HETA 94–0365–2563
Spartan Paving Company
Lansing, Michigan

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PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

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Health Hazard Evaluation Report 94–0365–2563
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EXECUTIVE SUMMARY

Approximately 285 million used tires are discarded in the United States each year, posing significant health, fire, and solid waste management problems. As one means of reducing these problems, considerable attention has been focused on the use of the scrap tire rubber in highway paving materials. In 1991, Congress enacted the Intermodal Surface Transportation Efficiency Act (ISTEA), which required each state to use a minimum quantity of "crumb rubber modified" (CRM) hot-mix asphalt (HMA) paving material, beginning at 5% of the HMA used in federally funded paving in 1993, and increasing to 20% in 1997 and thereafter. Because of public concerns over the lack of available information on the environmental and human health effects resulting from the use of CRM-HMA, along with the high cost of using this paving material, a temporary legislative moratorium was passed which precluded enforcement of the penalty provisions of the ISTEA legislation. This legislation also directed the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Transportation, Federal Highway Administration (FHWA) to evaluate the potential environmental and human health effects associated with the use of CRM asphalt. The recently passed National Highway System Designation Act of 1995 has eliminated the mandate requiring the use of CRM asphalt but continues to require research concerning CRM asphalt paving.

Approximately 300,000 workers are currently employed in the asphalt paving industry in the U.S. In June 1994, the National Institute for Occupational Safety and Health (NIOSH) entered into an Interagency Agreement with the FHWA to evaluate occupational exposures among asphalt workers. A research protocol developed by NIOSH included the following objectives:

- Characterize and compare occupational exposures to CRM asphalt and conventional asphalt.
- Develop and field test new methods to assess asphalt fume exposures.
- Evaluate potential health effects associated with CRM asphalt and conventional asphalt.

The protocol allows for up to eight individual site evaluations in different geographic regions of the country, enabling investigators to observe different asphalt pavement formulations, climatic conditions, and paving techniques.

One of the greatest challenges in conducting this study is the fact that asphalt is not a consistent product. Asphalt is composed of a highly complex mixture of paraffinic and aromatic hydrocarbons and heteroatomic compounds containing sulfur, nitrogen, and oxygen. The specific chemical content of asphalt products is dependent on the crude petroleum source, production techniques, and process temperatures. The addition of rubber further complicates the asphalt mixture as numerous additional substances present in tires (such as aromatic oils, accelerants, and antioxidants used during tire manufacturing) may become airborne during the asphalt heating and

mixing processes. Finally, there is a lack of available air sampling methods and occupational exposure limits for most of the compounds present in asphalt and the rubber tire components.

This report presents the findings from the first site evaluation conducted in Lansing, Michigan, during asphalt pavement construction on Interstate 96. The purpose of this report is not to draw definitive conclusions about CRM asphalt and conventional asphalt exposures, but rather to provide the site-specific information obtained at the Lansing, Michigan, project.

On August 30 and 31, 1994, approximately 2,495 metric tons of conventional asphalt were applied by ten workers of Spartan Paving Company; 1,787 metric tons of CRM asphalt were placed September 1 and 2 by the same workers. The rubber content was approximately 15% by weight of the asphalt binder. The field exposure assessment was performed during all four paving days. The evaluation included the collection of area air samples to characterize the asphalt fume emission, personal breathing zone (PBZ) air samples to evaluate worker exposures, and a medical component that included symptom questionnaires and lung function tests. To evaluate worst-case conditions and characterize the asphalt fume, the area air samples were collected above the screed auger of the paving vehicle and adjacent to the paver hopper.

