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Ron M. — something I've had in my files, belongs to D.2. Do you have final copy? Ron R.

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EVALUATION OF VOC EMISSIONS FROM HEATED ROOFING ASPHALT

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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.

SECTION 1

INTRODUCTION

The Control Technology Center (CTC) and the 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. 2 refs. ①

where are these described?

The asphalt can be delivered to the site in 2 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 100-lb blocks. The blocks are chopped into sections and added to the kettle as needed.

Don't want to confuse this with production of asphalt roofing (shingles, etc)

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 used for similar projects. In-house testing was performed to 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 (Internal Communication).

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 PROJECT DESCRIPTION

Asphalt roofing ~~material~~ 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 achieve EVT in order to transport the asphalt to the point of application. Q-ref (3)

need to provide some further discussion that these are usually mounted on trailers and hauled from site to site.

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 on the bottom of the kettle. The first temperature condition was defined by the melting of the asphalt. (typically 1st) 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 (what Temp?) 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 150 °F (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.

Were conditions 1, 2 and 3 done with the same sample of asphalt for each type? or was the kettle emptied and reloaded for each condition?

If the same sample was subjected to all 3 conditions, all (or most) of the volatiles may have been driven off before condition 3 was sampled. Therefore, condition 2's emissions would be cumulative because the samples were also exposed to the previous conditions.

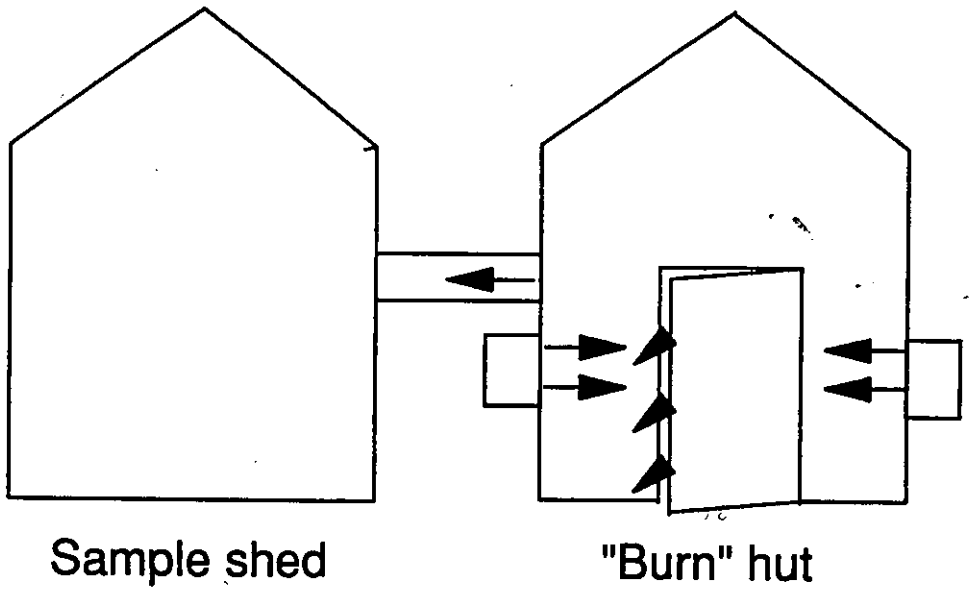
The same heating procedure was used for all 3 asphalt types. The temperatures inside the burn hut and sample transport duct also were monitored periodically. The asphalt block was replaced after each test after a significant weight loss was recorded. A baseline test using the torch, but no asphalt, was done with the VOST tubes and an XAD-2 canister 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. Volatile organic samples were collected with VOST tubes and the semi-volatile organics and particulates were collected with XAD-2 and Pallflex 142-mm filters. After the asphalt was heated, 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 gas chromatograph/mass selective detector (GC/MSD) for compound identification and 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. This 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 8-ft x 8-ft x 8-ft (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 1,200 ft^3/min (34.0 m^3/min). A deflector shield was located 4 ft (1.2 m) over the pit



(Arrows indicate air flow)

Figure 1. Sampling buildings.

to protect the ceiling and enhance ambient mixing. The sample duct, an 8-in O.D. (203-mm) 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 (EPA-600/2-89-054). 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 3/8-in O.D. (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 1/4-in O.D. (6.4-mm) Teflon tubing.

