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AP42 Section: 11.1

Reference Number: 363

Title: P. Kariher, M. Tufts, and L. Hamel, Evaluation Of VOC Emissions From Heated Roofing Asphalt,

EPA 600/2-91-061,

U. S. Environmental Protection Agency, Research Triangle Park, NC,

November 1991

L-5 5-3

United States
Environmental Protection
Agency

Control Technology Center

EPA-600/2-91-061 November 1991

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EVALUATION OF VOC EMISSIONS FROM HEATED ROOFING ASPHALT

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EPA-600/2-91-061
November 1991

EVALUATION OF VOC EMISSIONS FROM HEATED ROOFING ASPHALT

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ABSTRACT

A short-term, in-house project to characterize emissions from a simulated asphalt roofing kettle was performed at EPA/AEERL. Hot asphalt surfacing and resurfacing has been identified as a possible significant source of volatile organic compound (VOC) emissions that may affect human health and contribute to the ozone non-attainment problem.

The purpose of the study was to collect, identify, and semi-quantitate as many of the compounds as possible that are discharged during the open heating of roofing asphalt and relate them to the amount volatilized into the air.

Types 1, 2, and 3 mopping grade asphalts were chosen for this study. They constitute more than 90 percent of roofing asphalt used. Samples of each type of asphalt were placed in a simulated roofing kettle, heated to predetermined temperatures, and sampled for volatile and semi-volatile organic emissions. Compounds identified during this study were alkanes, aromatics, a ketone, and an aldehyde.

This work was done at the request of the Control Technology Center (CTC) steering committee to provide information to state and local agencies for use in responding to public concerns.

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ACKNOWLEDGEMENTS

The authors would like to recognize EPA/AEERL's Ray Steiber for his expertise in identifying compounds. The authors would like to thank Ken Krebs of Acurex for his analytical support and Ray Thomas of Acurex for his sampling support.

PREFACE

The Control Technology Center (CTC) was established by EPA's Office of Research and Development (ORD) and Office of Air Quality Planning and Standards (OAQPS) to provide technical assistance to state and local air pollution control agencies. Three levels of assistance can be accessed through the CTC. First, a CTC HOTLINE has been established to provide telephone assistance on matters relating to air pollution control technology. Second, more in-depth engineering assistance can be provided when appropriate. Third, the CTC can provide technical guidance through publication of technical guidance documents, development of personal computer software, and presentation of workshops on control technology matters.

The engineering assistance projects, such as this one, focus on topics of national or regional interest that are identified through contact with state and local agencies.

Metric to Nonmetric Conversions

Readers more familiar with nonmetric units may use the following factors to convert to that system.

Metric	Times	Yields Nonmetric
°C	1.8T + 32	°F
m^3	35.336	ft^3
mmHg	0.03937	in. Hg
kg	2.2026	lb
m^3/min	35.714	cfm

SECTION 1

INTRODUCTION

The Control Technology Center (CTC) and its Air Research Information Service Center (AIR RISC) information support system have received numerous calls on the health effects of asphalt roofing fumes. In response to these calls, the CTC steering committee initiated a parametric study of the emissions profile from asphalt roofing techniques.

Asphalt is produced near the end of the fractional distillation of crude oil. Roofing asphalt is produced by blowing air through the asphalt flux at different temperatures to derive the adhesives used for roof surfacing or resurfacing. Types 1, 2, and 3 were chosen for this study. They cover the roof range levels from flat to a 25 percent slope and constitute more than 90 percent of roofing asphalt used for mopping operations.[1]

The asphalt can be delivered to the site in two ways. It is either heated and transported in a tanker truck or heated in a container (kettle) on site. When the heated kettle method is used, the asphalt is purchased in paper-covered sections of approximately 45-kg* blocks. The blocks are chopped into sections and added to the kettle as needed.

Several emissions sources exist from the on site asphalt roofing process, but the heating kettle has been identified as a major point of emissions. A simulated heated roofing kettle was constructed and placed in a building (burn hut) used for similar projects. In-house testing was performed to

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* A conversion table has been provided for convenience on page viii.

characterize emissions from the simulated kettle. The data from this project can then be used to estimate the amount of organic compound volatilized into the air.

Previous work done by AEERL in this area included a cursory examination of emissions during reroofing of the Environmental Research Center, RTP, NC, in 1989. Although minimal compound identification was performed, the analytes detected included alkanes, alkenes, aromatics, alcohols, aldehydes, and a ketone.[2]

Asphalt roofing operations are a source of organic vapors that could affect human health both directly and indirectly. This study will provide information to state and local agencies for use in responding to public concerns.

SECTION 2

PROJECT DESCRIPTION

2.1 EXPERIMENTAL APPROACH

Asphalt roofing cement is used as a sealing medium for many buildings with relatively level roofs. The method of application of this material is to use a torch to heat the side of the kettle, until it reaches a viscosity that allows it to be mopped onto the roof surface. This viscosity is defined as the equiviscous temperature (EVT). The normal procedure is to heat the asphalt to temperatures considerably higher than needed to ensure EVT after the asphalt is transported to the point of application.[3]

The purpose of this study was to collect, identify, and estimate the quantities of as many of the compounds as possible that were discharged during the small-scale, open heating of roofing asphalt and relate them to the amount of roofing asphalt volatilized. A predetermined amount of one of the grades of roofing asphalt was placed in the heating kettle and heated with a torch applied to the bottom of the kettle. The first temperature condition was defined by the melting of the asphalt. At this temperature, the asphalt was not liquid enough to be applied with a mop, but was no longer a solid block. The temperature was recorded and heating was regulated to maintain a constant temperature in the asphalt. Samples were taken to determine the emissions at this condition. The second temperature condition was the EVT condition where the asphalt was the right consistency to mop onto a surface. The temperature was monitored and stabilized at this condition, and samples were taken. The third temperature was approximately 66 °C higher than the second condition. Heating the asphalt to this temperature is a common practice prior to transporting the asphalt to the application site. The

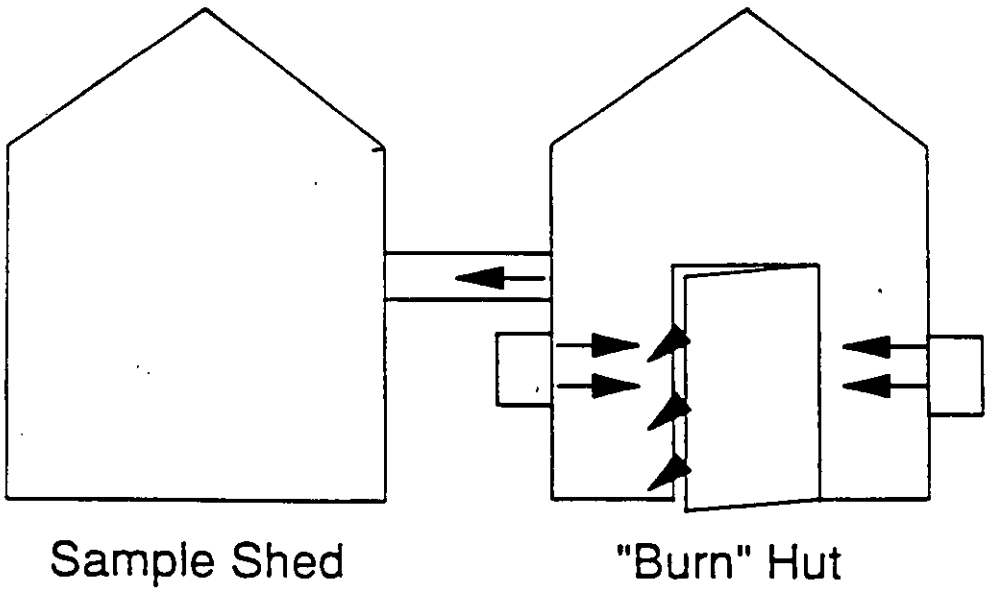
same heating procedure was used for all three asphalt types. The temperatures inside the burn hut and sample transport duct also were monitored periodically. The asphalt block was replaced after each test after a significant weight loss was recorded. A baseline test using the torch, but no asphalt, was to determine background compounds.

For each test, a selected representative roofing asphalt was heated in a controlled outbuilding designed for the simulation of the open burning or heating of similar products. To perform each test, a stainless steel bowl was filled with about 7 kg of asphalt, and the specific weight of the asphalt was measured. After the asphalt was melted, the diameter of the bowl was measured at the asphalt line, and sampling began. Volatile organic samples were collected with volatile organic sampling train (VOST) tubes, and the semi-volatile organics and particulates were collected with XAD-2 and Pallflex 142-mm filters. After each test was performed, the final weight of the asphalt was recorded. The volatile organic samples collected were analyzed by an adsorption and thermal desorption gas chromatograph/mass selective detector(GC/MSD) system. The semi-volatile organics were analyzed using GC/MSD for compound identification and a gas chromatograph/flame ionization detector (GC/FID) for compound quantitation. A total chromatographable organics (TCO) analysis provided the total organics in the boiling point range of 100-300 °C. A gravimetric (GRAV) analysis indicated the amount of organic material possessing boiling points greater than 300 °C. Both the VOST and TCO samples were analyzed by GC/MSD to provide compound class and compound specific identification. A representative portion of the identified compounds were semi-quantitated. The semi-quantitative information was coupled with collected sample volumes and material mass displacement to estimate gaseous emission concentrations and mass emissions based on total material volatilized.

2.2 EXPERIMENTAL APPARATUS

2.2.1 Burn Hut

The burn hut is an 2.4-m x 2.4-m x 2.4-m outbuilding modified for small-scale combustion experiments (Figure 1). The building has a cooled, dilution air handling system capable of delivering nominally 34.0 m^3/min. A deflector shield was located 1.2 m over the pit to protect the ceiling and



(Arrows indicate air flow)

Figure 1. Sampling buildings.

enhance ambient mixing. The sample duct, a 20.3-cm pipe, was located to the side of the deflector shield (Figure 2). Since the sample air was mixed thoroughly by the deflector shield and the air conditioner flow, the sample duct transported a representative portion (Figure 2) of the gaseous, particulate-containing sample to the sampling shed located adjacent to the burn hut (Figure 1). The portion of the gas transported through the sample duct was assumed to be representative of all the gas in the hut as was proven in previous experiments performed in the same shed.[4] The unheated duct was insulated when it exited the burn hut to minimize heat loss and condensation of organics. The door and window were open several inches to allow ventilation of the flow from the air conditioner and the mixed air. This allowed the sample duct to work at a slight negative pressure rather than at the pressure from the air conditioners that were supplying sample gas.

2.2.2 Sample Shed

The sample shed contained the majority of the associated sampling equipment: the volatile organic sampling train (VOST) system, the semi-volatile organics/particulate sample collection systems, and the particulate removal system.

All gaseous samples were extracted from a sampling manifold within the duct. The manifold consisted of 9.5-mm stainless steel probes positioned in the sample transport duct so the probe orifice faced the direction of sample flow. All samples were obtained at the same location (Figure 3). The sample stream was pulled from the burn hut into the sample shed under slight negative pressure by an induced draft (ID) fan located downstream of the sample manifold.

Volatile organics were collected using the Nutech Model 280 VOST system (Figure 4). For this application, the heated probe was not used. Other changes included the absence of the glass-lined probe. The connection from the sample manifold to the sampling train was made with an insulated section of 6.4-mm Teflon tubing.