Asphalt fume exposures have typically been measured as total particulate and the benzene soluble particulate fraction. However, since neither of these exposure markers measure exposure to a distinct chemical component or even a distinct class of chemicals, it is difficult to relate them to possible health effects. For example, many organic compounds are soluble in benzene, and any dust may contribute to total particulate levels. In an effort to address this problem, new or modified analytical methods were developed and included in this study to more definitively characterize asphalt fume exposures. For example, polycyclic aromatic compounds (PACs), which may be present in asphalt fume, were measured using a new analytical method. Some of the PACs are believed by NIOSH investigators to have irritative effects while other PACs are suspected to be carcinogenic. In addition to PACs, benzothiazole (a sulfur-containing compound present in rubber tires) along with other sulfur-containing compounds (suspected to be present as a result of the addition of rubber to the asphalt or from crude petroleum used for asphalt manufacturing) were also measured. Benzothiazole is of interest since it may be useful as a surrogate indicator for other CRM asphalt fume exposures while other sulfur-containing compounds may be associated with respiratory irritation. Samples were collected for selected organic compounds (toluene, benzene, and methyl isobutyl ketone) and total hydrocarbons (as Stoddard solvent). Elemental carbon was measured to determine if diesel exhaust could have contributed to the air contaminants measured at the paving site. The airborne particulate at the paving site was analyzed to determine the concentration of particles which were respirable. Air samples were collected for 28 different metals and minerals and direct-reading instruments were used to measure carbon monoxide, hydrogen sulfide, sulfur dioxide, and ozone. Finally, bulk air samples of asphalt fume were collected at the asphalt cement storage tank located at the hot mix asphalt plant and submitted for mutagenicity testing.

The area air sample results indicate that total particulate, respirable particulate, and benzene soluble particulate concentrations were higher during the CRM asphalt paving period as compared with the conventional asphalt paving period. Total PAC concentrations above the paver screed on CRM asphalt paving days were approximately three times the total PAC concentrations detected on conventional asphalt paving days. Furthermore, the CRM asphalt paving generated more benzothiazole and other sulfur-containing compounds than the conventional asphalt paving. Over 50 volatile organic compounds were detected in the asphalt emissions, however, only the most significant peaks were analyzed quantitatively. The concentrations of benzene, toluene, methyl isobutyl ketone, and total “other” hydrocarbons were orders of magnitude below their respective occupational exposure criteria in both types of asphalt. Extremely low or trace concentrations of the following metals were detected during all paving operations: aluminum, calcium, iron, magnesium, manganese, and titanium.

Personal breathing-zone (PBZ) air samples were collected on 11 workers during each of the four days of sampling. The PBZ samples were analyzed for total particulates, and for some workers, a second sample was analyzed for either total PACs, other sulfur compounds and benzothiazole, or for benzene soluble particulates. The PBZ exposures for total particulates ranged up to 1.2 milligrams per cubic meter (mg/m^3), but the highest exposures were not necessarily from workers whose jobs were in close proximity to asphalt fume emissions. All of the PBZ concentrations were well below the asphalt fume criteria of 5 mg/m^3 (measured as total particulate) currently recommended by NIOSH.

Seven of the ten workers directly associated with the asphalt paving operation (pavers) were included in a health assessment. Additionally, five workers performing jobs associated with road construction, but not exposed to asphalt fume (non-pavers), were included for comparison. Serial symptom questionnaires were administered to obtain information concerning the prevalence of acute symptoms (i.e., respiratory, eye, nose, throat, and skin symptoms) in relation to worksite exposures. Serial measurements of peak expiratory flow rate (PEFR) were conducted to evaluate acute changes in lung function in relation to worksite exposures. Among pavers, the acute symptom survey revealed an 8-fold increase in the number of reported health symptoms, and a 14-fold increase in the rate of reported symptoms per hour of estimated asphalt fume exposure during the CRM asphalt paving period as compared to the conventional asphalt paving period. Most notable was the increased reporting of nose and throat symptoms during CRM asphalt paving. Lower airway symptoms were reported by several workers in association with work exposures, but none of these symptoms were accompanied by significant bronchial lability. The PEFR results at this study site did not appear to show an association between measurable bronchospastic responses and asphalt paving work.

This study showed that asphalt fume emissions, as well as other exposure measurements, were below current NIOSH Recommended Exposure Limits or other relevant exposure limits for those substances with established occupational exposure criteria. Acute symptoms were reported by workers in association with asphalt paving exposures, with higher symptom responses associated with CRM asphalt paving. Presently, it is premature to draw definitive conclusions from this single site evaluation. Data provided from this evaluation are based on a very small sample size and may reflect production and weather conditions specific to this site. Additional site evaluations may enable more definitive conclusions to be drawn. A final composite report will be prepared after these additional site evaluations are completed.

