatile compounds in used engine oils. Polynuclear aromatic hydrocarbons (PAH) and nitrosoamines are potential products of the combustion process in internal combustion engines. The following method used in this program involves a column chromatography procedure to remove the aliphatic components of the oil and allow for the quantitation of PAH and nitrosoamines by GC/MS. The following conditions represent those used in this study, when different from the conditions stipulated in the Method 625 procedures.

MATERIALS/APPARATUS

1. Column - 200 mm x 10 mm ID glass with Teflon stopcock, water jacketed.
2. Silica gel - Davison Grade 950, 60-200 mesh; cleaned by sequential soxhlet extractions with methanol, methylene chloride, and pentane. Activated at 110°C for at least 2 hours, and cooled in a desiccator.
3. Gas Chromatograph/Mass Spectrometer operated under the following conditions:

<u>GC Conditions</u>

Column	SE54, 30-meter fused silica capillary
Temperature program	60°C held for 2 minutes and ramped at 10°C/minute to 260°C and held
Injector temperature	275°C
Injection volume	1 µl
Flow	0.5 ml/min

<u>MS Conditions</u>

Ionization voltage	70 eV
Emission voltage	300 µA
Source temperature	200°C
Scan rate	1.0 sec/scan
Range	45 to 450 m/Z

REAGENTS

1. Pentane - pesticide residue grade
2. Methylene Chloride - pesticide residue grade
3. Methanol - pesticide residue grade
4. Sodium Sulfate - anhydrous, reagent grade

PROCEDURE

Column Preparation

1. Slurry-pack the column with 6.0g (±0.2g) of Silica gel in pentane. When the column is fully prepared, allow the pentane to drain to the top of the Silica bed.

2. Add 3.0g (±0.2g) of sodium sulfate to the top of the column with several pentane washings. Drain pentane to top of sodium sulfate layer.

Sample Preparation

1. Weigh approximately 0.5g of a homogeneous waste oil sample into a 50 ml beaker to a precision of 0.1 mg.

2. Mix oil sample with sufficient silica gel to provide a relatively dry mix.

Fractionation

The following fractions are collected:

Fraction	Solvent	Volume
1	pentane	25.0 ml
2	50% methylene chloride/50% pentane	10.0 ml
3	95% methylene chloride/5% methanol	10.0 ml
4	50% methylene chloride/50% methanol	10.0 ml

1. Transfer oil/silica gel mix to head of column with several washings of the first elution solvent, 25.0 ml of pentane.

2. Elute with the remaining pentane and reserve the eluate in a 25.0-ml container. Bring to volume (25.0 ml) with pentane if necessary.

3. Repeat procedure for fractions 2, 3, and 4, bringing each separate fraction to the specified volume with the proper eluting solvent. Maintain an elution rate of 1.0 ml/min for reproducibility and adequate resolution.

4. Reduce (by Kuderna-Danish evaporation and nitrogen blow down) 5 ml of fractions 2, 3, and 4 to 0.5 ml. Combine the concentrates from fractions 3 and 4 for analysis by Method 625. Hold the remainder of the fractions in reserve.

5. Fraction 1 contains the aliphatic hydrocarbons that are responsible for the background interference in this sample matrix. The fraction is reserved though it is unsuitable for analysis without further preparation.

REFERENCE

Estes, E. D., W. F. Gutknecht, D. E. Lentsen, D. E. Wagoner. IERL-RTP Procedure Manual: Level 1 Environmental Assessment, 2nd ed., p. 144-148.

BASE/NEUTRALS, ACIDS AND PESTICIDES

(FEDERAL REGISTER METHOD 625)

1.0 SCOPE AND APPLICATION

This method is designed to detect and quantify most neutral, basic and acidic organic compounds which are soluble in methylene chloride and amenable to gas chromatography; the method may be used for water and wastewater samples. Method 625 has been approved for NPDES monitoring.

2.0 SUMMARY OF METHOD

The sample is extracted with methylene chloride using a separatory funnel. The extract is dried over sodium sulfate and concentrated to 1 to 2 mls using a Kuderna-Danish (K-D) evaporator. Quantitative analysis is performed by GC/MS.

3.0 SAMPLE COLLECTION AND PRESERVATION

Samples are collected in 1 gallon glass containers and stored at 4°C until the time of analysis. All samples must be extracted within 14 days and analyzed within 30 days of collection.

4.0 INTERFERENCES

A variety of interfering substances may be present in more complex samples such as industrial effluents. Method interferences may be caused by contaminants introduced by reagents or glassware; a method blank must be analyzed with each set of samples to detect any contamination.

5.0 REAGENTS

5.1 Sodium Hydroxide--6N solution

5.2 Sulfuric Acid--6N solution

5.3 Sodium Sulfate--Granular, anhydrous; rinse with methylene chloride (20 ml/g) and dry in fume hood.

5.4 Methylene Chloride--Burdick & Jackson "Distilled-in-Glass" or Baker "Resi-Analyzed" are acceptable grades of this solvent.

5.5 UHP Helium

5.6 Stock Standards--Stock standards for the compounds shown in Tables B-3, B-4 and B-5 are prepared at a concentration range of 200 to 400 ppb using assayed reference material (obtain from Chem Service)

TABLE B-3. CHARACTERISTIC IONS AND RETENTION TIMES OF THE BASE/NEUTRAL COMPOUNDS

Compound	Characteristic ion	Retention time (min)
Bis(2-chloroethyl ether)	93	7.3
1,3-Dichlorobenzene	146	7.7
1,4-Dichlorobenzene	146	7.8
1,2-Dichlorobenzene	146	8.2
Bis(2-chloroisopropyl) ether	45	8.5
N-nitroso-dipropyl amine	70	8.8
Hexachloroethane	117	8.9
Nitrobenzene	77	9.1
Isophorone	82	9.7
Bis(2-chloroethoxy)methane	93	10.3
1,2,4-Trichlorobenzene	180	10.6
Naphthalene	128	10.8
Hexachlorobutadiene	225	11.2
Hexachlorocyclopentadiene	237	13.0
2-Chloronaphthalene	162	13.7
Dimethyl phthalate	163	14.7
Acenaphthylene	152	14.7
2,6-Dinitrotoluene	165	14.9
Acenaphthene	154	15.2
2,4-Dinitrotoluene	165	15.8
Fluorene	166	16.5
Diethyl phthalate	149	16.5
4-Chlorophenyl phenyl ether	204	16.5
N-Nitrosodiphenyl amine	169	16.9
1,2-Diphenyl hydrazine	77	16.9
4-bromophenyl phenyl ether	248	17.8
Hexachlorobenzene	284	18.1
Phenanthrene	178	18.9
Anthracene	178	18.9-19.0
Dibutyl phthalate	149	20.6
Fluoranthene	202	21.9
Pyrene	202	22.5
Butyl benzylphthalate	149	24.5
Benz(a)anthracene	228	26.3
Bis(2-ethylhexyl)phthalate	149	27.0
Dioctyl phthalate	149	30.6
Benzo fluoranthene	252	32.4
Benz(a)pyrene	252	34.8
Dibenzo(a,h) anthracene	278	47.7