Semi-volatile organics and particulate were collected using a sample system modified for use in this study. A 3/8-in O.D. stainless steel tube was connected from the manifold to a particulate filter

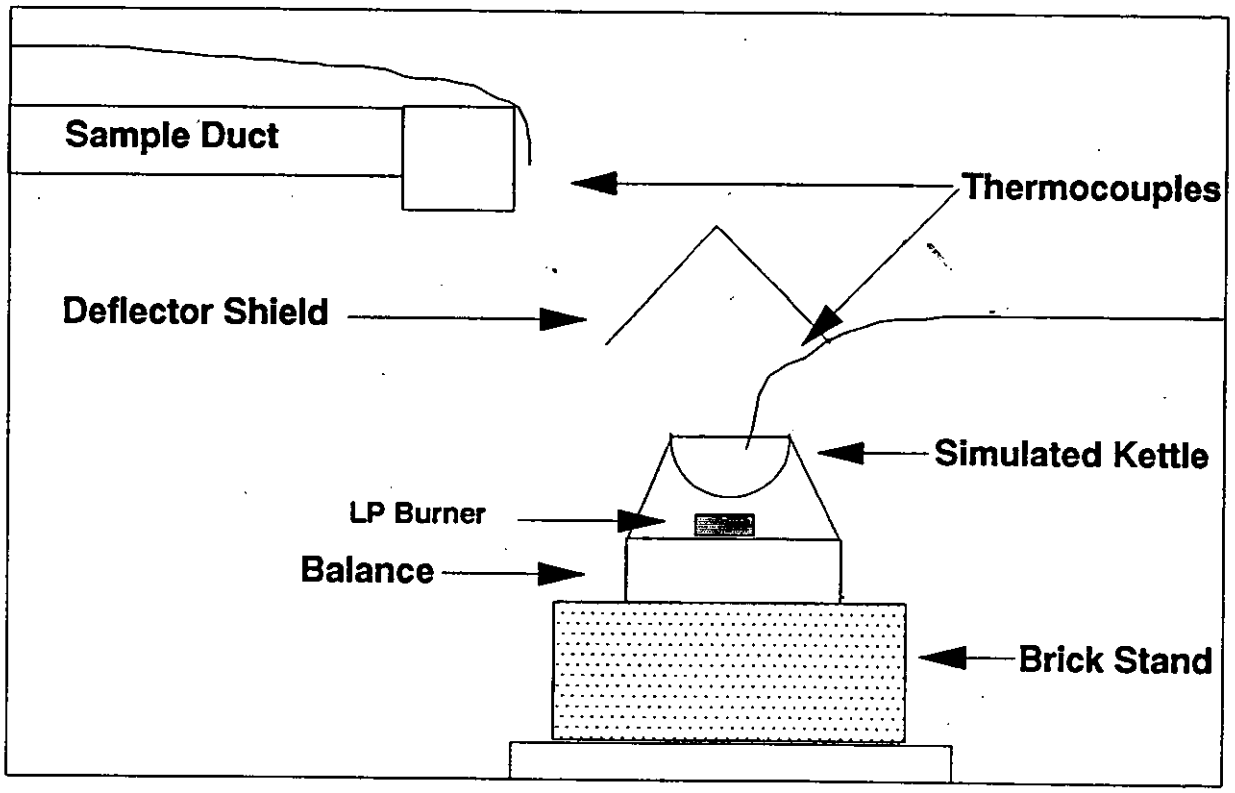


Figure 2. Heating apparatus in "Burn Hut".