Semi-volatile organics and particulate were collected using a sample system modified for use in this study. A 9.5-mm stainless steel tube was connected from the manifold to a particulate filter assembly. Particulate was collected on a 142-mm, Teflon-coated, glass fiber filter located in the filter

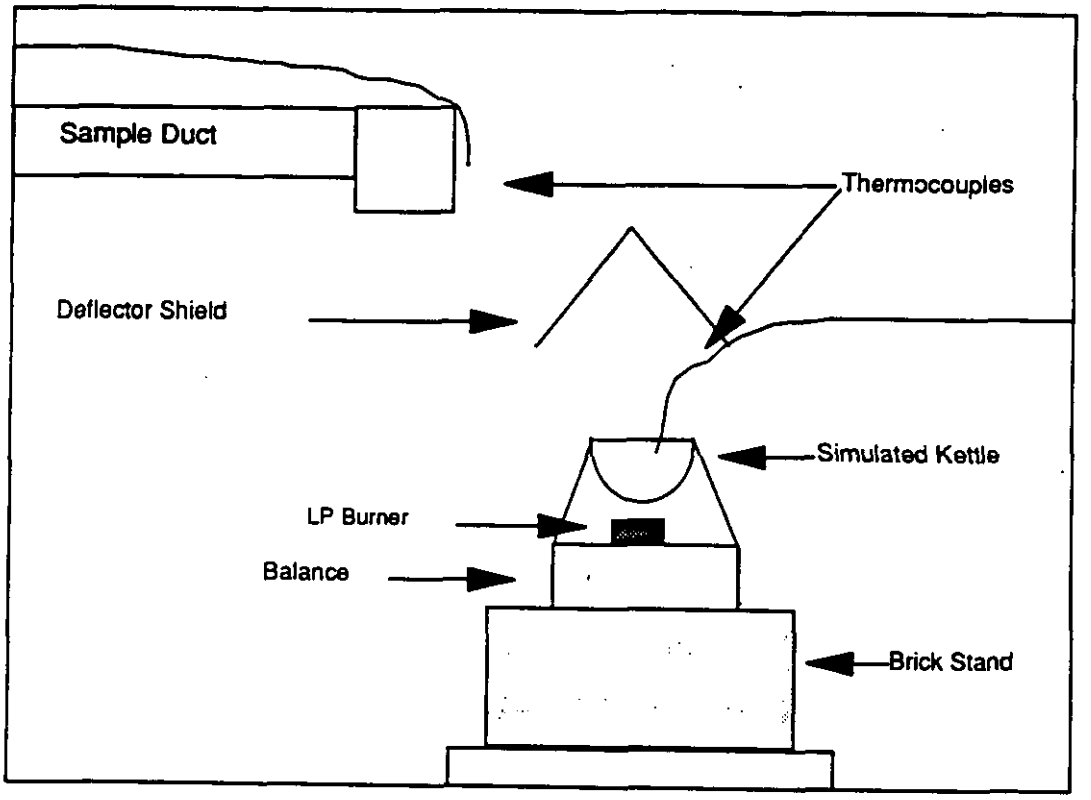


Figure 2. Heating Apparatus in "Burn Hut"

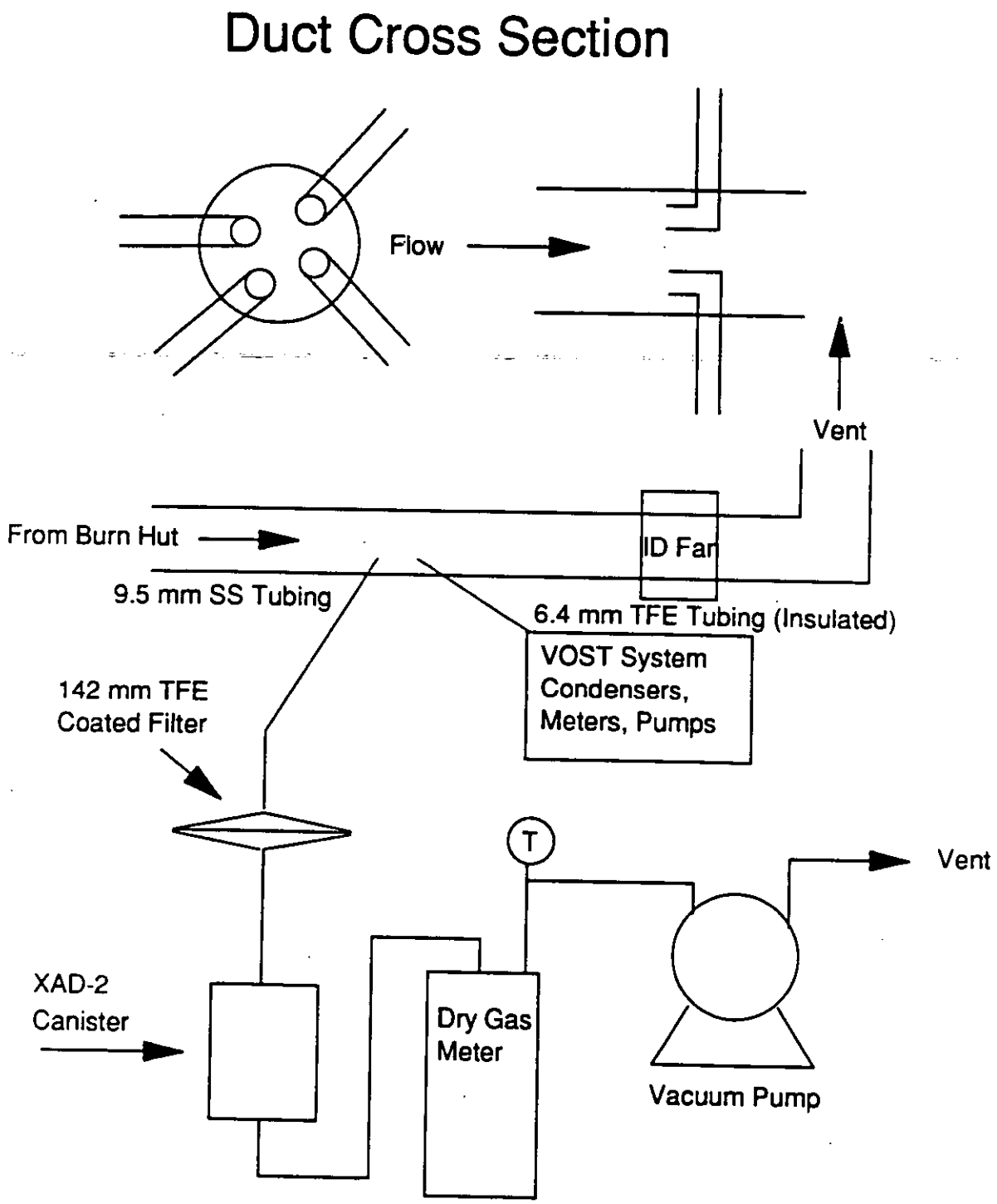


Figure 3. Diagram of sampling system used.

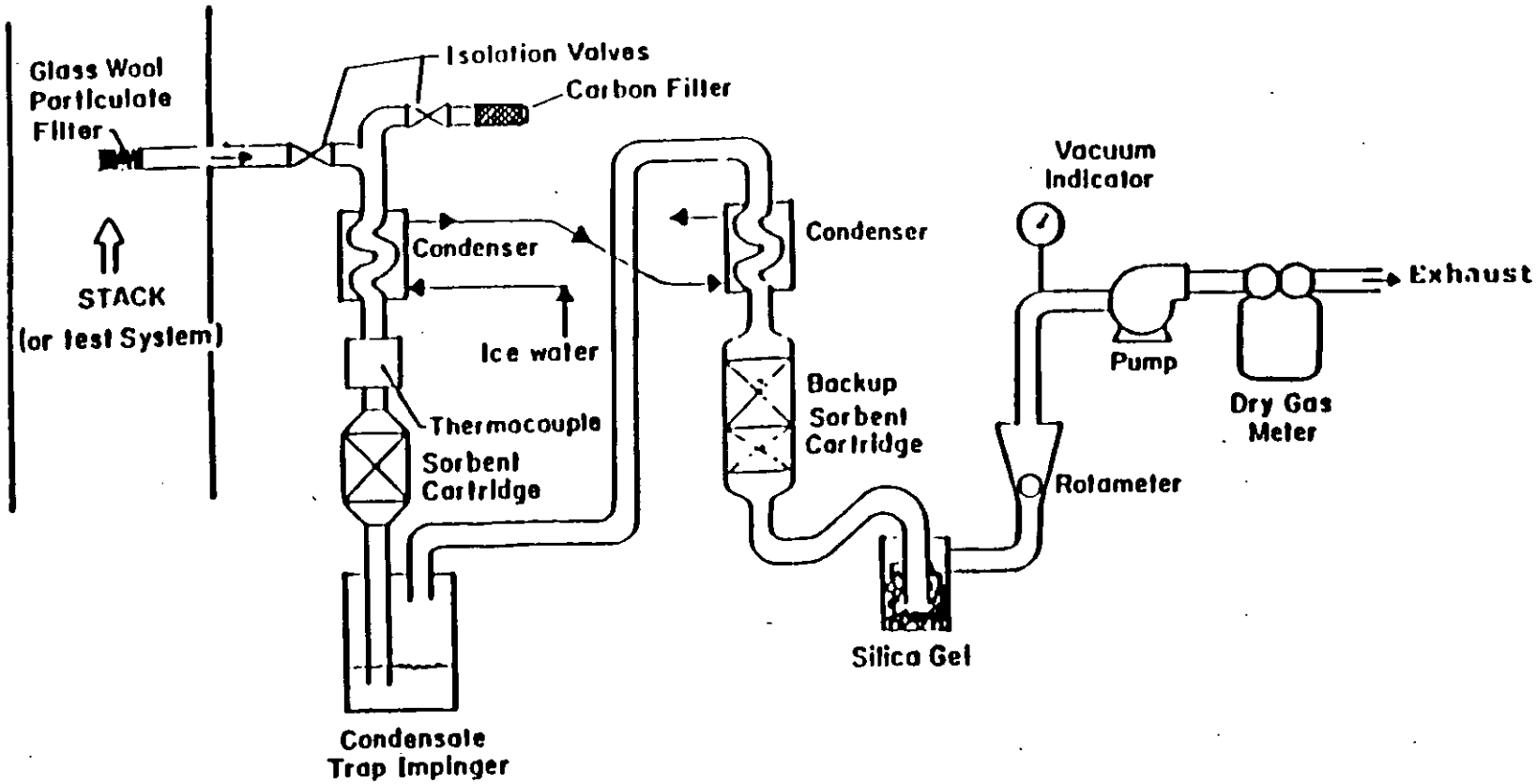


Figure 4. Schematic of volatile organic sampling train.

housing. This filter housing was connected to a XAD-2 canister that held roughly 150 g of the organic sorbent material. The exit of the canister was connected to a pump and metering system.