TABLE B-4. CHARACTERISTIC IONS AND RETENTION TIMES OF THE ACID COMPOUNDS

Compound	Characteristic ion	Retention time (min)
Phenol	94	7.2
2-chlorophenol	128	7.4
2-nitrophenol	139	9.9
2,4-dimethylphenol	107	10.1
2,4-dichlorophenol	162	10.5
p-chloro-o-cresol	142	12.4
2,4,6 trichlorophenol	198	13.4
2,4-dinitrophenol	184	15.6
4-nitrophenol	139	15.9
4,6-dinitro-o-cresol	198	16.9
Pentachlorophenol	266	18.7

TABLE B-5. CHARACTERISTIC IONS AND RETENTION TIMES OF PESTICIDES/PCBs

Compound	Characteristic ion	Retention time (min)
Aldrin	66	19.8
α-BHC[a]	183	18.5
ß-BHC	181	19.5
δ-BHC[a]	183	19.1
4,4'-DDD	235	23.6
4,4'-DDE	246	23.0
4,4'-DDT	235	25.0
Dieldrin	79	23.4
Endosulfan I[a]	201	---
Endosulfan II[a]	201	---
Endosulfan Sulfate	272	27.0
Endrin[a]	81	---
Endrin Aldehyde	250	24.3
Heptachlor	100	20.0
Heptachlor epoxide	353	22.0
PCB 1016[b]	186	19-22
PCB 1221[b]	188	20-23
PCB 1232[b]	188	20-23
PCB 1242[b]	258	21-24
PCB 1248[b]	292	21-24
PCB 1254[b]	326	22-25
PCB 1260[b]	360	22-25

[a] Subject to decomposition deriving from the alkaline conditions of the Method 625 extraction. Recoveries by this method are known to be low.

[b] Mixtures of isomers eluting over a 2- to 3-minute time period.

5.6.1 Dissolve the reference material in hexane or other suitable solvent. Dilute to volume in a 100 ml ground glass stoppered volumetric flask using hexane.

5.6.2 Transfer the stock solution to 15 ml Teflon lined screw cap vials. Mark with the date and refrigerate. PNA standards must be protected from light.

5.6.3 Check standards for signs of degradation or evaporation prior to preparing working standards. Prepare fresh standards as needed.

5.7 Working Standards--These are prepared by dilution of the stock solution to result in standards covering the range 20 to 400 ppb. Verify a new set of standards by analyzing the EPA QA samples for base/neutrals and acids.

5.8 Wide Range pH paper.

6.0 APPARATUS

6.1 Hewlett-Packard 5985 GC/MS with SE-54, 30m fused-silica capillary column.

6.2 Damon IEC centrifuge.

6.3 2000 ml separatory funnel.

6.4 Kuderna-Danish apparatus.

6.5 Concentrator tube, 15 ml. Ground glass stopper is used to prevent evaporation of extracts.

6.6 Drying Column--20 mm ID Pyrex chromatographic column equipped with a glass wool plug.

6.7 500 ml Evaporative Flash--Attach to connector tube with springs.

6.8 Snyder Columns--2 ball micro, 3 ball macro.

6.9 Teflon boiling chips, 10/40 mesh, pre-extracted.

6.10 Water Bath.

7.0 QUALITY CONTROL REQUIREMENTS

7.1 A method blank and a laboratory control sample must be taken through the entire extraction and analysis procedure with each group of 10 to 15 samples processed.

7.2 After calibrating the instrument, analyze the laboratory control sample. Enter the reported values in the instrument QC log. If the results are within acceptance limits (± 2s), the analysis may proceed. If the results are outside the acceptance limits analysis should be stopped and corrective action taken. After preparation of new standard solutions verify their concentration by analyzing the appropriate EPA QC samples.

8.0 PROCEDURE

8.1 Sample Extraction

8.1.1 Measure 1 liter of water into a 2 liter separatory funnel using a graduated cylinder. If only 1 liter was collected, the entire sample should be used.

8.1.2 Spike the sample with the surrogate compounds, for base neutrals, either Decafluorobiphenyl, 2-fluoroaniline or D_5-Bromobenzene may be used; for acids, use D_5 phenol. Adjust the sample pH to 11 or greater using 6N NaOH. Multirange pH paper can be used for pH measurement.

8.1.3 Rinse the graduated cylinder or sample bottle thoroughly with 60 ml methylene chloride and transfer the solvent rinse to the separatory funnel.

8.1.4. Extract the sample by shaking the funnel for 2 minutes, periodically venting to release excess vapor pressure. Allow organic layer to separate from the aqueous phase for a minimum of 10 minutes; if two distinct phases form, proceed to Step 8.1.5. If an emulsion forms which is more than one third the size of the solvent layers, the phase separation is completed by centrifugation according to the following procedure:

a. Place the methylene chloride layer in a centrifuge bottle.

b. Centrifuge for 10 to 15 minutes at approximately 3200 rpm.

c. Pour the sample into a 125 ml separatory funnel and collect the methylene chloride layer in a BOD bottle.

d. Pour the remaining sample back into the 2-liter separatory funnel, rinse the centrifuge bottle and the 125 ml sep. funnel with the next portion of methylene chloride and continue with Step 8.1.6 below.

8.1.5 Collect the methylene chloride layer in a BOD bottle.

8.1.6 Add a second 60 ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time. Add the second methylene chloride layer to the first in the BOD bottle.

8.1.7 Extract with a third 60 ml portion of methylene chloride adding this extract to the first two in the BOD bottle.

8.1.8 Pour the combined extracts through a drying column containing 3 to 4 inches of anhydrous sodium sulfate and collect it in a 500 ml K-D flask equipped with a 15 ml concentrator tube.