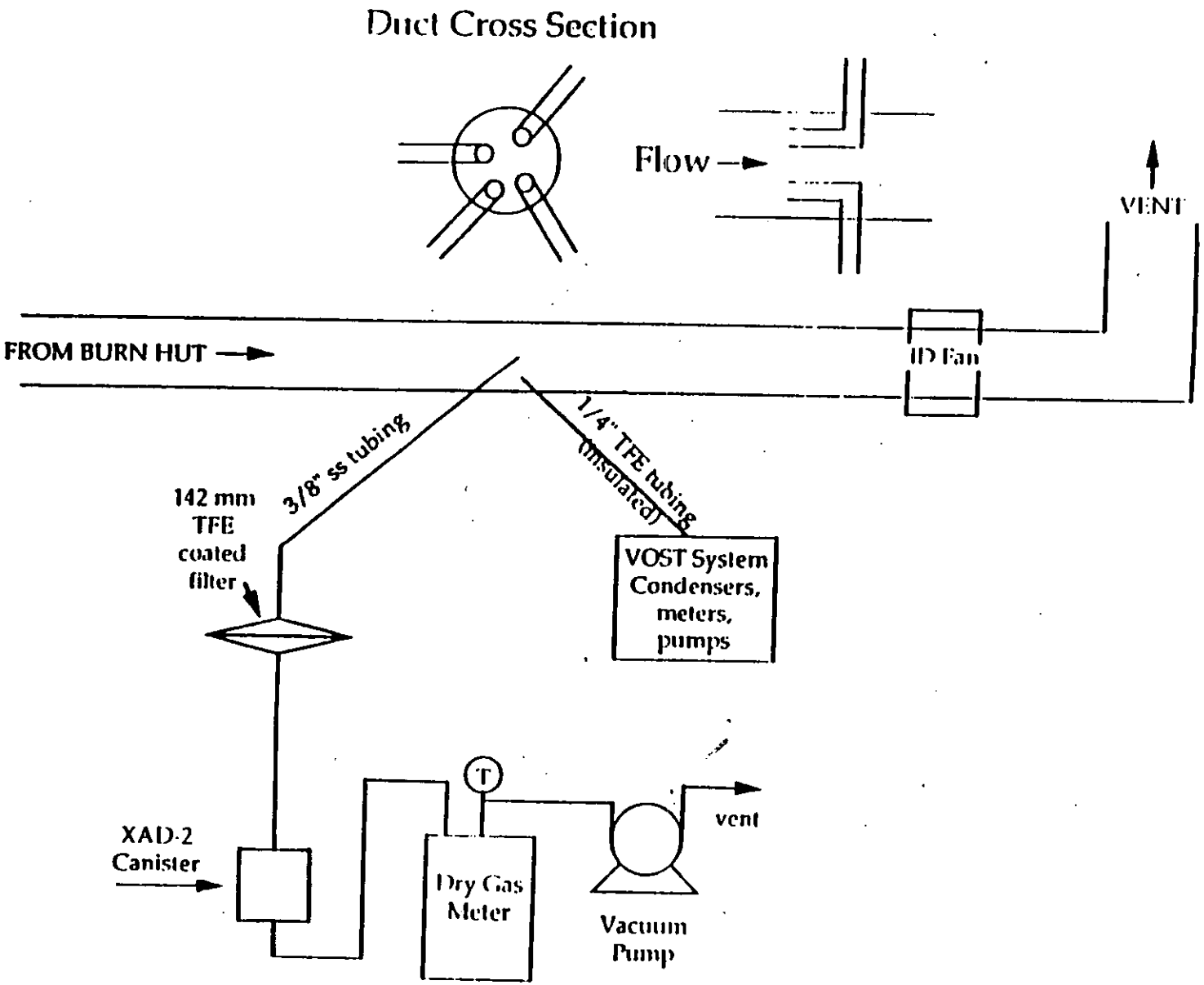


Figure 3. Diagram of sampling systems used.