2.3 EXPERIMENTAL METHODS AND PROCEDURES

2.3.1 Simulation of Open Air Asphalt Kettle Heating

Asphalt was obtained from local sources. Asphalt types 1 and 3 were supplied by Morton J.R. Company of Raleigh, NC. Type 2 asphalt was obtained from Bob Lyerly of Owens-Corning Fiberglass, Morehead City, NC. All three asphalt types were made by the Trumbull Asphalt Division of Owens-Corning Fiberglass Corporation. The asphalt was supplied in 45-kg cardboard or tin containers and required chopping before the asphalt could be put into the kettle. A known amount of asphalt was placed in the kettle and heated until melted but unmoppable. This temperature was determined to be unmoppable because the asphalt appeared to have a high viscosity but had just lost the solid appearance. This temperature was maintained and recorded as the first condition. The second temperature condition was the EVT condition where the asphalt was the right consistency to mop onto a surface. At this temperature the asphalt easily flowed and had a much lower viscosity than the first melting temperature. The third temperature was approximately 66 °C higher than the second condition. For each condition, once the desired temperature was obtained, the asphalt was maintained at that temperature and the sampling was performed. The conditions are listed in Table 15.

2.3.2 Volatile Organics Collection

Volatile organics were collected using a modified VOST technique. Organics were collected in triplicate on pairs of Tenax-GC-containing glass tubes. The VOST system was operated as described in EPA-600/8-84-007.[5] These tests were performed using a short section of 6.4-mm Teflon tubing to transport the gas sample from the sample duct to the VOST train. Sample flow rates and total volumes were determined during the shakedown tests. These tests included heating a sample of asphalt to determine asphalt sample sizes and sample volumes. A sample flow rate of 0.5 L/min for 10 min was determined to be optimum for the VOST tubes. These shakedown test samples were analyzed to prevent instrument overload on the GC/MSD.

The Tenax tubes were conditioned at 230 °C for at least 12 hr prior to use. At least 50 percent of the pairs of tubes were quality-control-checked (QC'd). The tubes were checked for organic contamination by GC/FID with a QC rejection of 100 ng total organics per set (based on system response to toluene) and an individual peak rejection of 50 ng. Following conditioning and QC, the tubes were sealed in pairs in a Teflon bag. The conditioned tubes were refrigerated at 4 °C until use. Following use, the tubes were returned to the Teflon bag, resealed and placed into a cryo-freezer until they were analyzed. The tubes were stored in two separate freezers to prevent contamination of conditioned tubes by the sampled tubes. All sampling information was collected on standardized data collection sheets (Figures 5 & 6).

The VOST collected samples were analyzed using an adsorption and thermal desorption GC/MSD system. The analytical method used in this study is found in EPA-600/8-84-007[5]. Our goal was to identify and semi-quantitate unknown compounds.

Collected VOST samples were analyzed in pairs. Three pairs were collected for each sample. The samples were desorbed in a clamshell heater at 190 °C for 10 min. Helium carried the vaporized analytes onto a cryogenically cooled trap at -150 °C. This trap focuses the sample prior to injection. The trap was rapidly heated to 225 °C with the sample directed onto a 30-m x 0.32-mm I.D. DB-624 capillary column. The oven temperature program was initially operated at 20 °C for 5 min, then heated at 3 °C/min until reaching 150 °C. The oven was then ramped at 5 °C/min until reaching 260 °C at which it was held for 15 min. All detector temperatures on the GC were held at 260 °C.

Simultaneous detection by the MSD and FID was attempted by using a splitter apparatus installed between the column exit and detectors. It was determined that the FID was unusable because the flame was extinguished on most of the samples. The MSD acquired sufficient spectral data such that each chromatographic peak was sampled at least 5 times over a 45-420 atomic mass unit (AMU) range. The resulting chromatogram was digitally stored for data interpretation. The MSD was calibrated for mass linearity using perfluorotributylamine (PFTBA). Several criteria were used to assist

AEERL/OCB SAMPLE LOG

Samples transferred by _____ Date _____

Signature of transferor _____

Samples received by _____ Date _____

Signature of transferee _____

Project _____ Analysis required _____

Sample ID	Sample contents/description	Date Collected	Date Prepped

For further information contact _____ at ( ) _____-_____

Figure 5. AEERL/OCB sample log.

Plant _____

Date _____

Location _____

Operator _____

Field Blank I.D.: Tenax _____

Tenax/Charcoal _____

Stack No. _____

Probe No. _____

VOST No. _____

Rotameter No. _____

Dry Gas Meter No. _____

Pair No.[a]	Leak Check	Cartridge I.D. Tenax	Cartridge I.D. Tenax/Charcoal	Rotameter Reading (l/min)	Time Initial	Time Final	Sampling Duration (min)	Probe Temp. (°C)	Barometric Pressure (in of Hg)	Condenser Outlet Temp. (°C)	(°C) Meter Temp. (Outlet)	(liters) Dry Gas Meter Initial	(liters) Dry Gas Meter Final	Gas Sample Volume (liters)	Comments

Condensate Samples:

Run No.	Sample I.D.	Comments

NOTES: [a] Refers to sample collection on one pair of Tenax/charcoal traps.

Figure 6. VOST field data sheet.

in compound identification. A mass spectral library (National Institute of Standards and Technology*) matching program was used extensively. The program was written so that, for each integrated peak, spectra were obtained both at the point of maximum intensity (peak top) and at the peak start (baseline). This baseline or background spectrum was subtracted from the peak spectra. This background-subtracted spectrum was compared to spectra in the library. The top five matches were presented and compared. An expert experienced in mass spectral interpretation evaluated the matches. In addition, several samples were prepared containing an alkane mix. This mix was analyzed by injection onto the adsorption media and then thermally desorbed. The elution order was used to generate a retention index that aided in compound identification and individual peak referencing. Standards were prepared for eight of the tentatively identified compounds to confirm identification and provide semi-quantitation.

Quantitation of volatile organics was performed from the MSD integration data. Response factors were calculated by dividing the known mass of a single compound by the area counts assigned to that compound from a 5-point calibration standard. Calibration checks were performed daily. The compounds in the 5-point calibration standard included benzene, toluene, xylene, decane, dodecane, tetradecane, and heptadecane. Because of the large number of compounds, quantitation based on individual standard calibrations was not possible. To accommodate this problem, calculated response factors from the standards were used for the compounds that were identified. A trend was seen in the response factors for the standards; the response factors were seen to increase as the retention time increased. This trend was used to assign response factors to those compounds that were not found in the standard calibration. Following analysis and compound identification, several standards were prepared to represent the alkane and aromatic compound classes. The response factors were calculated from the standard mix. The response factors were used to quantitate identified compounds in each compound class. Prior to sampling, the Tenax tube pairs were spiked with a known quantity of

* Formerly the National Bureau of Standards.

deuterated benzene (D6), an internal standard. Five mL of 48.8-ng/mL deuterated benzene in air was injected onto the pair of Tenax tubes. Recovery of the deuterated benzene from the samples varied considerably. The values ranged from 39 to 174 percent for the deuterated benzene.

2.3.3 Semi-volatile Organics and Particulate Collection

The sampling system used for the collection of semi-volatile organics and particulate was a modified system specifically fabricated for use on this project (Figure 3). Overall, the system was very similar in nature to that of the Source Assessment Sampling System (SASS) equipment used for stack sampling. A short length of 0.95-cm O.D. stainless steel tubing was used to connect the sample manifold to the filter assembly. The filter assembly held a 142-mm diameter, Teflon-coated, glass fiber filter. The filter assembly was connected to an XAD-2-filled stainless steel canister. This canister contained roughly 150 g of the organic sorbent material. A drying tube containing silica gel was connected after the canister for moisture removal before being attached to the dry gas meter. The dry gas meter was connected to the canister to measure total volume sampled. A sample pump was connected to the end of the dry gas meter and vented outside the shed.

The system was operated at a nominal sample rate of 0.06 m^3/min for 3 hr. The system was leak-checked up to the exit of the filter assembly before and after each sample period. All sampling information was recorded on standardized data collection sheets (Figure 7). Upon completion of the sample period, the train was dismantled and brought to the laboratory for sample retrieval.

The XAD-2 was packed in the canisters, capped, sealed in Teflon bags, and refrigerated at 4 °C until used. After use, the canisters were returned to the Teflon bag, resealed, and refrigerated in a cryo-freezer at -80 °C until extracted. The particulate filters were desiccated, tared, and stored in labeled aluminum foil envelopes until used. Following sampling, the filters were placed back in the foil envelopes with the loaded side facing upward. The filters were desiccated (with the foil open), weighed and stored in a desiccator until extracted.

The particulate filter and XAD-2 samples from each sample were extracted separately. Following sampling, the filters were extracted with methylene chloride in an ultrasonic bath. The XAD-2

SEMI-VOLATILE SAMPLING WORKSHEET

Run # _____

Date _____ Conditions _____

Tamb _____ (°C/°F) Pbar _____ (mm Hg/in Hg)

XAD-2 Run Canister # _____ XAD-2 Field Blank # _____

DGM I.D. # _____ Filter Field Blank # _____

Correction Factor _____

Filter I.D.	Start Time	Stop Time	Start DGM	Stop DGM	Total Time (min)	Total DGM (ft^3)
DGM Temp °C/°F	Time	Orifice delta P		Totals		
					Corrected ft^3	
					ft^3/min	
					Std ft^3/min	
					Std m^3/min	

Comments:

Figure 7. Semi-volatile sampling worksheet

canisters were extracted with methylene chloride by pump through elution. The particulate filter and XAD-2 extracts from the same samples were combined. The combined extracts were concentrated and filtered with a 0.45-mm filter and brought to a stock volume of 10 mL. Crystals were found in the concentrated samples after being stored in the cryo-freezer (-80 °C). The crystals had the appearance of frozen water. A 5-mL aliquot of each sample was passed through a bed of Na_2SO_4 to remove any residual water. The bed was then rinsed with methylene chloride. The rinsate was then concentrated to 5 mL. Crystallization still occurred in the samples when returned to the cryo-freezer, but the crystals appeared to be organic in nature.

A portion of sample solution was analyzed for TCO using a GC/FID analytical method. The TCO analysis determines the amount of organic material with boiling points between 100 and 300 °C based on the average system response to an alkane standard mix. The analysis was conducted using a reduced temperature ramp from the specified temperature program (5 °C/min as opposed to 20 °C/min) to obtain the greater peak separation needed for individual compound quantitation.

Compounds possessing boiling points greater than 300 °C were quantified using GRAV analysis. This procedure gravimetrically measures the organic material remaining after an aliquot of the liquid sample is allowed to evaporate in an aluminum pan.

Compound identification was performed by GC/MSD. The conditions were almost identical to those used in the TCO analysis. The compounds were separated using a 0.32-mm I.D. x 30-m DB-5 column with 5 °C/min temperature ramping program. This column was the same length used for the TCO analysis. Compounds were identified using a spectral library matching program similar to that used for volatile organics identification. These compound matches were examined and verified by an expert mass spectroscopist. Again, an alkane standard mix for establishing retention indices information was used to aid compound identification.

Quantitation of identified compounds was based on response factors calculated from a standard mix. The response factors were calculated from a 5-point calibration. Calibration checks were run before and after the samples were analyzed. The compounds in these calibration standards included

heptane, decane, dodecane, tetradecane, and heptadecane. Compounds were quantitated by using response factors from the standard mix and assigning the values to compounds with similar retention indices or the specific compound. The data from the standard mix combined with identification data from the MSD provided retention indices for the sample compounds. The retention indices were established from the alkane standards and were used to mark elution orders both from the MSD and FID runs, allowing cross-referencing of quantitative reports.