8.1.9 Rinse the BOD bottle with 20 to 40 ml of methylene chloride and pour this through the drying column. The collected extracts and rinsings are sealed and labeled as the base/neutral fraction.

8.1.10 Adjust the pH of the sample, which was previously extracted for base/neutrals, to 2 or below using 6N H_2SO_4.

8.1.11 Serially extract with three 60-ml portions of methylene chloride as before.

8.1.12 Collect and combine the extracts in a BOD bottle and dry by passing through a column of anhydrous sodium sulfate. Rinse the BOD bottle with 20 to 40 ml of methylene chloride and pour the rinse through the drying column collecting extracts and rinsings as before in a 500 ml K-D flask having a 15 ml concentrator tube. Seal and label as the acid fraction.

8.2 Concentration

8.2.1 To concentrate the base/neutral fraction, use the following procedure:

a. Add 1 or 2 clean boiling chips to the K-D flask and attach a 3-ball macro Snyder column. Prewet the Snyder column by adding approximately 1 ml of methylene chloride through the top.

b. Place the K-D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water and the entire lower rounded surface of the flask is bathed with water vapor.

c. Adjust the vertical position of the K-D flask and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column should actively chatter but the chambers should not flood.

d. When the liquid has reached a volume of less than 1 to 5 ml, remove the K-D apparatus and allow the solvent to drain for at least 10 minutes while cooling.

e. Rinse the Snyder column, the flask and its lower joint into the concentrator tube with 10 ml of methylene chloride.

f. Add a clean boiling chip and attach a two ball micro Synder column to the concentrator tube. Prewet the column by adding about 0.5 ml methylene chloride through the top.

g. Place the K-D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood.

h. When the liquid reaches an apparent volume of 0.5 ml, remove the K-D from the water bath and allow the solvent to drain and cool for at least 10 minutes.

i. Remove the micro Synder column and rinse its lower joint into the concentrator tube with approximately 0.2 ml of methylene chloride. Adjust the volume to 1.0 ml with methylene chloride and place in a 2.0 ml vial with Teflon lined cap. Rinse the concentrator tube with 1.0 ml hexane and combine with the methylene chloride portion. The final volume will be 2.0 ml. Label as the base neutral fraction. Use the same procedure for the concentration of the acid fraction.

8.3 GC/MS Analysis

8.3.1 Tune the instrument daily by bleeding in PFTBA using the following criteria.

Mass	Ion Abundance Criteria
69	100%
131	32 to 37% of Mass 69
219	23 to 29% of Mass 69

The ion abundance values for mass 131 and mass 219 should differ by 6 to 10 percent.

8.3.2 The following instrument operating conditions are used:

GC Conditions

Temperature program	50°C held for 2 min, then 10°/min to 260°C and held
Injection volume	Typically 1 µl
Injection temperature	275°C
Column flow	UHP helium, 0.5 ml/min

MS Conditions

Emission	300 µa
Electron energy	70 eV
Scan rate	1.0 sec/scan
Mass Interval	45 to 450 amu

8.3.3 Adjust the system sensitivity by injecting phenanthrene. The sensitivity varies as a function of multiplier, column, injector and source interface characteristics. The optimum electron multiplier setting is that which will yield approximately 50X the detection limit but less than one-fourth of the value where serious saturation occurs for 50 ng of phenanthrene. For the HP 5985, the total ion count for the 188 peak should be about 20,000.

8.3.4 Program the instrument to operate in the Extracted Ion Current Profile (EICP) mode and collect EICP for the characteristic 100 percent ion shown in Tables B-3, B-4 and B-5 for each compound being measured.

8.3.5 Operating in the EICP mode, calibrate the system using the internal standard method.

a. Determine the response factor using the following equation:

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where A_s = the integrated area or peak height of the characteristic ion for the pollutant standard.

A_{is} = the area of the characteristic ion for the internal standard.

C_{is} = the amount (µg) of the internal standard.

C_s = the amount (µg) of the pollutant standard.

b. Prepare a calibration curve by plotting the response factor against the standard concentration using a minimum of three standards in the range of interest. The concentration of the upper standard should be in the range of 200 to 300 ppb, the concentration of the lower standard should be one-tenth that of the upper standard or 20 to 30 ppb.

c. Verify the calibration curve daily; if significant drift has occurred, a new curve should be prepared.

d. To quantify, add the internal standard to the concentrated sample extract. The following compounds are used as internal standards:

d_8-naphthalene
d_{10}-anthracene
d_{12}-chrysene

e. Calculate the concentration of each compound present using the following equation:

$$\text{Concentration } (\mu g/l) = \frac{(A_s)(C_{is})}{(A_{is})(RF)}$$

where A_s = area of the primary characteristic ion of the compound to be measured.

C_{is} = concentration of the internal standard in µg/l in the samples.

A_{is} = area of the primary characteristic ion of the internal standard.

RF = response factor of the compound being quantified.

These calculations are normally performed by the HP 5985 computer.

9.0 REFERENCE

1. Method 625, Federal Register, Monday, December 3, 1979, 40 CFR Part 136.

PCBs IN OIL

The procedure used in this program for the determination of PCBs in Oil was a modification of EPA Method 608. The modifications used in sample preparation are shown below; the full text of Method 608 is contained in the following pages.

PREPARATION PROCEDURE

1. Take an aliquot of oil weighing approximately 1.0 g, add 5 ml hexane and 5 ml concentrated sulfuric acid.
2. Shake the sample for approximately 1 minute. If the sample extract is not clear, it must be applied to a Florisil column as described in Section 8.2 of EPA Method 608.
3. Analyze as described in Section 9.0 of Method 608; report results as μg/g.

PESTICIDES AND PCBs

(FEDERAL REGISTER METHOD 608)

1.0 SCOPE AND APPLICATION

This method may be used in the determination of certain organochlorine pesticides and polychlorinated biphenyls (PCBs) in water and wastewater. This method has been approved for NPDES monitoring.

2.0 SUMMARY OF METHOD

A 1-liter sample is extracted with methylene chloride using separatory funnel techniques. The extract is dried, concentrated and solvent exchanged into hexane. If necessary, sample concentrates are cleaned by Florisil chromatography to remove interferences. Identification and quantitation is performed using a gas chromatograph equipped with an electron capture detector.

3.0 SAMPLE COLLECTION AND PRESERVATION

Grab samples are collected in 1 liter glass containers following normal sample collection procedures; the bottle should not be prewashed with sample prior to collection. If composite samples are collected the samples should be placed in refrigerated glass containers. Tygon tubing should not be used in sampling equipment.