Keywords: SIC 1611 (Highway and Street Construction), asphalt fume, bitumen, crumb rubber modifier, CRM, recycled tires, paving, interstate highways, polycyclic aromatic compounds, PACs, polynuclear aromatic hydrocarbons, PAH, total particulate, respirable particulate, benzene soluble particulate, volatile organic compounds, hydrocarbons, elemental carbon, eye irritation, respiratory irritation.

TABLE OF CONTENTS

PROCESS OVERVIEW

There are three basic steps in constructing an asphalt pavement - manufacture of the hot mix asphalt (HMA), placement of the mix onto the ground, and compaction. The asphalt mix contains two primary ingredients, a binder which is typically an asphalt cement, and an aggregate which is usually a mixture of coarse and fine stones, gravel, sand, and other mineral fillers. The mix design establishes the proportions of the aggregate materials and sizes to the amount of asphalt cement to obtain the appropriate pavement properties (flexibility, drainage, durability, etc.).

The purpose of an HMA plant is to blend the aggregate and asphalt cement to produce a homogenous paving mixture at a hot temperature so that it can be easily applied and compacted. Asphalt cement is typically received from a refinery by tractor trailer tankers and is transferred into heated storage tanks. Aggregate of different materials and sizes is blended through a series of belt conveyors and a dryer (a heated drum mixer). Once the aggregate is sufficiently blended and dried, asphalt cement is applied so that a continuous thin film of cement covers the aggregate evenly. The finished HMA is then placed in a storage silo until it can be dispensed into trucks that haul the material to the paving site. At the paving site the following equipment is typically used:

- **Tack truck**: A vehicle which precedes the paver and applies a low viscosity asphalt ("tack" coat) to the roadway to improve adhesion prior to the HMA placement.

- **Paver**: A motorized vehicle which receives the HMA from the delivery trucks and distributes it on the road in the desired width and depth. The HMA may be directly transferred from the delivery truck to the paver by: (1) directly pouring HMA into a hopper located in the front of the paver; (2) dumping HMA in a line onto the road where it is picked up by a windrow conveyor and loaded into the paver hopper; or (3) conveying the mix with a material transfer vehicle.

- **Screed**: Located at the rear of the paver, the screed distributes the HMA onto the road to a preselected width and depth and grades the HMA mix to the appropriate slope as the paving vehicle moves forward.

- **Rollers**: Typically two or three roller vehicles follow the paver to compact the asphalt.

Paving crews normally consist of eight to ten workers. Job activities include a foreman who supervises the crew; a paver operator who drives the paver; one or two screed operators who control and monitor the depth and width of the HMA placement; one or two rakers who shovel excess HMA, fill in voids and prepare joints; laborers who perform miscellaneous tasks; roller operators who drive the rollers; and a tackman who applies the tackcoat. The paver operators and roller operators do not usually perform different jobs, while the screed operators, rakers, and laborers may perform a variety of tasks throughout the workday.

For purposes of this report, workers associated with the asphalt paving operation (i.e., workers with potential exposure to HMA fume) will be referred to as "pavers." This definition may include workers not specifically employed by the paving contractor (i.e., state highway inspectors) but who are associated with the paving operation and could be exposed to HMA fume during paving. Additionally, some workers who performed jobs associated with road construction, but <u>not</u> exposed to HMA fume (i.e., foremen, laborers, heavy equipment operators, and road surveyors), participated as a control group for the pavers and will be referred to as "non-pavers."

SITE DESCRIPTION

On August 29 through September 2, 1994, NIOSH investigators conducted a study at Spartan Paving Company in Lansing, Michigan, during asphalt pavement construction on Interstate 96. The same

10-person paving crew was evaluated throughout the survey and consisted of a foreman, a paver operator, an operator trainee, a screed operator, a raker, a laborer, three roller operators, and a tackman.

During this survey, both the conventional hot mix asphalt (hereafter referred to as "conventional asphalt") and crumb rubber modified hot mix asphalt (subsequently referred to as "CRM asphalt") were manufactured at the same plant from the same petroleum crude source. The conventional asphalt was placed on August 30 and 31 while the CRM asphalt was used on September 1 and 2. All of the paving occurred on the east-bound lanes of I-96 with the traffic diverted to the west-bound lanes.