SECTION 3

DATA, RESULTS, AND DISCUSSION

3.1 VOLATILE ORGANIC EMISSION DATA

Problems keeping the FID flame lit resulted in the loss of data for several VOST tubes. Because the FID and the MSD acquired data simultaneously, it was possible to use only the MSD integration data to quantify. Most of the compounds from the VOST tubes were identified by the GC/MSD instrument. The majority of these compounds were alkanes, aromatics, and aldehydes (Table 1). This was expected because of the petroleum-type chemicals used in the manufacture of asphalt. The alkanes ranged from heptane to heptadecane and included all the straight chain alkanes between these two ranges. The aromatic compounds found were benzene, toluene, xylene, and substituted naphthalenes. The only aldehyde found was benzaldehyde, and a ketone (1-phenyl-ethanone), both of which may be contaminants from the oxidation of Tenax. Large concentrations of dichloromethane were found in the samples and may be attributed to the XAD-2 solvent wash. Because the outlet of the XAD-2 canister was flowing into the sampling shed, the methylene chloride may have contaminated the Tenax tubes during exchanging. Because of the large variations in recovery for the dueterated benzene, the sample concentrations were not scaled. Table 2 presents the data for the average deuterated benzene areas for the three pairs of VOST tubes collected for each condition.

The data tables are arranged so each asphalt type may be examined at each temperature. In each category, the average gaseous concentration, estimated emissions, and emissions per area of the kettle are presented (Tables 3-11). Sampling data also are available in Table 12.

TABLE 1. COMPOUNDS IDENTIFIED BY GC/MS FROM VOST RUNS

Compound Identified	Formula
Methane, dichloro-	CH_2Cl_2
Benzene	C_6H_6
Heptane	C_7H_{16}
Benzene, methyl-	C_7H_8
Octane	C_8H_{18}
Benzene, dimethyl-	C_8H_{10}
Nonane	C_9H_{20}
Decane	$C_{10}H_{22}$
Benzene, trimethyl-	C_9H_{12}
Benzaldehyde	C_7H_6O
Undecane	$C_{11}H_{24}$
Benzene, tetramethyl-	$C_{10}H_{14}$
Ethanone, 1-phenyl-	C_8H_8O
Dodecane	$C_{12}H_{26}$
Undecane, dimethyl-	$C_{13}H_{28}$
Naphthalene	$C_{10}H_8$
Tridecane	$C_{13}H_{28}$
Tetradecane	$C_{14}H_{30}$
Naphthalene, dimethyl-	$C_{11}H_{10}$
Pentadecane	$C_{15}H_{32}$
Hexadecane	$C_{16}H_{34}$
Heptadecane	$C_{17}H_{36}$
Naphthalene, trimethyl-	$C_{13}H_{14}$

TABLE 2. D-BENZENE DATA

	Nanograms of Deuterated Benzene		
	Type 1	Type 2	Type 3
Condition 1	230	426	111
2	96	362	225
3	140	180	205

Average	219 ng
Standard Deviation	104 ng
Actual	244 ng

TABLE 3. TYPE 1 (VOST) CONDITION 1

Type 1 Asphalt (VOST) Condition 1	Weight Loss (kg)	0.0010
	Time (h)	4.0167
	Temperature (C)	117
	Sample Volume (L)	4.79

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Methane, dichloro	0	0.0000	0	0
Benzene	0	0.0000	0	0
Heptane	0	0.0000	0	0
Benzene, methyl	13	0.0027	23	42
Octane	0	0.0000	0	0
Benzene, dimethyl	0	0.0000	0	0
Nonane	0	0.0000	0	0
Decane	21	0.0043	37	66
Benzene, trimethyl	0	0.0000	0	0
Benzaldehyde	30	0.0062	53	95
Undecane	0	0.0000	0	0
Benzene, tetramethyl	0	0.0000	0	0
Ethanone, 1-phenyl	0	0.0000	0	0
Dodecane	25	0.0052	44	80
Undecane, dimethyl	0	0.0000	0	0
Naphthalene	0	0.0000	0	0
Tridecane	147	0.0306	260	470
Tetradecane	0	0.0000	0	0
Naphthalene, dimethyl	0	0.0000	0	0
Pentadecane	0	0.0000	0	0
Hexadecane	0	0.0000	0	0
Heptadecane	0	0.0000	0	0
Naphthalene, trimethyl	0	0.0000	0	0
		Total	417	

TABLE 4. TYPE 1 (VOST) CONDITION 2

Type 1 Asphalt (VOST)	Weight Loss (kg)	0.0020
Condition 2	Time (h)	3.5833
	Temperature (C)	163
	Sample Volume (L)	4.57

4.83 gm/m² hr
.08 gm/m² min
80 mg/m² min
T = 325 F

Compound			nc.	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Methane, dic				1285*	5200
Benzene				78	315
Heptane				0	0
Benzene, me				0	0
Octane				0	0
Benzene, dim				0	0
Nonane				0	0
Decane				12	49
Benzene, trim				0	0
Benzaldehyde		0.0117		44	180
Undecane	31	0.0068		26	104
Benzene, tetramethyl	55	0.0120		46	185
Ethanone, 1-phenyl	0	0.0000		0	0
Dodecane	28	0.0061		23	93
Undecane, dimethyl	0	0.0000		0	0
Naphthalene	0	0.0000		0	0
Tridecane	11	0.0024		9	38
Tetradecane	0	0.0000		0	0
Naphthalene, dimethyl	0	0.0000		0	0
Pentadecane	33	0.0073		28	112
Hexadecane	31	0.0068		26	105
Heptadecane	0	0.0000		0	0
Naphthalene, trimethyl	0	0.0000		0	0
			Total	292**	1181

* Contaminant
** Dichloro methane not included

TABLE 5. TYPE 1 (VOST) CONDITION 3

Type 1 Asphalt (VOST) Condtion 3	Weight Loss (kg)	0.0337
	Time (h)	3.133333
	Temperature (C)	246
	Sample Volume (L)	4.77

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Methane, dichloro	451	0.0943	19	1449
Benzene	155	0.0324	6	498
Heptane	97	0.0203	4	312
Benzene, methyl	111	0.0233	5	358
Octane	94	0.0196	4	301
Benzene, dimethyl	115	0.0242	5	371
Nonane	111	0.0232	5	357
Decane	167	0.0350	7	538
Benzene, trimethyl	0	0.0000	0	0
Benzaldehyde	278	0.0581	11	893
Undecane	201	0.0421	8	647
Benzene, tetramethyl	87	0.0182	4	279
Ethanone, 1-phenyl	0	0.0000	0	0
Dodecane	258	0.0541	11	831
Undecane, dimethyl	0	0.0000	0	0
Naphthalene	0	0.0000	0	0
Tridecane	258	0.0541	11	831
Tetradecane	296	0.0619	12	951
Naphthalene, dimethyl	452	0.0947	19	1454
Pentadecane	739	0.1547	30	2376
Hexadecane	359	0.0751	15	1153
Heptadecane	0	0.0000	0	0
Naphthalene, trimethyl	286	0.0598	12	919
		Total	188	

TABLE 6. TYPE 2 (VOST) CONDITION 1

Type 2 Asphalt (VOST)	Weight Loss (kg)	0.0015	
Condition 1	Time (h)	3.9667	
	Temperature (C)	132	
	Sample Volume (L)	4.77	

2.41 gm/M²hr
0.040 gm/M² min
40 mg/M² min
T = 269°F

Comp	Compound	Average Gaseous Conc. (g/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Meth		.0197	111	303
Benz		.0000	0	0
Hepta		.0000	0	0
Benze		.0049	27	75
Octan		.0000	0	0
Benze		.0000	0	0
Nonar		.0000	0	0
Decar		.0000	0	0
Benze		.0000	0	0
Benza		.0232	130	356
Undec		.0113	63	173
Benzene, tetramethyl	0	0.0000	0	0
Ethanone, 1-phenyl	28	0.0059	33	90
Dodecane	61	0.0128	72	197
Undecane, dimethyl	0	0.0000	0	0
Naphthalene	0	0.0000	0	0
Tridecane	51	0.0107	60	164
Tetradecane	61	0.0129	72	198
Naphthalene, dimethyl	27	0.0056	32	87
Pentadecane	22	0.0046	26	70
Hexadecane	74	0.0154	87	237
Heptadecane	24	0.0051	28	78
Naphthalene, trimethyl	45	0.0094	53	145
		Total	794	

TABLE 7. TYPE 2 (VOST) CONDITION 2

Type 2 Asphalt (VOST) Condition 2		Weight Loss (kg)	0.0138	
		Time (h)	3.3667	
		Temperature (C)	170	
			5.10	
		33.3 gm/M² hr		
		1.99 gm/M² min		
		1998 mg/M² min		
Compound	Co Ma (ng	T = 338°F		Emissions per Area (mg/sq m h)
Methane, dichloro	4			1210
Benzene	2			614
Heptane				0
Benzene, methyl	1			593
Octane				0
Benzene, dimethyl	1			433
Nonane				0
Decane	143	0.0281	15	432
Benzene, trimethyl	0	0.0000	0	0
Benzaldehyde	357	0.0701	36	1077
Undecane	133	0.0261	14	401
Benzene, tetramethyl	208	0.0409	21	628
Ethanone, 1-phenyl	121	0.0238	12	365
Dodecane	267	0.0524	27	805
Undecane, dimethyl	0	0.0000	0	0
Naphthalene	83	0.0162	8	249
Tridecane	235	0.0460	24	707
Tetradecane	157	0.0308	16	473
Naphthalene, dimethyl	34	0.0066	3	102
Pentadecane	91	0.0178	9	274
Hexadecane	89	0.0174	9	267
Heptadecane	0	0.0000	0	0
Naphthalene, trimethyl	0	0.0000	0	0
		Total	291	9062

TABLE 8. TYPE 2 (VOST) CONDITION 3

Type 2 Asphalt (VOST) Condtion 3	Weight Loss (kg)	0.0297
	Time (h)	4.05
	Temperature (C)	246
	Sample Volume (L)	4.99

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Methane, dichloro	1141	0.2287	66	3512
Benzene	0	0.0000	0	0
Heptane	62	0.0124	4	190
Benzene, methyl	82	0.0165	5	254
Octane	69	0.0139	4	214
Benzene, dimethyl	65	0.0130	4	200
Nonane	98	0.0196	6	301
Decane	109	0.0218	6	335
Benzene, trimethyl	0	0.0000	0	0
Benzaldehyde	248	0.0497	14	764
Undecane	137	0.0275	8	422
Benzene, tetramethyl	39	0.0078	2	120
Ethanone, 1-phenyl	0	0.0000	0	0
Dodecane	183	0.0367	11	564
Undecane, dimethyl	65	0.0130	4	200
Naphthalene	0	0.0000	0	0
Tridecane	124	0.0249	7	382
Tetradecane	0	0.0000	0	0
Naphthalene, dimethyl	21	0.0043	1	66
Pentadecane	110	0.0220	6	338
Hexadecane	98	0.0196	6	301
Heptadecane	51	0.0101	3	156
Naphthalene, trimethyl	19	0.0039	1	60
		Total	158	

TABLE 9. TYPE 3 (VOST) CONDITION 1

Type 3 Asphalt (VOST) Condition 1	Weight Loss (kg)	0.0010	
	Time (h)	2.7333	
	Temperature (C)	163	
	Sample Volume (L)	19.09*	