The samples should be stored at 4°C until extraction. Samples must be extracted within 14 days and analyzed within 30 days of collection.

4.0 INTERFERENCES

Contamination may be introduced by reagents or inadequate glassware cleaning. A variety of interfering substances may be present in more complex samples such as industrial effluents. Contact with plastics must be avoided since phthalate esters can be a major interference. Prior to use, all glassware should be cleaned using the following procedure:

4.1 Solvent rinse immediately after use.

4.2 Wash thoroughly with soap and hot water.

4.3 Rinse with hot water, deionized water, acetone and pesticide quality hexane.

4.4 Heavily contaminated glassware may require treatment by heating at 400°C for 15 to 30 minutes. However certain high boiling materials such as PCBs may not be eliminated by this treatment; contaminated Class A volumetric glassware (e.g. pipets, volumetric flasks) must not be cleaned by this method.

4.5 Clean glassware should be capped with aluminum foil prior to storage.

4.6 Immediately before use; rinse the glassware with methylene chloride or hexane.

5.0 REAGENTS

5.1 Preservatives:

5.1.1 Sodium hydroxide, J. T. Baker, 10 N in distilled water.

5.1.2 Sulfuric acid, J. T. Baker reagent grade 1+1 with distilled water.

5.2 Methylene Chloride--Baker "Resi-Analyzed" or Burdick and Jackson "Distilled-in-Glass."

5.3 Hexane--Baker "Resi-Analyzed" or Burdick and Jackson "Distilled-in-Glass."

5.4 Sodium Sulfate--Granular anhydrous, soxhlet extract with a mixture of 85 percent hexane, 15 percent methylene chloride and dry in a fume hood.

5.5 Stock Standards--Prepare stock standards at concentrations of 1.0 μg/μl by dissolving 0.010g of assayed reference material in pesticide quality hexane and diluting to volume in a 10 ml ground glass stoppered volumetric flask. Transfer the stock solution to screw-capped reagent bottles and store in a refrigerator. Prior to preparing working standards, check the stock solution for signs of degradation or evaporation.

5.6 Working Standards--Prepare mixed working standards at concentrations that will bracket the working range of the chromatographic system, usually 1 ng/ml to 100 ng/ml.

5.7 Diethyl ether--Burdick and Jackson Distilled-in-Glass, must be free of peroxides as indicated by EM Quant Test Strips (EM Laboratores, Inc., 500 Executive Blvd., Elmsford, NY 10523)

5.8 Florisil--PR grade (60/100 mesh), purchase activated at 1250°F. Soxhlet extract in hexane and dry in a fume hood. Store in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 hours at 130°C in a foil covered glass container.

5.9 Multi-range pH paper.

6.0 APPARATUS

6.1 Hewlett Packard 5840 Gas Chromatograph with Ni^{63} electron capture detector and HP 7671A automatic sampler.

6.2 Columns: Primary Column--1.5 percent OV-17/1-95 percent, on 100/120 Chromosorb WHP, 6 ft x 2 mm
Confirmatory Column--5 percent SP 2401 on 100/120 Supelcoport, 6 ft x 2 mm.

6.3 Büchi-Brinkmann Rotary Evaporator.

6.4 Beroza Trap, 24/40 fitting.

6.5 Damon IEC Centrifuge

6.6 Separatory Funnel--2000 ml with Teflon stopcock.

6.7 Drying Column--20 mm I.D. Pyrex chromatographic column with coarse frit.

6.8 Boiling Flask--250-ml with 24/40 ground glass fitting.

6.9 Teflon Boiling Chips--10/40 mesh, pre-extracted.

6.10 Volumetric Glassware--flasks, pipets.

6.11 Water bath.

7.0 QUALITY CONTROL REQUIREMENTS

7.1 A method blank and a laboratory control sample must be taken through the entire extraction and analysis procedure with each group of 10 to 15 samples processed. EPA-EMSL concentrates containing pesticides and PCBs are available.

7.2 After calibrating the instrument, analyze a laboratory control sample. Enter the reported values in the instrument QC log. If the results are within acceptable limits (±2S), the analysis may proceed. If the results are outside the acceptable limits, analysis should be stopped and corrective action taken.

8.0 PROCEDURE

8.1 Sample Extraction

8.1.1 Measure 1 liter of water into a 2 liter separatory funnel using a graduated cylinder. If only 1 liter of sample was collected, the entire amount should be used.

8.1.2 Check the pH of the sample using wide-range pH paper. If necessary, adjust the pH to within the range of 5 to 9 with sodium hydroxide or sulfuric acid.

8.1.3 Rinse the graduated cylinder and/or sample bottle thoroughly with 60 ml methylene chloride and transfer the solvent rinse to the separatory funnel.

8.1.4 Extract the sample by shaking the funnel for 2 minutes, periodically venting to release excess vapor pressure. Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes; if two distinct phases form, proceed to Step 8.1.5. If an emulsion forms which is more than one third the size of the solvent layers, phase separation is completed by centrifugation according to the following procedure:

a. Place the methylene chloride layer in a centrifuge bottle.

b. Centrifuge for 10 to 15 minutes at approximately 3200 rpm.

c. Pour the sample into a 125 ml separatory funnel and collect the methylene chloride layer in a BOD bottle.

d. Pour the remaining sample back into the 2-liter separatory funnel. Rinse the centrifuge bottle and the 125 ml separatory funnel with the next portion of methylene chloride and continue the extraction as in Step 8.1.6, below.

8.1.5 Collect the methylene chloride layer in a BOD bottle.

8.1.6 Add a second 60 ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time. Add the second methylene chloride layer to the first in the BOD bottle.

8.1.7 Extract with a third 60 ml portion of methylene chloride adding this extract to the first two in the BOD bottle.

8.1.8 Pour the combined extracts through a drying column containing 3 to 4 inches of anhydrous sodium sulfate and collect it in a 250 ml boiling flask.

8.1.9 Rinse the BOD bottle with methylene chloride and pour the rinse through the drying column collecting the rinse in the boiling flask.

8.1.10 Place the 250-ml boiling flask on the rotary evaporator with a 30 to 36°C water bath. Evaporate to a volume of 1 to 5 ml.

8.1.11 Solvent exchange into hexane; add 50 ml of hexane to the boiling flask and raise the temperature of the water bath to 40 to 45°C. Evaporate to a volume of less than 10 ml.