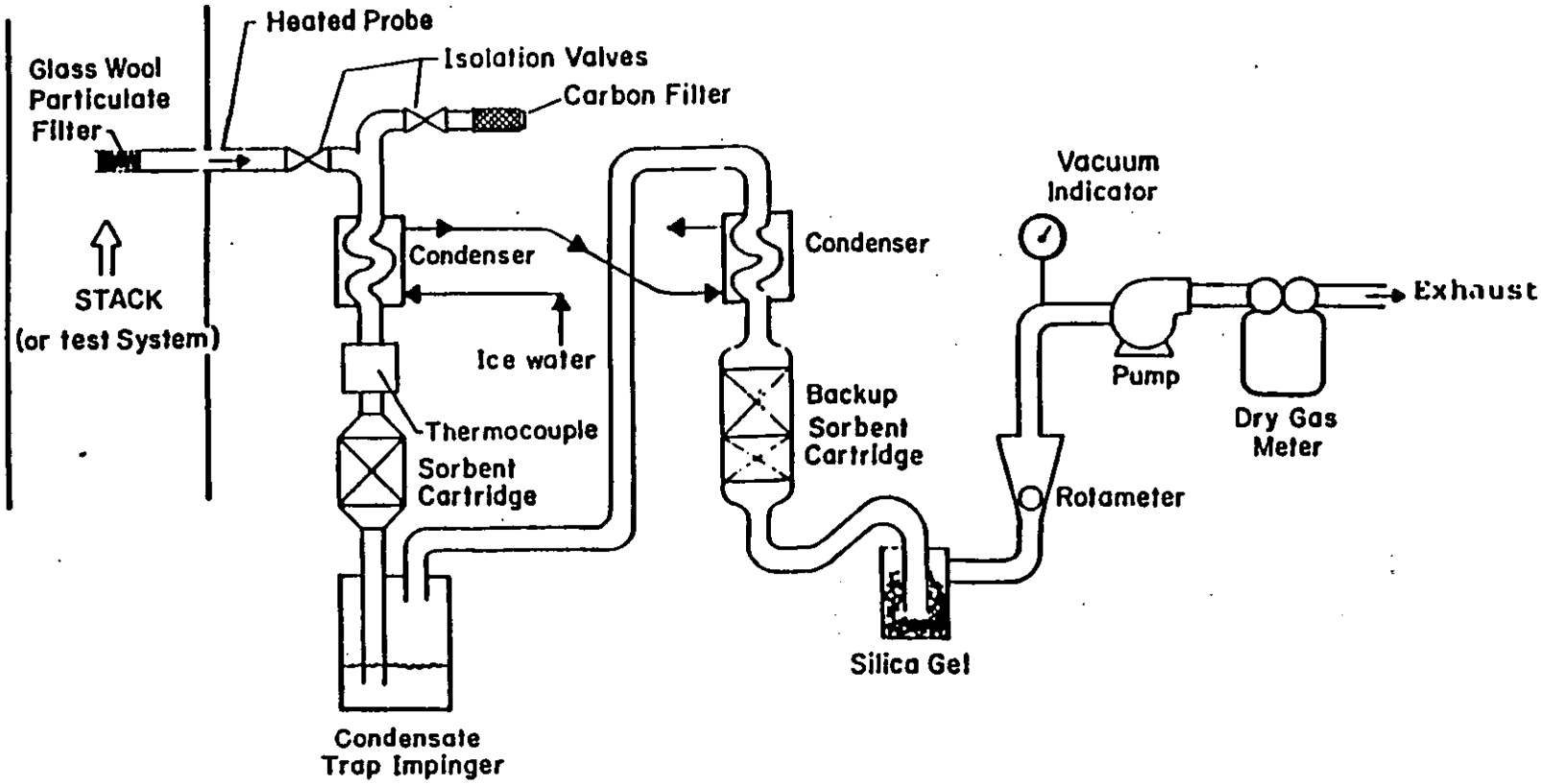


Figure 4. Schematic of volatile organic sampling train.

assembly. Particulate was collected on a 142-mm, Teflon-coated, glass fiber filter located in the filter 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 Fiber Glass, Morehead City, NC. All 3 asphalt types were made by the Trumbull Asphalt Division of Owens-Corning Fiberglass Corporation. The asphalt was supplied in 100-lb 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 150 °F (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.

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 1/4-in (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

3 hr was determined to be the optimum volume 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 hours 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 quality control (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 2 separate freezers to prevent contamination of conditioned tubes by the sampled tubes. All sampling information was collected on standardized data collection sheets.