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Methane, dichloro	1044	0.0547	317	840
Benzene	843	0.0442	256	679
Heptane	58	0.0030	18	47
Benzene, methyl	200	0.0105	61	161
Octane	45	0.0024	14	36
Benzene, dimethyl	64	0.0033	19	51
Nonane	57	0.0030	17	46
Decane	79	0.0042	24	64
Benzene, trimethyl	0	0.0000	0	0
Benzaldehyde	311	0.0163	94	251
Undecane	97	0.0051	30	78
Benzene, tetramethyl	0	0.0000	0	0
Ethanone, 1-phenyl	395	0.0207	120	318
Dodecane	118	0.0062	36	95
Undecane, dimethyl	0	0.0000	0	0
Naphthalene	61	0.0032	18	49
Tridecane	64	0.0034	19	52
Tetradecane	49	0.0026	15	39
Naphthalene, dimethyl	0	0.0000	0	0
Pentadecane	28	0.0014	8	22
Hexadecane	0	0.0000	0	0
Naphthalene, trimethyl	0	0.0000	0	0
		Total	1066	

*Sample volume different because initial volumes were still being determined

TABLE 10. TYPE 3 (VOST) CONDITION 2

Type 3 Asphalt (VOST) Condition 2	Weight Loss (kg)	0.0134
	Time (h)	3.9833
	Temperature (C)	218
	Sample Volume (L)	4.83

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Methane, dichloro	2153	0.4429	279	6803
Benzene	20	0.0041	3	63
Heptane	57	0.0117	7	180
Benzene, methyl	159	0.0327	21	503
Octane	53	0.0109	7	168
Benzene, dimethyl	83	0.0171	11	262
Nonane	89	0.0183	12	281
Decane	106	0.0218	14	335
Benzene, trimethyl	27	0.0056	4	86
Benzaldehyde	353	0.0726	46	1116
Undecane	222	0.0456	29	701
Benzene, tetramethyl	0	0.0000	0	0
Ethanone, 1-phenyl	156	0.0320	20	492
Dodecane	170	0.0351	22	539
Undecane, dimethyl	52	0.0107	7	165
Naphthalene	0	0.0000	0	0
Tridecane	738	0.1519	96	2334
Tetradecane	122	0.0251	16	386
Naphthalene, dimethyl	70	0.0145	9	223
Pentadecane	120	0.0247	16	380
Hexadecane	0	0.0000	0	0
Heptadecane	0	0.0000	0	0
Naphthalene, trimethyl	0	0.0000	0	0
		Total	619	

TABLE 11. TYPE 3 (VOST) CONDITION 3

Type 3 Asphalt (VOST) Condtion 3	Weight Loss (kg)	0.1180
	Time (h)	4.0333
	Temperature (C)	288
	Sample Volume (L)	5.12

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Methane, dichloro	2623	0.5126	37	7873
Benzene	148	0.0289	2	444
Heptane	351	0.0686	5	1054
Benzene, methyl	354	0.0692	5	1063
Octane	325	0.0635	5	975
Benzene, dimethyl	567	0.1108	8	1702
Nonane	437	0.0854	6	1311
Decane	175	0.0342	2	526
Benzene, trimethyl	817	0.1596	12	2452
Benzaldehyde	0	0.0000	0	0
Undecane	539	0.1053	8	1618
Benzene, tetramethyl	438	0.0856	6	1315
Ethanone, 1-phenyl	0	0.0000	0	0
Dodecane	618	0.1207	9	1855
Undecane, dimethyl	233	0.0455	3	699
Naphthalene	0	0.0000	0	0
Tridecane	332	0.0648	5	996
Tetradecane	239	0.0467	3	718
Naphthalene, dimethyl	156	0.0305	2	469
Pentadecane	226	0.0442	3	680
Hexadecane	0	0.0000	0	0
Heptadecane	0	0.0000	0	0
Naphthalene, trimethyl	0	0.0000	0	0
		Total	121	

TABLE 12. SAMPLING DATA

Date	Asphalt Type	Condition	Ambient Temp (C)	Barometric Pressure(mmHg)
10-24-90		Background	24	752
10-25-90	3	1	22	753
11-9-90	3	2	35	757
11-13-90	3	3	33	759
11-19-90	2	3	35	751
11-20-90	2	1	28	761
11-21-90	2	2	32	759
11-27-90	1	1	24	763
11-28-90	1	2	29	779
11-29-90	1	3	34	768

The original experiments were conducted while the experimental setup measuring the weight under the simulated kettle was malfunctioning, rendering the weights uncertain. In an effort to verify the weight data, several run conditions were reported with weights taken before and after the runs. Runs are numbered as: type 1 condition 3, type 2 conditions 2 and 5, and type 3 conditions 2 and 3.

The retested weights were used to produce the results of the calculations presented on the following pages. The average gaseous concentrations were found by dividing the milligrams of compound by the volume of sample drawn through the VOST tubes. The masses of compounds found in the background were subtracted from the masses found in samples. The background was sampled before the test. The average gaseous concentrations for the compounds found in the background samples are presented in Table 13. The blanks were not incorporated into the data since they contained the same compounds in the background in roughly the same concentrations except for dichloro methane. Table 14 provides the data for the blanks so that the data may be compared with the results of the samples. The estimated emissions were found by multiplying the average gaseous concentrations by the amount of air introduced to the burn hut by the air conditioners. This value was multiplied by the time of sampling, then divided by the weight loss of the asphalt. The air conditioner system flow rate was measured twice, and the velocity was assumed to be constant for the entire

TABLE 13. BACKGROUND DATA (VOST)

Compound	Area	Rf	Mass (ng)	Average Gaseous Conc. (mg/cu m)
Methane, dichloro	40803473	0.000005	224	0.011758
Benzene	2015041	0.000005	11	0.000580
Benzene, methyl	1905582	0.000004	9	0.000449
Benzaldehyde	9070293	0.000005	51	0.002661
Ethanone, 1-phenyl	15010602	0.000005	84	0.004404

sampling period. The measurement for the air conditioner flow was performed using a pitot tube traverse. The weight loss of the asphalt was calculated by subtracting the final weight from the beginning weight on the load cell. The TCO and GRAV masses are presented in Figures 8 and 9 and in Table 15.

The emissions per area were calculated by multiplying the average gaseous concentration by the air conditioner flow rate and dividing by the surface area of the kettle. The average diameter of the bowl at the asphalt level was found to be 419 mm. This value allows the calculation of the emissions for a specific compound for a kettle with a known surface area over a period of time. The emission rates also allow the calculation of emissions for each of the asphalt grades and temperature conditions. Example calculation:

This calculation is for type 1 asphalt, condition 1, for toluene. The air conditioner flow rate was 2119 m^3/h, the surface area of the kettle was 0.1380 m^2, the weight loss was 0.0010 kg, and the time of sampling was 4.0167 h. There was 13 ng of toluene found in the VOST tubes and 4.79 L of air was sampled.

Average Gaseous Concentration = VOST Tube Conc. / Sampling Volume

Average Gaseous Concentration = 13 ng/ 4.79 L = 0.0027 mg/m^3

Emission Rate = Weight Loss / Sampling Time

Emission Rate = (0.0010 kg)/ (4.0167 h) = 0.00025 kg/h

Estimated Emissions = (Average Gaseous Conc.)(AC Flow Rate)/(Emission Rate)

Estimated Emissions = (0.0027 mg/m^3)(2119 m^3/h)/(0.00025 kg/h) = 22885 mg of toluene emitted/kg of asphalt lost

Emissions per Area = (Average Gaseous Conc.)(AC Flow rate)/(Surface Area of Kettle)

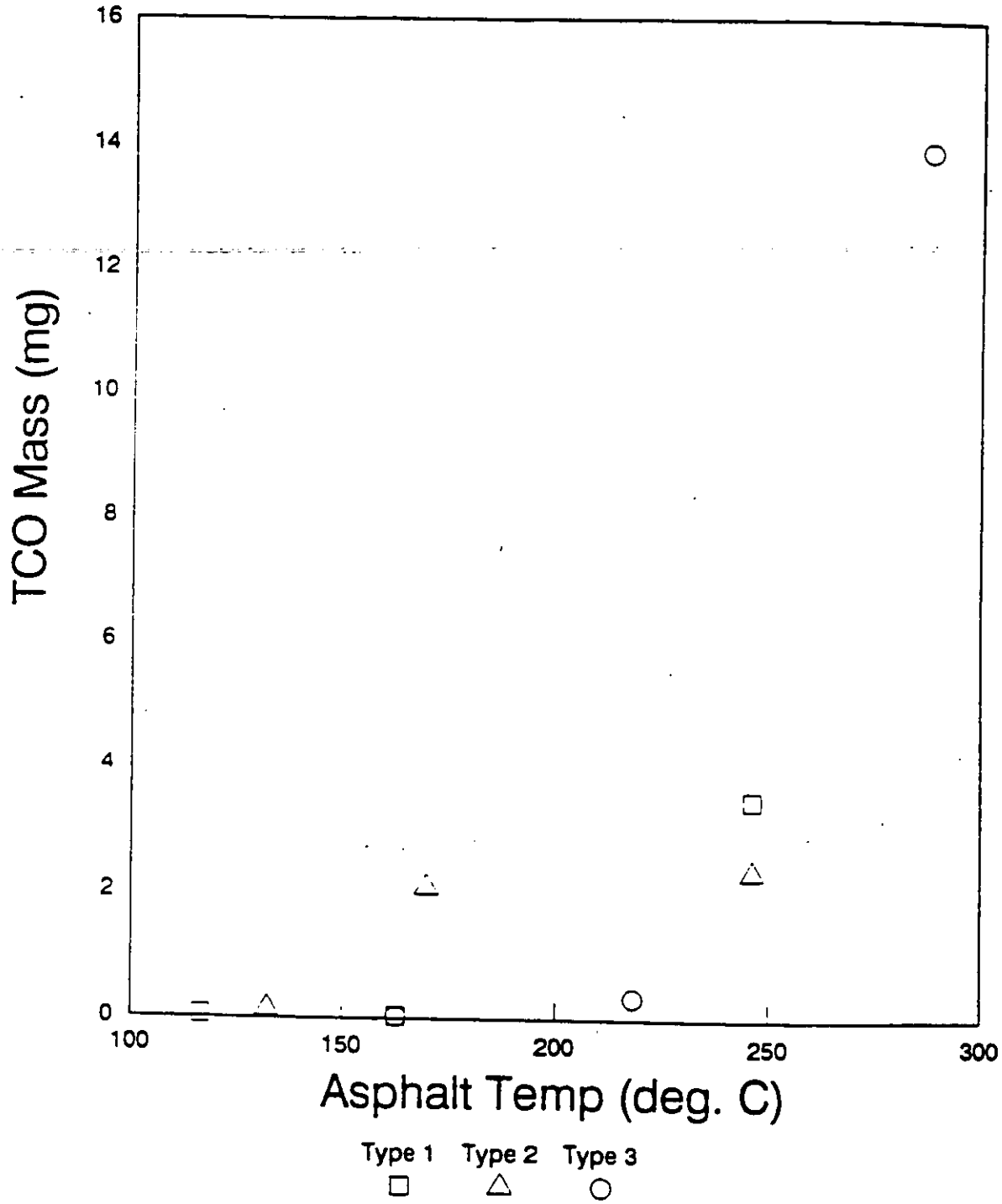
Emissions per Area = (0.0027 mg/m^3)(2119 m^3/h)/(0.1380 m^2) = 41.5 mg/h m^2

TABLE 14. BLANK DATA (VOST)

Compound	Nanograms of Compound in Blank VOST Tubes								
	T1 C1	T1 C2	T1 C3	T2 C1	T2 C2	T2 C3	T3 C1	T3 C2	T3 C3
Methane, dichloro	6106	502	5171	7657	7884	0	7994	10358	12111
Benzene	0	0	0	0	0	0	74	0	0
Benzene, methyl	0	0	0	0	0	0	41	0	0
Benzaldehyde	0	58	0	0	NM*	0	322	0	0
Ethanone, 1-phenyl	0	45	0	0	NM*	0	728	0	0

Compound	Average Gaseous Concentration in Blank VOST Tubes (mg/cu m)								
	T1 C1	T1 C2	T1 C3	T2 C1	T2 C2	T2 C3	T3 C1	T3 C2	T3 C3
Methane, dichloro	1.2746	0.1099	1.0823	1.6043	1.5474	0.0000	0.4188	2.1310	2.3668
Benzene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0039	0.0000	0.0000
Benzene, methyl	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0021	0.0000	0.0000
Benzaldehyde	0.0000	0.0127	0.0000	0.0000	NM*	0.0000	0.0169	0.0000	0.0000
Ethanone, 1-phenyl	0.0000	0.0098	0.0000	0.0000	NM*	0.0000	0.0381	0.0000	0.0000

* NM = Not measured (Compound present but integrator not working)



* A conversion table is provided on page viii

Figure 8. TCO mass data.