8.1.12 Wash the extract from the boiling flask into a 10 ml volumetric with hexane; dilute to volume with hexane and label as the pesticide/PCB fraction.

8.2 Cleanup and Separation

8.2.1 Add a weight of Florisil (nominally 21 grams) predetermined by calibration to a chromatographic column. Settle the Florisil by tapping the column; add sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep. Add 60 ml of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to the exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatography column. Discard the eluate.

8.2.2 Adjust the sample extract to an appropriate volume and transfer it from the volumetric flask to the Florisil column. Rinse the flask with 1 to 2 ml hexane and add each rinse to the column.

8.2.3 Place a 250-ml round bottom flask under the chromatography column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 ml of 6 percent ethyl ether in hexane (Fraction 1) using a drop rate of about 5 ml/min. Remove the flask and set aside.

8.2.4 Elute the column again using 200 mls of 15 percent ethyl ether in hexane (Fraction 2); collect in a second 250 ml round bottom flask.

8.2.5 Perform the third elution using 200 ml of 50 percent ethyl ether in hexane (Fraction 3). The elution patterns for the pesticides and PCBs are shown in Table B-6.

8.2.6 Concentrate the eluates by rotary evaporation using a water bath at about 85°C. Adjust the final volume to equal the volume initially applied to the Florisil column.

8.3 Analysis

8.3.1 Calibrate the instrument using a minimum of three calibration standards.

8.3.2 The following instrument conditions are used:

Temperature	175°C
Injector temperature	270°C
Injection volume	4.0 μl
Detector temperature	270°C
Run time	45 min
Carrier flow	UHP argon/methane, 50 ml/min

8.3.3 Record the volume injected to the nearest 0.05 μl and the resulting peak size in area units.

TABLE B-6. DISTRIBUTION AND RECOVERY OF CHLORINATED PESTICIDES AND PCBs USING FLORISIL COLUMN CHROMATOGRAPHY

Parameter	Recovery (percent) by fraction 1 (6%)	2 (15%)	3 (50%)
Aldrin	100		
α-BHC	100		
β-BHC	97		
δ-BHC	98		
γ-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan Sulfate	0	0	106
Endrin	4	96	
Endrin Aldehyde	0	68	26
Heptachlor	100		
Heptachlor Epoxide	100		
Toxaphene	96		
PCB 1016	97		
PCB 1221	97		
PCB 1232	95	4	
PCB 1242	97		
PCB 1248	103		
PCB 1254	90		
PCB 1260	95		

8.3.4 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

8.3.5 If measurement of the peak area is prevented by the presence of interferences, further sample cleanup is required.

8.3.6 The compounds determined by this procedure, their retention times and detection limits are shown in Table B-7.

9.0 QUALITATIVE AND QUANTITATIVE DETERMINATION

9.1 Identification and quantitation is performed by comparison of the retention times and area counts noted for the sample with those of the standard.

9.2 Linear regression data are obtained by entering the standard concentrations and area counts into the Texas Instruments Programmable 58C Calculator; the slope, intercept and correlation coefficient are recorded.

9.3 The sample concentration is determined using the equation for a line, $y = mx + b$ and solving for x:

$$x = \frac{y - b}{m}$$

where x = sample concentration, ng/ml

y = area counts of the compound of interest in the sample

b = y intercept

m = slope

9.4 The final sample concentration is determined by the following calculation:

Final concentration (ng/ml) =

$$\frac{\text{ng/ml in extract x extract vol (ml) x dilution factor}}{\text{initial sample volume (ml)}}$$

10.0 REFERENCE

10.1 Method 608, Federal Register, Monday, December 3, 1979, 40 CFR Part 136.

TABLE B-7. GAS CHROMATOGRAPHY OF PESTICIDES AND PCBs

Parameter	Retention time (min) Column 1	Column 2	Detection limit (μg/l)
Aldrin	4.08	2.73	0.01
α-BHC	2.07	2.13	0.01
ß-BHC	3.29	2.41	0.01
δ-BHC	3.81	2.73	0.01
γ-BHC	2.73	2.13	0.01
Chlordane	a	a	0.04
4,4'-DDD	13.24	9.21	0.01
4,4'-DDE	8.96	5.45	0.01
4,4'-DDT	15.64	10.19	0.01
Dieldrin	9.15	7.40	0.01
Endosulfan I	7.62	6.18	0.01
Endosulfan II	13.21	10.91	0.01
Endosulfan Sulfate	13.21	10.91	0.01
Endrin	10.83	8.65	0.01
Endrin Aldehyde	17.08	17.04	0.01
Heptachlor	3.35	2.41	0.01
Heptachlor Epoxide	6.24	4.85	0.01
Toxaphene	a	a	0.40
PCB 1016	a	a	0.10
PCB 1221	a	a	0.10
PCB 1232	a	a	0.10
PCB 1242	a	a	0.10
PCB 1248	a	a	0.10
PCB 1254	a	a	0.10
PCB 1260	a	a	0.10

[a] Multiple peak response, refer to Federal Register Method 608, pages 69505-69509.

APPENDIX C

QUALITY CONTROL

INTRODUCTION

Quality Control (QC) protocols implemented for this program included the use of method blanks, laboratory control samples, replicate analyses, surrogate spikes, EPA Quality Control samples and National Bureau of Standards Standard Reference Materials (SRMs). A brief synopsis of each of these control elements is provided below. A more detailed discussion of each element including the results for each of the respective categories is provided in subsequent portions of this section.

Blank Samples

Method Blanks--

Method blanks were carried through each analytical scheme with project samples to assess spurious contamination arising from reagents and glassware used in the analysis. All reported values have been corrected by an appropriate method blank.

Calibration Blanks--

These are blanks used in instrument calibration which contain all reagents, other than the standard material, used in the preparation of calibration standards.

Laboratory Control Samples

These are quality control samples which are processed through all preparation and analysis procedures with project samples. Laboratory control samples include replicate analyses, which are used to assess analytical precision, and matrix spikes and EPA and NBS reference materials which are used to assess analytical accuracy.

Instrument Check Samples

These are usually prepared from an EPA quality control concentrate and are used on a daily basis to verify instrument calibration.

Surrogate Spikes

A series of deuterated analogues of the components of interest are spiked into program samples scheduled for GC/MS analysis. These components serve to assess the behavior of actual components in individual program samples during the entire preparative and analysis scheme.