The VOST collected samples were analyzed using an adsorption and thermal desorption GC/MSD system. The analytical method used in this study was found in EPA-600/8-84-007. This procedure may be found in the QAPP. 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 (-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 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 in compound identification. A mass spectral library (NBS) matching program was used extensively. The program was written so that for each integrated peak, spectra was 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 5 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 8 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. One-point calibrations 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 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 3/8-in 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 a 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 2 ft^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. 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 use. 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 (in a method

similar to QAPP IACP study Roanoke, VA, November 1988, Appendix B). The XAD-2 canisters were extracted with methylene chloride by pump through elution (AEERL ROP #41). 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. The bed was then rinsed with methylene chloride to remove any residual water. 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 (AEERL ROP #13). 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 the GRAV analysis (AEERL ROP #12). 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 referenced procedure found in the Quality Assurance Project Plan (QAPP) was used for the analysis. 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. One-point calibrations were run before and after the samples were analyzed. The compounds in these calibration standards included heptadecane, 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 dueterated benzene areas for the 3 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. In order to confirm several of the weights from the volatilized asphalt, 5 of the conditions were repeated to test for

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-	$C_{13}H_{28}$
Napthalene	$C_{10}H_8$
Tridecane	$C_{13}H_{28}$
Tetradecane	$C_{14}H_{30}$
Napthalene, dimethyl-	$C_{11}H_{10}$
Pentadecane	$C_{15}H_{32}$
Hexadecane	$C_{16}H_{34}$
Heptadecane	$C_{17}H_{36}$
Napthalene, trimethyl-	$C_{13}H_{14}$

TABLE 2. D-BENZENE DATA

	Nanograms of Dueterated 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 (F)	242
	Sample Volume (L)	4.79

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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
Napthalene	0	0.0000	0	0
Tridecane	147	0.0306	260	470
Tetradecane	0	0.0000	0	0
Napthalene, dimethyl	0	0.0000	0	0
Pentadecane	0	0.0000	0	0
Hexadecane	0	0.0000	0	0
Heptadecane	0	0.0000	0	0
Napthalene, trimethyl	0	0.0000	0	0
		Total	417	

TABLE 4. TYPE 1 (VOST) CONDITION 2

Type 1 Asphalt (VOST) Condition 2	Weight loss (kg)	0.0020
	Time (h)	3.5833
	Temperature (F)	325
	Sample Volume (L)	4.57

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm h)
Methane, Dichloro	1545	0.3385	1285*	5200
Benzene	94	0.0205	78	315
Heptane	0	0.0000	0	0
Benzene, methyl	0	0.0000	0	0
Octane	0	0.0000	0	0
Benzene, dimethyl	0	0.0000	0	0
Nonane	0	0.0000	0	0
Decane	15	0.0032	12	49
Benzene, trimethyl	0	0.0000	0	0
Benzaldehyde	53	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
Napthalene	0	0.0000	0	0
Tridecane	11	0.0024	9	38
Tetradecane	0	0.0000	0	0
Napthalene, dimethyl	0	0.0000	0	0
Pentadecane	33	0.0073	28	112
Hexadecane	31	0.0068	26	105
Heptadecane	0	0.0000	0	0
Napthalene, trimethyl	0	0.0000	0	0
		Total	292**	

* Contaminant
**Methylene Chloride 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 (F)	475
	Sample Volume (L)	4.77

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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
Napthalene	0	0.0000	0	0
Tridecane	258	0.0541	11	831
Tetradecane	296	0.0619	12	951
Napthalene, dimethyl	452	0.0947	19	1454
Pentadecane	739	0.1547	30	2376
Hexadecane	359	0.0751	15	1153
Heptadecane	0	0.0000	0	0
Napthalene, trimethyl	286	0.0598	12	919
		Total	168	

TABLE 6. TYPE 2 (VOST) CONDITION 1

Type 2 Asphalt (VOST) Condition 1	Weight loss (kg)	0.0015
	Time (h)	3.9667
	Temperature (F)	270
	Sample Volume (L)	4.77

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm h)
Methane, Dichloro	94	0.0197	111	303
Benzene	0	0.0000	0	0
Heptane	0	0.0000	0	0
Benzene, methyl	23	0.0049	27	75
Octane	0	0.0000	0	0
Benzene, dimethyl	0	0.0000	0	0
Nonane	0	0.0000	0	0
Decane	0	0.0000	0	0
Benzene, trimethyl	0	0.0000	0	0
Benzaldehyde	111	0.0232	130	356
Undecane	54	0.0113	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
Napthalene	0	0.0000	0	0
Tridecane	51	0.0107	60	164
Tetradecane	61	0.0129	72	198
Napthalene, dimethyl	27	0.0056	32	87
Pentadecane	22	0.0046	26	70
Hexadecane	74	0.0154	87	237
Heptadecane	24	0.0051	28	78
Napthalene, trimethyl	45	0.0094	53	145
		Total	792	

Is this included in totals now?