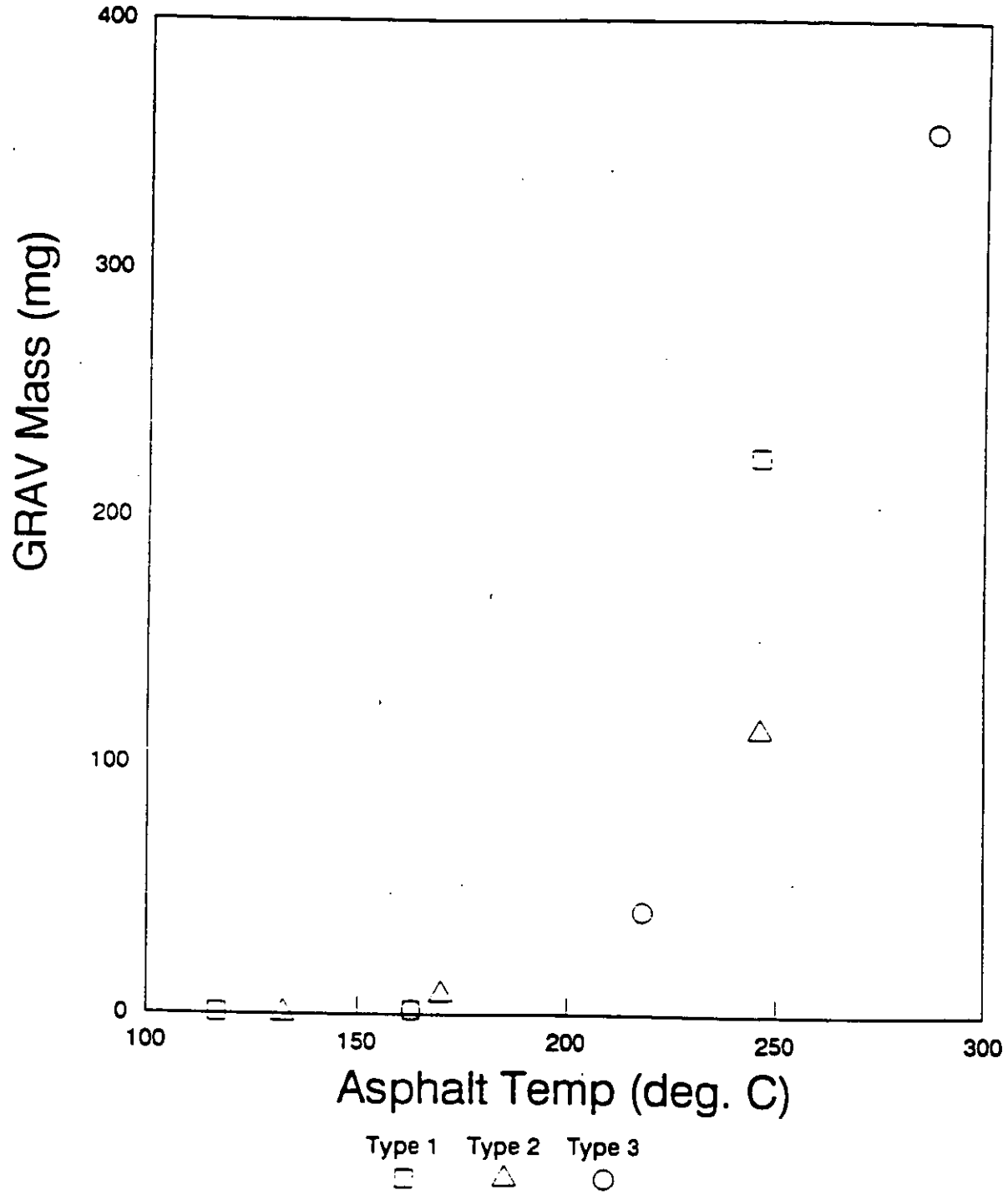


Figure 9. GRAV mass data.

TABLE 15. GRAV MASS DATA

Sample Identification	Asphalt Temp (°C)	100-300 °C TCO Mass (mg)	>300 °C GRAV Mass (mg)	Total Mass (mg)	Real Weight Loss (kg)
Type 1 Condition 1	117	0.04	0.5	1.0	0.001
Type 1 Condition 2	163	0.03	1.6	1.6	0.002
Type 1 Condition 3	246	3.48	223.8	227.3	0.034
Type 2 Condition 1	132	0.13	0.9	1.0	0.002
Type 2 Condition 2	170	2.08	7.9	10.0	0.014
Type 2 Condition 3	246	2.34	113.6	115.9	0.030
Type 3 Condition 1	163	0.03	1.8	1.8	0.001
Type 3 Condition 2	218	0.34	41.0	41.3	0.013
Type 3 Condition 3	288	13.91	355.4	369.3	0.018

3.2 SEMI-VOLATILE ORGANIC EMISSIONS DATA

Compounds were identified by the same identification program as the volatile organics. The identification data showed only straight chain alkanes (Table 16). The alkanes started from nonane and progressed through hentriacontane. Because the method used to extract the filters and XAD-2 samples had been proven to have excellent recoveries, it was assumed that all the compounds were extracted, although some of the compounds above C-24 may have had less recovery. Aromatics and aldehydes were not found in any of the samples. Quantitation was made from weight data. The calibration check of the GC/FID was done by analyzing a calibration standard as the first and last sample. The data between the two were compared for continuity, and response factors were computed from this data and the 5-point calibration. The MSD data were used only for compound identification. The masses of compounds found in the background were subtracted from the masses found in samples for the TCOs. The GRAV background weight was not subtracted because the weight was below detection limits. Compounds were then matched by retention time and retention indices. The average gaseous concentration increased as the temperature increased (Tables 17-25). The average gaseous concentration, emission rate, and emissions per area were calculated using the same formulas as the volatile organics. The sample time for the canisters and filters was 3 hours and is reflected in the

TABLE 16. COMPOUNDS IDENTIFIED BY MS FROM XAD AND FILTER EXTRACT RUNS

Compound Name	Formula
Nonane	C_9H_{20}
Decane	$C_{10}H_{22}$
Undecane	$C_{11}H_{24}$
Dodecane	$C_{12}H_{26}$
Tridecane	$C_{13}H_{28}$
Tetradecane	$C_{14}H_{30}$
Pentadecane	$C_{15}H_{32}$
Hexadecane	$C_{16}H_{34}$
Octadecane	$C_{18}H_{38}$
Nonadecane	$C_{19}H_{40}$
Icosane	$C_{20}H_{42}$
Henicosane	$C_{21}H_{44}$
Docosane	$C_{22}H_{46}$
Tricosane	$C_{23}H_{48}$
Tetracosane	$C_{24}H_{50}$
Pentacosane	$C_{25}H_{52}$
Hexacosane	$C_{26}H_{54}$
Heptacosane	$C_{27}H_{56}$
Octacosane	$C_{28}H_{58}$
Nonacosane	$C_{29}H_{60}$
Triacontane	$C_{30}H_{62}$
Hentriacontane	$C_{31}H_{64}$

calculations. Table 26 presents the ASTM standards for roofing asphalt.[6]

TABLE 17. TYPE 1 (TCO) CONDITION 1

Type 1 Asphalt (TCO) Condition 1	Weight Loss (kg)	0.0010
	Temperature (C)	117
	Sample Volume (cu m)	9.49

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Nonane	0	0.00e+00	0	0
Decane	0	0.00e+00	0	0
Undecane	0	0.00e+00	0	0
Dodecane	0	0.00e+00	0	0
Tridecane	0	0.00e+00	0	0
Tetradecane	0	0.00e+00	0	0
Pentadecane	0	0.00e+00	0	0
Hexadecane	6895	7.27e-04	5	11
Heptadecane	10996	1.16e-03	7	18
Octadecane	8710	9.18e-04	6	14
Nonadecane	508	5.36e-05	0	1
Icosane	0	0.00e+00	0	0
Henicosane	0	0.00e+00	0	0
Docosane	0	0.00e+00	0	0
Tricosane	0	0.00e+00	0	0
Tetracosane	12354	1.30e-03	8	20
Pentacosane	0	0.00e+00	0	0
Hexacosane	0	0.00e+00	0	0
Heptacosane	0	0.00e+00	0	0
Octacosane	0	0.00e+00	0	0
Nonacosane	0	0.00e+00	0	0
Triacontane	0	0.00e+00	0	0
Hentriacontane	0	0.00e+00	0	0
		Total	26	

TABLE 18. TYPE 1 (TCO) CONDITION 2

Type 1 Asphalt (TCO)	Weight Loss (kg)	0.0020	
Condition 2	Temperature (C)	163	
	Sample Volume (cu m)	9.58	

Compound	Compound Mass (ng)	Average Gasmous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Nonane	0	0.00e+00	0	0
Decane	0	0.00e+00	0	0
Undecane	0	0.00e+00	0	0
Dodecane	0	0.00e+00	0	0
Tridecane	0	0.00e+00	0	0
Tetradecane	0	0.00e+00	0	0
Pentadecane	0	0.00e+00	0	0
Hexadecane	0	0.00e+00	0	0
Heptadecane	2667	2.78e-03	9	43
Octadecane	918	9.58e-04	3	15
Nonadecane	174	1.82e-04	1	3
Icosane	78	8.15e-05	0	1
Henicosane	646	6.74e-04	2	10
Docosane	0	0.00e+00	0	0
Tricosane	0	0.00e+00	0	0
Tetracosane	923	9.63e-04	3	15
Pentacosane	0	0.00e+00	0	0
Hexacosane	0	0.00e+00	0	0
Heptacosane	0	0.00e+00	0	0
Octacosane	0	0.00e+00	0	0
Nonacosane	0	0.00e+00	0	0
Triacontane	0	0.00e+00	0	0
Nonane	0	0.00e+00	0	0
		Total	18	