INORGANIC ANALYSES

Metals

Quality control protocols for the determination of metals in oil and particulate samples included the analysis of replicates and NBS Standard Reference Materials. NBS Standard Reference Materials 1634a (Trace Elements in Fuel Oil) and 1085 (Wear Metals in Lubricating Oil) were used to monitor the analysis of oil samples during this program; these results are presented in Tables C-1 and C-2, respectively. NBS Standard Reference Material 1648 (Urban Particulate) was analyzed with particulate samples submitted during this program. Table C-3 presents results from the analysis of SRM 1648.

In addition, replicate aliquots of two oil samples were carried through the entire preparation and analysis procedure to assess analytical precision using actual program samples. Results from duplicate analyses of BC-4, Recycling Process (GCA No. 22165) and triplicate analyses of BO-SS-1, Feed Stock (GCA No. 27106) are shown in Tables C-4 and C-5, respectively.

At the start of each analysis session, the ICAP was standardized and an EPA quality control concentrate was analyzed to verify the accuracy of the calibration standards; the results of this analysis were then entered into the instrument log book.

Sulfur in Oil

Quality control protocols for the determination of sulfur in oil samples included the analysis of National Bureau of Standards Standard Reference Material 1619, Sulfur in Residual Fuel Oil and the analysis of replicate samples. These results are presented in Tables C-6 and C-7.

Prior to analysis of samples, instrument calibration was verified by analysis of an EPA quality control concentrate. The reported values for this sample were entered in the instrument log book.

Total Chlorine in Oil

Quality control procedures for the determination of total chlorine in oil (measured as chloride) included the analysis of spiked samples and replicates. Samples of mineral oil spiked with dibromochloromethane were carried through the preparation and analysis procedures to assess method accuracy; these results are presented in Table C-8.

Duplicate aliquots of GCA No. 22205 (PS-1, Recycling Process) were prepared by Parr Bomb combustion and analyzed by ion chromatography. Both aliquots were found to contain 850 μg/g total chlorine.

ORGANIC ANALYSES

Volatile Organics

Quality control procedures for the analysis of volatile organics in oil included the analysis of method blanks, spiked samples and replicates.

Samples of a well characterized oil were spiked to contain known quantities of a number of volatile compounds and were analyzed with project samples using the tetraglyme procedure described in Appendix B. The results of these analyses are shown in Tables C-9, C-10 and C-11.

Replicate analyses were performed on three samples; these results are presented in Tables C-12, C-13 and C-14.

Instrument calibration was verified on each day of analysis through the use of EPA quality control concentrates. The results of these analyses were entered in the instrument log book.

Semivolatile Organics

Quality control procedures implemented for the analysis of semivolatile organics included the use of method blanks, spiked samples, surrogates and analysis of NBS Standard Reference Material 1580, Organics in Shale Oil.

NBS Standard Reference Material 1580, Organics in Shale Oil was analyzed in duplicate using the procedures outlined in Appendix B of this report. The results of these analyses are presented in Table C-15.

Samples of a well-characterized oil were spiked with a mixture containing a number of the compounds of interest and analyzed with program samples. These results are presented in Tables C-16 and C-17. Recoveries of semivolatile organics vary significantly by compound; certain compounds, such as hexachlorobenzene, are known to be lost in the preparation procedure.

Program samples submitted for semivolatile organic analysis were spiked with a mixture of deuterated surrogate compounds, d_5-phenol and d_8-naphthalene. It was anticipated that these components would assess the behavior of actual components in individual program samples during the entire preparative and analysis scheme. Surrogate recovery data are presented in Table C-18.

Instrument calibration was verified on each analysis day through the use of an EPA quality control concentrate. The results of these analyses were entered in the instrument log book.

Polychlorinated Biphenyls (PCBs)

Quality control protocols for the determination of PCBs in oil included the use of method blanks and analysis of replicate aliquots of an EPA quality control samples (WP380, concentrate 2, PCBs in Oil). Results from the analysis of the EPA quality control sample are shown in Table C-19.

Instrument calibration was verified daily by analysis of an EPA quality control concentrate. These results were entered in the instrument log book.

TABLE C-1. ANALYSIS OF NBS STANDARD REFERENCE MATERIAL 1634a (TRACE ELEMENTS IN FUEL OIL)

Element	NBS value (μg/g)	Reported (μg/g) 11/30/82	12/21/82	2/11/83	2/11/83	$\overline{X}$	S_x	Relative standard deviation (%)	Average recovery (%)
Calcium	16[a]	15.3	18.3	18.4	17.9	17.5	1.47	8.4	114
Cobalt	0.3[a]	0.222	0.392	0.245	0.341	0.300	0.080	27	100
Chromium	0.7[a]	0.644	0.727	0.667	0.660	0.675	0.036	5.3	96
Iron	31[a]	25.3	27.7	34.1	26.9	28.5	3.86	14	92
Nickel	29 ± 1[b]	23.8	50.6[c]	25.3	23.8	24.3	0.866	3.6	84
Sodium	87 ± 4[b]	73.9	81.8	67.6	73.9	74.3	5.78	7.8	85
Vanadium	56 ± 2[b]	46.9	53.3	53.0	46.9	50.0	3.61	7.2	89
Zinc	2.7 ± 0.2[b]	2.97	3.07	2.01	2.52	2.64	0.485	18	98

[a] NBS supplemental information.

[b] NBS Certified Value.

[c] Rejected as outlier using Dixon Criteria for Testing of Extreme Observation (Quality Assurance Handbook for Air Pollution Measurement Systems, Volume 1, EPA-600/9-76-005, U.S. EPA, Environmental Monitoring and Support Laboratory, Research Triangle Park, NC.)