TABLE 7. TYPE 2 (VOST) CONDITION 2

Type 2 Asphalt (VOST) Condition 2	Weight loss (kg)	0.0138
	Time (h)	3.3667
	Temperature (F)	338
	Sample Volume (L)	5.10

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm h)
Methane, Dichloro	401	0.0788	41	1210
Benzene	204	0.0400	21	614
Heptane	0	0.0000	0	0
Benzene, methyl	197	0.0386	20	593
Octane	0	0.0000	0	0
Benzene, dimethyl	143	0.0282	15	433
Nonane	0	0.0000	0	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
Napthalene	83	0.0162	8	249
Tridecane	235	0.0460	24	707
Tetradecane	157	0.0308	16	473
Napthalene, dimethyl	34	0.0066	3	102
Pentadecane	91	0.0178	9	274
Hexadecane	89	0.0174	9	267
Heptadecane	0	0.0000	0	0
Napthalene, trimethyl	0	0.0000	0	0
		Total	291	

TABLE 8. TYPE 2 (VOST) CONDITION 3

Type 2 Asphalt (VOST) Condtion 3	Weight loss (kg)	0.0297
	Time (h)	4.05
	Temperature (F)	475
	Sample Volume (L)	4.99

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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
Napthalene	0	0.0000	0	0
Tridecane	124	0.0249	7	382
Tetradecane	0	0.0000	0	0
Napthalene, dimethyl	21	0.0043	1	66
Pentadecane	110	0.0220	6	338
Hexadecane	98	0.0196	6	301
Heptadecane	51	0.0101	3	156
Napthalene, 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 (F)	325
	Sample Volume (L)	19.09*

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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
Napthalene	61	0.0032	18	49
Tridecane	64	0.0034	19	52
Tetradecane	49	0.0026	15	39
Napthalene, dimethyl	0	0.0000	0	0
Pentadecane	28	0.0014	8	22
Hexadecane	0	0.0000	0	0
Napthalene, 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 (F)	425
	Sample Volume (L)	4.83

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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
Napthalene	0	0.0000	0	0
Tridecane	738	0.1519	96	2334
Tetradecane	122	0.0251	16	386
Napthalene, dimethyl	70	0.0145	9	223
Pentadecane	120	0.0247	16	380
Hexadecane	0	0.0000	0	0
Heptadecane	0	0.0000	0	0
Napthalene, trimethyl	0	0.0000	0	0
		Total	616	

TABLE 11. TYPE 3 (VOST) CONDITION 3

Type 3 Asphalt (VOST) Condtion 3	Weight loss (kg)	0.1180
	Time (h)	4.0333
	Temperature (F)	550
	Sample Volume (L)	5.12

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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
Napthalene	0	0.0000	0	0
Tridecane	332	0.0648	5	996
Tetradecane	239	0.0467	3	718
Napthalene, dimethyl	156	0.0305	2	469
Pentadecane	226	0.0442	3	680
Hexadecane	0	0.0000	0	0
Heptadecane	0	0.0000	0	0
Napthalene, trimethyl	0	0.0000	0	0
		Total	121	

TABLE 12. SAMPLING DATA

Date	Asphalt Type	Condition	Ambient Temp (F)	Barometric Pressure (in Hg)
10-24-90		Background	75	29.60
10-25-90	3	1	72	29.65
11-9-90	3	2	95	29.80
11-13-90	3	3	92	29.88
11-19-90	2	3	95	29.58
11-20-90	2	1	83	29.95
11-21-90	2	2	89	29.87
11-27-90	1	1	75	30.02
11-28-90	1	2	85	30.66
11-29-90	1	3	94	30.22

reproducibility. For the calculations presented below, the retested weights were used to produce these results. 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 concentration 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 concentration except for methylene chloride. 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 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 Table 15.