TABLE 19. TYPE 1 (TCO) CONDITION 3

Type 1 Asphalt (TCO) Condtion 3	Weight Loss (kg)	0.0337
	Temperature (C)	246
	Sample Volume (cu m)	9.60

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Nonane	5592	5.83e-03	1	89
Decane	5353	5.58e-03	1	86
Undecane	5171	5.39e-03	1	83
Dodecane	5237	5.45e-03	1	84
Tridecane	5563	5.80e-03	1	89
Tetradecane	7948	8.28e-03	2	127
Pentadecane	11620	1.21e-02	2	186
Hexadecane	14912	1.55e-02	3	239
Heptadecane	19259	2.01e-02	4	308
Octadecane	19459	2.03e-02	4	311
Nonadecane	27406	2.85e-02	5	439
Icosane	55778	5.81e-02	11	892
Henicosane	64582	6.73e-02	13	1033
Docosane	61621	6.42e-02	12	986
Tricosane	59342	6.18e-02	12	949
Tetracosane	66264	6.90e-02	13	1060
Pentacosane	67365	7.02e-02	13	1078
Hexacosane	67031	6.98e-02	13	1073
Heptacosane	45177	4.71e-02	9	723
Octacosane	50389	5.25e-02	10	806
Nonacosane	32859	3.42e-02	6	526
Triacontane	23600	2.46e-02	5	378
Nonane	21066	2.19e-02	4	337
		Total	146	

TABLE 20. TYPE 2 (TCO) CONDITION 1

Type 2 Asphalt (TCO), Condition 1	Weight Loss (kg)	0.0015
	Temperature (C)	132
	Sample Volume (cu m)	9.40

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Nonane	0	0.00e+00	0	0
Decane	0	0.00e+00	0	0
Undecane	0	0.00e+00	0	0
Dodecane	301	3.20e-04	1	5
Tridecane	385	4.09e-04	2	6
Tetradecane	472	5.02e-04	2	8
Pentadecane	530	5.64e-04	2	9
Hexadecane	1034	1.10e-03	5	17
Heptadecane	991	1.05e-03	4	16
Octadecane	624	6.64e-04	3	10
Nonadecane	0	0.00e+00	0	0
Icosane	0	0.00e+00	0	0
Henicosane	0	0.00e+00	0	0
Docosane	0	0.00e+00	0	0
Tricosane	0	0.00e+00	0	0
Tetracosane	1079	1.15e-03	5	18
Pentacosane	0	0.00e+00	0	0
Hexacosane	0	0.00e+00	0	0
Heptacosane	0	0.00e+00	0	0
Octacosane	0	0.00e+00	0	0
Nonacosane	0	0.00e+00	0	0
Triacontane	0	0.00e+00	0	0
Hentriacontane	0	0.00e+00	0	0
		Total	24	

TABLE 21. TYPE 2 (TCO) CONDITION 2

Type 2 Asphalt (TCO) Condition 2	Weight Loss (kg)	0.0138	
	Temperature (C)	170	
	Sample Volume (cu m)	9.72	

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Nonane	2279	2.34e-03	1	36
Decane	2544	2.62e-03	1	40
Undecane	3110	3.20e-03	1	49
Dodecane	3781	3.89e-03	2	60
Tridecane	4602	4.73e-03	2	73
Tetradecane	6017	6.19e-03	3	95
Pentadecane	7879	8.10e-03	4	124
Hexadecane	8300	8.54e-03	4	131
Heptadecane	5483	5.64e-03	3	87
Octadecane	2990	3.08e-03	1	47
Nonadecane	1444	1.49e-03	1	23
Icosane	1818	1.87e-03	1	29
Henicosane	2073	2.13e-03	1	33
Docosane	746	7.67e-04	0	12
Tricosane	0	0.00e+00	0	0
Tetracosane	1470	1.51e-03	1	23
Pentacosane	0	0.00e+00	0	0
Hexacosane	0	0.00e+00	0	0
Heptacosane	0	0.00e+00	0	0
Octacosane	0	0.00e+00	0	2
Nonacosane	0	0.00e+00	0	0
Triacontane	0	0.00e+00	0	0
Hentriacontane	0	0.00e+00	0	0
		Total	26	

TABLE 22. TYPE 2 (TCO) CONDITION 3

Type 2 Asphalt (TCO) Condition 3	Weight Loss (kg)	0.0297
	Temperature (C)	246
	Sample Volume (cu m)	9.80

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Nonane	5850	5.97e-03	1	92
Decane	5335	5.44e-03	1	84
Undecane	5124	5.23e-03	1	80
Dodecane	4877	4.98e-03	1	76
Tridecane	4696	4.79e-03	1	74
Tetradecane	5995	6.12e-03	1	94
Pentadecane	7229	7.38e-03	2	113
Hexadecane	8481	8.65e-03	2	133
Heptadecane	8681	8.86e-03	2	136
Octadecane	7360	7.51e-03	2	115
Nonadecane	9893	1.01e-02	2	155
Icosane	15769	1.61e-02	3	247
Henicosane	17984	1.84e-02	4	282
Docosane	16039	1.64e-02	4	251
Tricosane	13604	1.39e-02	3	213
Tetracosane	14583	1.49e-02	3	229
Pentacosane	16870	1.72e-02	4	264
Hexacosane	16607	1.69e-02	4	260
Heptacosane	13206	1.35e-02	3	207
Octacosane	13440	1.37e-02	3	211
Nonacosane	14406	1.47e-02	3	226
Triacontane	14555	1.49e-02	3	228
Hentriacontane	15279	1.56e-02	3	239
		Total	56	

TABLE 23. TYPE 3 (TCO) CONDITION 1

Type 3 Asphalt (TCO) Condition 1	Weight Loss (kg)	0.0010	
	Temperature (C)	163	
	Sample Volume (cu m)	10.14	

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Nonane	0	0.00e+00	0	0
Decane	0	0.00e+00	0	0
Undecane	0	0.00e+00	0	0
Dodecane	0	0.00e+00	0	0
Tridecane	0	0.00e+00	0	0
Tetradecane	0	0.00e+00	0	0
Pentadecane	0	0.00e+00	0	0
Hexadecane	0	0.00e+00	0	0
Heptadecane	0	0.00e+00	0	0
Octadecane	0	0.00e+00	0	0
Nonadecane	0	0.00e+00	0	0
Icosane	0	0.00e+00	0	0
Henicosane	0	0.00e+00	0	0
Docosane	0	0.00e+00	0	0
Tricosane	0	0.00e+00	0	0
Tetracosane	760	7.49e-04	5	12
Pentacosane	0	0.00e+00	0	0
Hexacosane	0	0.00e+00	0	0
Heptacosane	0	0.00e+00	0	0
Octacosane	0	0.00e+00	0	0
Nonacosane	0	0.00e+00	0	0
Triacontane	0	0.00e+00	0	0
Hentriacontane	0	0.00e+00	0	0
		Total	5	

TABLE 24. TYPE 3 (TCO) CONDITION 2

Type 3 Asphalt (TCO) Condition 2		Weight Loss (kg)	0.0134
		Temperature (C)	218
		Sample Volume (cu m)	9.67

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Nonane	1172	1.21e-03	1	19
Decane	1074	1.11e-03	1	17
Undecane	1230	1.27e-03	1	20
Dodecane	1335	1.38e-03	1	21
Tridecane	1455	1.51e-03	1	23
Tetradecane	1771	1.83e-03	1	28
Pentadecane	2094	2.17e-03	1	33
Hexadecane	2722	2.82e-03	1	43
Heptadecane	3633	3.76e-03	2	58
Octadecane	3829	3.96e-03	2	61
Nonadecane	4050	4.19e-03	2	64
Icosane	9187	9.50e-03	5	146
Henicosane	9379	9.70e-03	5	149
Docosane	7782	8.05e-03	4	124
Tricosane	6617	6.85e-03	3	105
Tetracosane	7093	7.34e-03	3	113
Pentacosane	5503	5.69e-03	3	87
Hexacosane	4785	4.95e-03	2	76
Heptacosane	3855	3.99e-03	2	61
Octacosane	3401	3.52e-03	2	54
Nonacosane	2528	2.61e-03	1	40
Triacontane	1669	1.73e-03	1	27
Hentriacontane	966	9.99e-04	0	15
		Total	45	

TABLE 25. TYPE 3 (TCO) CONDITION 3

Type 3 Asphalt (TCO) Condtion 3	Weight Loss (kg)	0.1180
	Temperature (C)	288
	Sample Volume (cu m)	9.95

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sq m h)
Nonane	17169	1.73e-02	1	265
Decane	16047	1.61e-02	1	248
Undecane	14763	1.48e-02	1	228
Dodecane	13355	1.34e-02	1	206
Tridecane	12549	1.26e-02	1	194
Tetradecane	12872	1.29e-02	1	199
Pentadecane	11537	1.16e-02	1	178
Hexadecane	8760	8.81e-03	0	135
Heptadecane	9290	9.34e-03	1	143
Octadecane	7182	7.22e-03	0	111
Nonadecane	10412	1.05e-02	1	161
Icosane	20150	2.03e-02	1	311
Henicosane	19163	1.93e-02	1	296
Docosane	21364	2.15e-02	1	330
Tricosane	23799	2.39e-02	1	368
Tetracosane	26128	2.63e-02	1	403
Pentacosane	31687	3.19e-02	2	489
Hexacosane	34520	3.47e-02	2	533
Heptacosane	29898	3.01e-02	2	462
Octacosane	40861	4.11e-02	2	631
Nonacosane	36991	3.72e-02	2	571
Triacontane	36785	3.70e-02	2	568
Hentriacontane	38475	3.87e-02	2	594
		Total	28	

TABLE 26. ASTM STANDARDS

ANSI Guidelines for Roofing Asphalt (ASTM D312-78)*

Type 1 includes asphalts that are relatively susceptible to flow at roof temperatures with good adhesive and "self-healing" properties. They are generally used in slag- or gravel-surfaced roofs on inclines up to 4.17 percent (½ in/ft) slope.

Type 2 includes asphalts that are moderately susceptible to flow at roof temperatures. They are generally for use in built-up roof construction on inclines from approximately 4.17 percent (½ in/ft) slope to 12.5 percent (1½ in/ft) slope.

Type 3 includes asphalts that are relatively nonsusceptible to flow at roof temperatures for use in the construction of built-up roof construction on inclines from approximately 8.3 percent (1 in/ft) slope to 25 percent (3 in/ft) slope.

ANSI Physical Requirements of Asphalt in Roofing*

	Type 1		Type 2		Type 3	
Property	Min	Max	Min	Max	Min	Max
Softening Point C (F)	57 (135)	66 (151)	70 (158)	80 (176)	85 (185)	96 (205)
Flash Point C (F)	225 (437)	...	225 (437)	...	225 (437)	...
Penetration Units						
at 0 C (32 F)	...	6	...	6	...	
at 25 C (77 F)	18	60	18	40	15	35
at 46 C (115 F)	90	180	...	100	...	90
Ductility at 25 C (77 F) cm	10	...	3	...	1.5	...
Solubility in Trichloro-ethylene, %	99	...	99	...	99	...