TABLE C-2. ANALYSIS OF NBS STANDARD REFERENCE MATERIAL 1085 (WEAR METALS IN LUBRICATING OIL)

Element	NBS value (µg/g)	Reported (µg/g)											Relative standard deviation (%)	Average recovery (%)
		3/11/83			3/21/83		3/26/83							
		A	B	C	A	B	A	B	C	D	$\overline{X}$	S_x		
Aluminum	296 ± 4	263	267	267	274	225	284	278	260	257	264	17.0	6.4	89
Chromium	298 ± 5	222	244	249	280	286	292	278	247	260	260	24.6	9.5	87
Copper	295 ± 10	250	259	263	266	263	262	253	239	239	255	10.3	4.0	86
Iron	300 ± 4	254	261	261	274	280	268	252	226	241	257	16.7	6.5	86
Lead	305 ± 8	304	304	304	343	337	298	300	300	301	310	17.1	5.5	102
Magnesium	299 ± 3	278	280	280	300	303	327	327	287	289	297	19.2	6.5	100
Molybdenum	292 ± 11	288	291	292	317	286	286	282	282	284	290	10.8	3.7	99
Nickel	303 ± 7	271	277	276	298	270	298	300	250	259	278	17.8	6.4	92

TABLE C-3. ANALYSIS OF NBS STANDARD REFERENCE MATERIAL 1648 (URBAN PARTICULATE)

	Concentration, μg/g[a]				
		Reported values			Average recovery (%)
Element	NBS value	8/19/82	1/31/83	$\bar{X}$	
Aluminum (%)	3.42 ± 0.11[b]	2.98	1.90	2.44	71
Antimony	45[c]	32.1	34.0	33.1	74
Arsenic	115 ± 10[b]	120	109	115	100
Barium	737[c]	637	Not reported	-	-
Cadmium	75 ± 7[b]	59.1	65.0	62.1	83
Chromium	403 ± 12[b]	116	119	118	29
Copper	609 ± 27[b]	513	552	533	88
Iron (%)	3.91 ± 0.10[b]	3.17	3.19	3.18	81
Lead (%)	0.655 ± 0.008[b]	0.480	0.643	0.562	86
Magnesium (%)	0.8[c]	0.670	0.505	0.588	74
Nickel	82 ± 3[b]	100	76.0	88	107
Sodium (%)	0.425 ± 0.002[b]	0.268	0.219	0.244	57
Titanium (%)	0.40[c]	0.280	0.334	0.307	77
Vanadium	140 ± 3[b]	96.5	102	99.3	71
Zinc (%)	0.476 ± 0.014[b]	0.336	0.581	0.459	96

[a] Except as noted.

[b] NBS Certified Value.

[c] NBS Non-certified Value.

TABLE C-4. DUPLICATE ANALYSES OF GCA 22165 (BC-4, RECYCLING PROCESS)

Element	Reported (μg/g) GCA No. 22165A	GCA No. 22165B	Percent difference
Aluminum	54.5	55.7	2.2
Antimony	2.76	0.23	170
Arsenic	11.5	12.2	5.9
Barium	153	154	0.65
Beryllium	0.219	0.217	0.92
Boron	22.2	39.3	56
Cadmium	1.31	1.93	38
Calcium	2470	2450	0.81
Chromium	18.8	20.1	6.7
Cobalt	2.21	2.22	0.45
Copper	47.3	49.2	3.9
Iron	788	800	1.5
Lead	1530	1510	1.3
Magnesium	726	729	0.41
Manganese	37.9	38.8	2.3
Molybdenum	6.61	6.75	2.1
Nickel	13.0	12.8	1.6
Sodium	578	576	0.35
Strontium	4.44	4.52	1.8
Tin	155	162	4.4
Titanium	4.84	6.34	27
Vanadium	12.3	12.6	2.4
Zinc	1250	1240	0.80

TABLE C-5. TRIPLICATE ANALYSES OF GCA 27106 (BO-SS-1, FEED STOCK)

Element	Reported ($\mu g/g$)					Relative standard deviation (%)
	27106A	27106B	27106C	$\overline{X}$	S_x	
Aluminum	644	636	612	631	16.7	2.6
Antimony	1.1	0.27	0.67	0.68	0.42	62
Arsenic	4.5	1.1	2.1	2.6	1.7	65
Barium	83.8	78.0	78.6	80.1	3.19	4.0
Beryllium	0.37	0.26	0.44	0.36	0.091	25
Boron	11.0	10.4	11.5	11.0	0.55	5.0
Cadmium	0.99	1.12	1.14	1.08	0.081	7.5
Calcium	1030	1030	1010	1020	11.5	1.1
Chromium	18.4	17.2	17.5	17.7	0.62	3.5
Cobalt	1.23	1.14	1.31	1.23	0.085	6.9
Copper	126	117	115	119	5.86	4.9
Iron	1300	1520	1520	1450	130	9.0
Lead	347	386	377	370	20.4	5.5
Magnesium	238	247	236	240	5.86	2.4
Manganese	27.5	26.4	26.5	26.8	0.61	2.3
Molybdenum	12.7	12.7	12.2	12.5	0.29	2.3
Nickel	25.7[a]	17.1	17.4	17.3	-	-
Sodium	449	446	459	451	6.81	1.5
Strontium	3.40	3.24	3.24	3.29	0.092	2.8
Tin	16.6	16.0	7.77[a]	16.3	-	-
Titanium	20.8	21.6	21.0	21.1	0.42	2.0
Vanadium	7.5	6.5	7.2	7.1	0.51	7.2
Zinc	343	390	367	367	23.5	6.4

[a] Rejected as outlier using Dixon Criteria for Testing of Extreme Observation.

TABLE C-6. ANALYSIS OF NBS STANDARD REFERENCE MATERIAL 1619 (SULFUR IN RESIDUAL FUEL OIL)

Sample	NBS value (sulfur wt %)	Date	Reported (sulfur wt %)
NBS SRM 1619	0.719 ± 0.007	07/15/82	0.65
		07/15/82	0.82
		07/15/82	0.65
		07/29/82	0.85
		10/18/82	0.72
		10/18/82	0.86
		11/01/82	0.88
		11/16/82	0.68
		02/08/83	0.66
		02/10/83	0.64

Average ($\bar{X}$)	0.74% sulfur
Standard deviation (S_x)	0.099
Relative standard deviation	13%
Average recovery	103%

TABLE C-7. ANALYSIS OF REPLICATE SAMPLES FOR SULFUR

GCA Number	Sample identification	Reported Sulfur, wt %		Percent difference
		A	B	
22155	DH-1 recycling process	0.70	0.65	7.4
27106	Feed stock BO-SS-1	0.69	0.65	6.0
27266	WO-BS-21 base stock oil	0.66	0.66	0
27330	WO-BS-22 base stock oil	0.64	0.61	4.8

TABLE C-8. ANALYSIS OF SPIKED MINERAL OIL

Sample identification	Total chlorine (μg/g)		Percent recovery
	Reported	Expected	
QC-A	231	229	101
QC-B	219	229	96

TABLE C-9. TETRAGLYME SPIKES (JUNE 1982)

	Concentration (μg/l)[a]				
		Observed			Average recovery (%)
Component	Expected	QC 858	QC 859	$\bar{X}$	
1,1-dichloroethane	90	91	50	71	78
Chloroform	108	80	50	70	65
1,1,1-trichloroethane	100	130	83	110	110
Carbon Tetrachloride	100	88	43	66	66
Bromodichloromethane	120	89	110	100	83
Trichloroethylene	100	85	110	98	98
Bromoform	100	89	81	85	85
Tetrachloroethylene	100	59	53	56	56

[a] Reported in ppb (μg/l) of tetraglyme.