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

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 16.5 in. 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 = .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) = 23338 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) = 42.1 mg/h m^2

TABLE 14. BLANK DATA

Compound	T1 C1	T1 C2	T1 C3	T2 C1	T2 C2	T2 C3	T3 C1	T3 C2	T3 C3
	Nanograms of Compound in Blank VOST Tubes								
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	T1 C1	T1 C2	T1 C3	T2 C1	T2 C2	T2 C3	T3 C1	T3 C2	T3 C3
	Average Gaseous Concentration in Blank VOST Tubes (mg/cu m)								
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)

TABLE 15. GRAV MASS DATA

Sample Identification	Asphalt Temp (°C)	TCO MASS (mg)	GRAV MASS (mg)	TOTAL MASS (mg)	Real Weight Loss (kg)
Type 1 Condition 1	242	0.04	0.5	1.0	0.001
Type 1 Condition 2	325	0.03	1.6	1.6	0.002
Type 1 Condition 3	475	3.48	223.8	227.3	0.034
Type 2 Condition 1	270	0.13	0.9	1.0	0.002
Type 2 Condition 2	338	2.08	7.9	10.0	0.014
Type 2 Condition 3	475	2.34	113.6	115.9	0.030
Type 3 Condition 1	325	0.03	1.8	1.8	0.001
Type 3 Condition 2	425	0.34	41.0	41.3	0.013
Type 3 Condition 3	550	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 2 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 calculations. Table 26 presents the ASTM standards for roofing asphalt.

TABLE 16. COMPOUNDS IDENTIFIED BY MS FROM XAD AND FILTER EXTRACTS 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	$C_{31}H_{64}$

TABLE 17. TYPE 1 (TCO) CONDITION 1

Type 1 Asphalt (TCO)	Weight loss (kg)	0.0010	
Condition 1	Temperature (F)	242	
	Sample Volume (cu m)	9.49	

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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 (F)	325	
	Sample Volume (cu m)	9.58	

Compound	Compound Mass (ng)	Average Gasmous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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 (F)	475
	Sample Volume (cu m)	9.60

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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)	Weight loss (kg)	0.0015	
Condition 1	Temperature (F)	270	
	Sample Volume (cu m)	9.40	

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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)	Weight loss (kg)	0.0138
Condition 2	Temperature (F)	338
	Sample Volume (cu m)	9.72

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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	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 22. TYPE 2 (TCO) CONDITION 3

Type 2 Asphalt (TCO) Condtion 3	Weight loss (kg)	0.0297
	Temperature (F)	475
	Sample Volume (cu m)	9.80

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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 (F)	325
	Sample Volume (cu m)	10.14

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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)	Weight loss (kg)	0.0134	
Condition 2	Temperature (F)	425	
	Sample Volume (cu m)	9.67	

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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	43	

TABLE 25. TYPE 3 (TCO) CONDITION 3

Type 3 Asphalt (TCO) Condtion 3	Weight loss (kg)	0.1180
	Temperature (F)	550
	Sample Volume (cu m)	9.95

Compound	Compound Mass (ng)	Average Gaseous Conc. (mg/cu m)	Estimated Emissions (g/kg)	Emissions per Area (mg/sqm 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	27	

TABLE 26. ASTM STANDARDS

ANSI Guidelines for Roofing Asphalt (ASTM D312-78)

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

Type III 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 I		Type II		Type III	
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	...

SECTION 4

SUMMARY AND CONCLUSIONS

The purpose of this study was to characterize and 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 3 types of asphalt behave at the melting point, the equiviscous temperature, and an overheated temperature. Compounds identified during this study showed alkanes, aromatics, a ketone, and an aldehyde. Although alcohols were found in the cursory study performed in 1989, the absence of these compounds may be attributed to a difference in asphalt brand or a change in sampling procedures. The unheated sample duct 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.