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SECTION 4

SUMMARY AND CONCLUSIONS

The purpose of this study was to characterize and semi-quantitate the volatile organic emissions from a heated roofing asphalt kettle. The results show the types of emissions produced by the three most common types of roofing asphalt used today. The data also show how the three types of asphalt behave at the melting point, the equiviscous temperature, and an overheated temperature. Compounds identified during this study were alkanes, aromatics, a ketone, and an aldehyde. Although alcohols were found in the cursory study performed in 1989[2], the absence of these compounds may be attributed to a difference in asphalt brand or a change in sampling procedures. The unheated sample duct used in this study may have condensed the compounds before they reached the adsorbing material.

By having the samples collected through an unheated duct several feet away from the asphalt kettle, it may be possible to compare these results to the average gaseous concentrations of volatile organics compounds found at a typical roofing asphalt project. These results show that, as the roofing asphalt is heated through higher temperature ranges, more compounds are emitted at higher concentrations. Useful emission factors also are provided in the data to help characterize the emissions either by the mass of asphalt lost by heating or by the size of the kettle over a period of time.

SECTION 5

REFERENCES

1. Asphalt Roofing Manufacturing Industry-Background Information for Promulgated Standards. EPA-450/3-80-021b (NTIS PB82-257726), July 1982.
2. Internal Communication with Bobby Daniel, 1990.
3. Health and Safety Guide for the Commercial Roofing Industry. DHEW (NIOSH) Publication No. 278-194. National Institute for Occupational Safety and Health. Cincinnati, Ohio. September 1978. pp. 77.
4. Ryan, J.V., "Characterization of Emissions from the Simulated Open Burning of Scrap Tires," EPA-600/2-89-054 (NTIS PB90-126004), October 1989.
5. Hansen, E.M., "Protocol for the Collection and Analysis of Volatile POHCs Using VOST," EPA-600/8-84-007 (NTIS PB84-170042), March 1984.
6. ASTM D312-78, Annual Book of ASTM Standards, Part 15.

APPENDIX A

QUALITY CONTROL EVALUATION REPORT

ACCURACY AND PRECISION

Accuracy and precision were calculated using the following formulas:

Accuracy:

$$Percent\ bias = \frac{measured\ concentration - known\ concentration}{known\ concentration} * 100$$

or

$$Percent\ recovery = \frac{measured\ concentration}{known\ concentration} * 100$$

Precision:

$$Relative\ precision\ data = \frac{(C_1 - C_2)}{(C_1 + C_2)/2} * 100$$

Where: C_1 = larger of the 2 measured values
C_2 = smaller of the 2 measured values

or

$$Relative\ standard\ deviation = \frac{standard\ deviation\ of\ replicate\ measurements}{average\ of\ replicate\ measurements} * 100$$

$$Standard\ deviation = \sqrt{\sum \frac{(V_i - average)}{n}}$$

Where: V_i = i^{th} item
average = average of values
n = number of items

Two XAD-2 and one filter laboratory blank was run. The laboratory blanks included injecting an internal standard on both the filter and the XAD-2 cartridges. The results of the extracts were compared to those of a straight injection of the same compounds for either the TCO or the GRAV analysis. It was determined that there was a recovery of 120 percent for the XAD-2 cartridges and 109 percent for the filter. This met the data quality objective (DQO) of 50-150 percent recovery.

TABLE A-1 PERCENT BIAS FOR VOST PEAS

Compound	True (ng)	Measured (ng)	Percent Bias
Benzene	122	142.5	+17
Toluene	147	196	+33
Ethyl Benzene	184	300.5	+63
Xylene	161	369	+129

VOLATILE ORGANIC DATA

Accuracy for this project was not assessed by spike recovery of the analyte for any of the methods. However a measure of accuracy can be assessed by looking at the data for the internal standard, deuterated benzene, in the VOST samples. A concentration of 244 ng of deuterated benzene was spiked onto all the tubes before sampling. The average measured concentration was 219 ng for 27 samples. This gives a bias of 10.2 percent. Bias was also calculated by examining the results of performance evaluation audit (PEA) samples from an external audit. Table A-1 shows the results for benzene, toluene, xylene, and ethyl benzene.

As can be seen from Table A-1, there is increasing positive bias with increasing retention time. This is probably caused by using a single response factor in calculating the analyte mass. This trend was not taken into account when calculating the response factors for the PEAs. The actual asphalt samples, however, were calculated on the basis of individual response factors from standards. The DQO for quantitation accuracy for the volatile organics of ±50 percent was not met for ethyl benzene or xylene, but was met for benzene and toluene.

The PEAs for the VOST tubes were also judged on the number of compounds identified correctly. On average, 91 percent of the compounds were identified correctly meeting the DQO of greater than 75 percent.

Precision for the volatile organics can be determined by the percent RSD of the internal standard spikes for the VOST samples. The standard deviation for the deuterated benzene was 104 ng. The concentration of the compound was 244 ng.

$$RSD = \frac{104}{219} * 100 = 47 \ percent$$

The DQO of 25 percent was not met for the samples in this project. Another measure of precision were the external audits. These were submitted in duplicate with the results as seen in Table A-2.

These DQOs for precision of 25 percent were met 50 percent of the time for the PEAs. If the DQO had been 50 percent, it would have been met. Under the circumstances of the project, in consideration of the many sources of error, this may have been a more realistic goal. Same day analysis or a different collection medium than Tenax may have allowed the project to meet the DQO. Fifty percent is the normal error for VOST analysis.

The QC checks on the Tenax tubes all passed the parameters for clean tubes set forth in the Quality Assurance Project Plan.

SEMI-VOLATILE DATA

The filters and XAD-2 cartridges were not spiked with an internal standard. The PEA filters were spiked at too low a concentration to be measured. The QC check standards were run four times a day with the TCOs. The data presented in Table A-3 provide the accuracy and precision for these standards.

The values for accuracy met the DQO of 20 percent while the precision never met the DQO of 15 percent. Accuracy and precision data were calculated from the recovery data for the spiked laboratory blanks. The replications called for in the QAPjP were not done, as agreed before sampling began. The spiking solutions to characterize TCO and GRAV measurements were not used. QC check samples as called for in the QAPjP for GRAV samples were not used. The deuterated naphthalene internal standard as called for in the QAPjP was not used to determine the recovery for the semi-volatiles from the XAD-2 resin.

TABLE A-2. RESULTS OF EXTERNAL AUDIT

Compound	Average (ng)	Standard Deviation (ng)	Percent RSD
Benzene	142.5	60.1	42.1
Toluene	196	2.8	1.4
Ethyl Benzene	300.5	85.6	28.5
Xylene	367	46.7	12.7

TABLE A-3. ACCURACY AND PRECISION DATA FOR SEMI-VOLATILES

Compound	True (mg)	Measured (mg)	Percent Bias	RPD*
Decane	0.023949	0.021871	-8.67818	24.42864
Dodecane	0.023478	0.023322	-0.66562	20.62726
Tetradecane	0.022179	0.025493	14.94403	19.98598
Heptadecane	0.021536	0.025376	17.83194	25.71266

* RPD = Relative Precision Data

COMPLETENESS

$$Completeness = \frac{Amount\ of\ valid\ data}{Amount\ of\ planned\ data} * 100 =$$

Volatiles = 89 percent or 24 of 27 Blanks = 100 percent or 9 of 9
Semi-volatiles = 100 percent or 9 of 9 Blanks = 75 percent or 3 of 4

Three volatile samples were not analyzed because they were broken during analysis. DQO for the volatiles was set at better than 75 percent, whereas the semi-volatiles were 100 percent. The results of the volatile blanks are presented in Table 14 of the basic report. The decision not to run semi-volatiles in duplicate was made before the project began. The semi-volatile field blank was not collected although a background sample was collected. It was determined that there were no compounds present in the background and that the GRAV mass was below detection limits.

REPRESENTATIVENESS

The design of the burn hut and sampling shed ensured good mixing of the asphalt fumes with ambient air before being sampled, ensuring representativeness. Using ambient pressures, air flows, and temperatures ensured that the air reaching the sampling equipment was representative of possible breathing zones. Also, studies in October 1989, "Characterization of Emissions from the Simulated Open Burning of Scrap Tires," proved representative sampling using the same techniques performed in this project.

COMPARABILITY

This study cannot be compared to studies of asphalt fumes in which sampling was done directly over an open kettle. Those studies found significant concentrations of polyaromatic hydrocarbons, for instance, which were not found in this study. This is thought to be due to the circumstances of the sampling which was designed to simulate the compounds reaching the breathing zones of people in the area of the kettle.

SUMMARY

It can be seen from the accuracy and precision data for the project that the DQOs for the project may have been set for slightly unrealistic goals. An approved QAPjP was in place prior to data collection thus stating the DQO. Several audits were performed during the course of the program. These included a technical systems audit, performance evaluation audits, and an audit of data quality. The technical systems audit evaluated the project organization and personnel, calibration procedures, the facilities and equipment, the sample handling equipment, analytical procedures, quality control procedures, data processing and validation procedures, and record keeping. The performance evaluation audits included spiked samples for both the volatiles and semi-volatiles. The results of both are stated above. The data quality audit was performed by reviewing the data for proper data recording, calculations, and discussion of data quality indicators. These audits were performed externally by EPA/AEERL QA.

After reviewing the data obtained form the load cell it was determined that several of the run conditions should be repeated for comparability. All of the high temperatures (condition 3) and the medium temperatures for types 2 and 3 were repeated. These tests were performed by heating a new block of asphalt to the desired temperature and maintaining it for a period of time. No air sampling was repeated for these tests.

All of the audits were passed with minor recommendations although many of the DQOs were not met. Since the margin by which the DQOs failed was very small it could be seen that the DQOs for the project may have been set unrealistically.

TECHNICAL REPORT DATA
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1. REPORT NO. EPA-600/2-91-061	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Evaluation of VOC Emissions from Heated Roofing Asphalt		5. REPORT DATE November 1991
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Peter Kariher, Michael Tufts, and Larry Hamel		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Acurex Corporation P. O. Box 13109 Research Triangle Park, North Carolina 27709		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-D0-0141, Task 91-001
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED Task Final; 4/90 - 8/91
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL Task Officer is Bobby E. Daniel, Mail Drop 61, 919/541-0908.

16. ABSTRACT The report gives results of a short-term in-house project to characterize emissions from a simulated asphalt roofing kettle, performed at EPA/AEERL. Hot asphalt surfacing and resurfacing has been identified as a possible significant source of volatile organic compound (VOC) emissions that may affect human health and contribute to the ozone non-attainment problem. The purpose of the study was to collect, identify, and semi-quantitate as many compounds as possible that are discharged during the open heating of roofing asphalt and relate them to the amount volatilized into the air. Types 1, 2, and 3 mopping grade asphalts were chosen for this study. They constitute more than 90% of roofing asphalt used. Samples of each type of asphalt were placed in a simulated roofing kettle, heated to predetermined temperatures, and sampled for volatile and semi-volatile organic emissions. Compounds identified during the study were alkanes, aromatics, a ketone, and an aldehyde.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Aromatic Compounds	Pollution Control	13B
Asphalts	Ketones	Stationary Sources	08G, 13C
Organic Compounds	Aldehydes	Volatile Organic Compounds (VOCs)	07C
Volatility			20M
Ozone			07B
Alkanes			

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 65
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

U.S. ENVIRONMENTAL PROTECTION AGENCY
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