TABLE C-10. TETRAGLYME SPIKES (JULY 1982)

	Concentration (µg/l)[a]					
		Observed				Average recovery (%)
Component	Expected	7/1/82	7/6/82	7/30/82	$\bar{X}$	
1,1-dichloroethane	65	78	74	54	69	106
Chloroform	78	85	79	110	91	117
1,1,1-trichloroethane	73	95	85	86	89	121
Carbon Tetrachloride	73	82	78	84	81	111
Bromodichloromethane	94	110	100	82	97	103
Trichloroethylene	73	84	75	100	86	118
Bromoform	74	78	76	76	77	104
Tetrachloroethylene	74	75	65	91	77	104

[a] Reported in ppb (µg/l) of tetraglyme.

TABLE C-11. TETRAGLYME SPIKES (JANUARY 1983)

Component	Concentration (mg/kg)						% Recovery
	QC 298		QC 299		QC 300		
	Reported	Expected	Reported	Expected	Reported	Expected	
Chloroform	3500	4200	2800	3100	3600	3600	91
Trichloroethylene	3300	3200	2300	2400	3100	2800	100
Tetrachloroethylene	4900	4200	3200	3100	4200	3600	110
Toluene	3900	4500	2800	3400	3100	3900	88

TABLE C-12. REPLICATE ANALYSES OF GCA 19765 (WO-BS-13, WASTE OIL)

Component	Reported (mg/kg)				Relative standard deviation (%)
	19765A	19765B	19765C	$\bar{X}$	
Benzene	Trace	Trace	Trace	-	-
Toluene	1300	1900	1700	1600	19
Ethylbenzene	180	270	260	240	20

TABLE C-13. REPLICATE ANALYSES OF GCA 22033 (W-BSB-1, FUEL OIL)

Component	Concentration (mg/kg)		
	GCA 22033A	GCA 22033B	$\bar{X}$
Tetrachloroethylene	17	22	20
Toluene	230	250	240
Ethylbenzene	240	280	260

TABLE C-14. REPLICATE ANALYSES OF GCA 22034 (W-BS-1, WASTE OIL)

Component	Concentration (mg/kg)		
	GCA 22034A	GCA 22034B	$\bar{X}$
Chloroform	25	ND	-
1,2-Dichloroethane	190	200	200
1,1,1-Trichloroethane	1700	1500	1600
Trichloroethylene	55	51	53
Benzene	160	160	160
Tetrachloroethylene	200	170	190
Toluene	>5100	>4400	-
Ethylbenzene	1300	1000	1200

TABLE C-15. ANALYSIS OF SRM 1580 (ORGANICS IN SHALE OIL)

Component	NBS value (μg/g)	Reported (μg/g) QC 891a	QC 891b	$\overline{X}$	Average percent recovery
Phenol	407	250	250	250	61
Pyrene	104	51	61	56	54
Benzo(a)pyrene	21.5	20	20	20	93
Fluoranthene	54	17	19	18	33
Dimethylphenol	175	320	180	250	140

TABLE C-16. ANALYSIS OF SPIKED OIL SAMPLES FOR SEMIVOLATILE ORGANICS

	Concentration (mg/kg)				
	QC 342		QC 351		
Compound	Expected	Reported	Expected	Reported	Average Recovery
2-Chlorophenol	320	140	360	140	41
Nitrobenzene	370	260	420	230	63
2-Chloronaphthalene	370	250	420	210	59
2,4,6-Trichlorophenol	280	100	320	320	68
Acenaphthene	400	200	460	220	49
Hexachlorobenzene	420	2.8	480	6.6	1
Butylbenzylphthalate	330	78	380	120	28
Pyrene	410	250	470	170	49
Benz(a)anthracene	410	292	470	250	62
PCBs	54	54	18	19	106

TABLE C-17. ANALYSIS OF SPIKED OIL FOR SEMIVOLATILE ORGANICS (QC694)

Component	μg Spiked	μg Detected	Recovery (%)
Bis-(2-chloroethyl)ether	550	560	100
1,3-Dichlorobenzene	540	220	41
N-nitrosodipropylamine	600	350	58
Bis-(2-chloroisopropyl)ether	370	190	50
Isophorone	550	460	84
Bis-(2-chloroethoxy)methane	700	650	93
Hexachlorobutadiene	640	---	--
Hexachlorocyclopentadiene	520	---	--
Acenaphthylene	460	510	110
2,6-dinitrotoluene	430	---	--
2,4-dinitrotoluene	520	---	--
N-nitrosodiphenylamine	440	460	110
4-chlorophenyl phenyl ether	480	340	71
1,2-diphenyl hydrazine	560	450	81
4-bromophenylphenylether	340	250	75
Phenanthrene	420	560	130
Benzofluoranthene	690	490	71

TABLE C-18. SURROGATE RECOVERY DATA

GCA Control No.	Sample identification	Surrogate recoveries (%)	
		d_5-phenol	d_8-naphthalene
18919	Waste oil WO-BS-5	8.6	110
18921	Waste oil WO-BS-7	70	86
18922	Waste oil WO-BS-8	52	70
19500	Waste oil WO-BS-9	100	59
19501	Waste oil WO-BS-10	82	56
19763	Waste oil WO-BS-11	70	49
19764	Waste oil WO-BS-12	70	51
19765	Waste oil WO-BS-13	3.6	60
19941	Waste oil WO-BS-14	ND	60
22174	Recycling process RO-1	59	66
22175	Recycling process RO-2	63	42
22176	Recycling process RO-3	56	54
22206	Recycling process SS-1	85	46
QC694	Laboratory control spike	88	120
QC718	Laboratory control spike	58	ND
QC722	Laboratory control spike	40	ND

ND = Not detected.

TABLE C-19. ANALYSIS OF EPA QUALITY CONTROL CONCENTRATE FOR PCBs IN OIL (WP380, NO. 2)

Aroclor	EPA value (mg/kg)	Reported (mg/kg)			$\overline{X}$	Average recovery (%)	Relative standard deviation (%)
		QC337	QC338	QC900			
1260	54	45	43	54	47	87	13