An examination of the estimated emissions for the VOST and the XAD-2 shows 2 trends. The volatile organics decreased in concentration as the temperature rose, whereas the semi-volatiles rose in concentration with temperature. This characteristic of the volatile organics may attributed to the compounds being completely volatilized from the asphalt and diluted more rapidly at the higher

temperatures. This trend of the semi-volatiles may occur because the temperatures needed to volatilize these higher molecular weight compounds may be present only at the higher temperatures. These results indicate that human breathing zones may be affected only by volatile organics and lower-boiling-point semi-volatiles. The more carcinogenic semi-volatiles and poly-aromatic hydrocarbons may be condensing or precipitating before reaching people in the area. The people most affected by the vapors may be the workers handling the asphalt operations, such as kettle maintenance or asphalt pouring and mopping.

SECTION 5

REFERENCES

1. Internal Communication with Bobby Daniel , 1990.
2. "Characterization of Emissions from the Simulated Open Burning of Scrap Tires," EPA–600/2–89–054, October, 1989.
3. Hansen, E.M., "Protocol for the Collection and Analysis of Volatile POHCs Using VOST," EPA-600/8–84–007 (NTIS PB84-170042), March 1984.
4. 40-CFR Part 60, Appendix A, Method 5.
5. Method 8270SW-846 in Test Methods for Evaluating Solid Wastes, Vol. II, Field Manual Physical/Chemical Methods, EPA, November 1986.
6. 40-CFR Part 136, Method 610-Polynuclear Aromatic Hydrocarbons.
7. QAPP IACP study Roanoke, VA, November 1988, Appendix B.
8. AEERL ROP #41.
9. AEERL ROP #13.
10. AEERL ROP #12.
11. ASTM D312-78, Annual Book of ASTM Standards, Part 15.

APPENDIX A

QUALITY CONTROL EVALUATION REPORT

A Quality Assurance Project Plan (QAPP) was set forth to ensure that the collected data represented a simulated roofing asphalt kettle. All the objectives and procedures used during testing sampling and analysis are found in the QAPP (QTRAK No. 90020, AEERL Category III).

The accuracy and precision for the volatile organics were calculated from performance evaluation audit samples prepared by Research Triangle Institute (RTI). Three VOST tubes were received for analysis, two containing sample and one blank. After the results of the analysis were reported to RTI, a report was issued describing the quality of the results. The precision was 60.7 percent high for the tubes, but the accuracy was only 21.2 percent high. The identification by GC/MS of the compounds spiked on the Tenax tubes shows that 91 percent of the compounds were identified correctly. Eighty-nine percent of the VOST tubes were analyzed for the project. Completeness for all other aspects of the project was 100 percent analyzed.

Performance evaluation audit samples also were received from RTI for the semi-volatile organics analysis. The samples were received on 142-mm Teflon-coated, fiber glass filters. The filters were placed in a desiccator to allow the samples to dry before extraction. The samples were extracted and analyzed by TCO and GRAV. Neither technique determined whether any compounds were present in the samples. The extractions then were evaporated with nitrogen and analyzed by GC/MSD and, again, no compounds were found. The samples were belived to be spiked in concentrations below the detection limits for the instrument.

Prior to sampling, all dry gas meters were calibrated using an NBS traceable calibration system. Correction factors were determined for each meter. The dilution air volumes for the burn hut were determined using a pitot measuring system. Thermocouples were calibrated using freezing water and boiling water to test for accuracy. All samples were tracked using sample log forms to track sample custody (Figure 5). Sample conditions and sample IDs were recorded on field data sheets for volatile and semi-volatile samples (Figures 6-7).

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. 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.[b]	Leak Check	Cartridge I.D.		Rotameter Reading (l/min)	Time		Sampling Duration (min)	Probe Temp. (°C)	Barometric Pressure (in of Hg)	Condenser Outlet Temp. (°C)	Meter Temp. (Outlet)	Dry Gas Meter		Gas Sample Volume (liters)	Comments
		Tenax	Tenax/ Charcoal		Initial	Final						Initial	Final		

Condensate Samples:

Run No.	Sample I.D.	Comments

NOTES: [a]Reading should be tabulated at the beginning of a run and every five minutes thereafter.
[b]Refers to sample collection on one pair of Tenax and Tenax/charcoal traps.

Figure 6. VOST field data sheet.

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.