A summary of the paving activities and equipment used at the I-96 site are contained in Table 1. Both of the projects required the placement of a '2C' base course using a dense gradation (i.e., an evenly distributed aggregate gradation containing particle sizes ranging from 75 micrometers [µm] up to 2.5 centimeters [1 inch] in diameter. While most of the granulated rubber was manufactured by Rouse Industries, a small percentage was provided by the Baker Rubber Company. The rubber content of the CRM asphalt was approximately 15% by weight of the asphalt cement. A 85/100 penetration grade was used in the conventional mix while, in contrast, a 200/250 penetration grade was used for the CRM mix (to reduce its viscosity).

The HMA plant for this construction project was located in East Lansing, approximately 30 to 40 minutes from the I-96 paving sites. During the first two days of conventional asphalt paving, the HMA was hauled to the paving site by eight "flowboy" trailer trucks (the capacity of these bottom conveyor trailers is approximately 45 metric tons [50 short tons] of HMA). This resulted in an average paving production rate of approximately 172 metric tons/hour during conventional asphalt paving. In contrast, on the first day of CRM asphalt paving, the HMA was hauled to the site using only five tandem axle dump trucks (the total capacity of each tandem dump truck was 36 metric tons (40 short tons). The use of smaller and fewer trucks reduced the average paving production rate to approximately 109 metric tons (120 short tons/hour). However, on the second CRM asphalt paving day, asphalt was again hauled to the paving site using eight flowboy trailers, increasing the average production rate to 172 metric tons/hour (190 short tons/hour).

The conventional asphalt was used to construct the mainline (traffic lanes) and shoulders, whereas the CRM asphalt was used to construct ramps, ramp shoulders, and a mainline shoulder. Approximately 1,340 and 1,155 metric tons of conventional asphalt were applied on August 30 and 31, respectively, compared to 869 and 918 metric tons of CRM asphalt placed, respectively, during September 1 and 2. The mean temperatures for the asphalt mix as it was applied were 142°C (287°F), 147°C (296°F), 134°C (273°F), and 147°C (296°F) for days 1 through 4. The depth of both the conventional asphalt and CRM asphalt course was approximately 10 centimeters (4 inches); the width of the paving was typically about 3 meters (approximately 10 feet) wide.

Two paving vehicles (auxiliary and primary) were used during the conventional asphalt period. The auxiliary paver received the HMA mix directly into its hopper from the flowboy trucks. This paver then placed the material onto the road in a windrow approximately 1.5 meters (5 feet) wide and 0.5 meters (1.5 feet) high. The primary paver, following directly behind the auxiliary paver, used a windrow conveyor to pick up the conventional asphalt from the road and load it into the hopper. The primary paver then placed the asphalt on to the ground with a screed attachment. In contrast, during the CRM asphalt placement, the HMA mix was transferred directly from the delivery trucks into the hopper of the primary paver that contained a screed placement attachment.

INDUSTRIAL HYGIENE EVALUATION DESIGN

Previous research efforts by NIOSH investigators and other researchers have attempted to characterize asphalt fume exposures among road paving workers. Asphalt fume exposures have typically been measured as total particulates and benzene soluble particulate fraction. Correspondingly, occupational exposure criteria for asphalt fume have been expressed in terms of total particulates and the benzene soluble fraction of the particulates. However, since neither of these exposure markers measure exposure to a distinct chemical component or even a distinct class of chemicals, it is difficult to relate them to possible health effects. For example, many organic compounds are soluble in benzene, and any dust may contribute to total particulate levels. In an effort to address this situation, new or modified sampling and analytical methods were developed and included in this study. For example, polycyclic aromatic compounds (PACs) which may be present in asphalt fume were measured using a new analytical method. Some of the PACs are believed to have irritative effects while other PACs are suspected to be carcinogenic. In addition to PACs, benzothiazole (a sulfur-containing compound present in rubber tires) along with other sulfur-containing compounds (suspected to be present as a result of the addition of rubber to the asphalt or from high sulfur crude petroleum used for asphalt manufacturing) were also measured. Benzothiazole is of interest since it may be useful as a surrogate indicator for other CRM asphalt fume exposures while other sulfur-containing compounds may be associated with respiratory irritation. Samples were collected for selected organic solvents (toluene, benzene, and methyl isobutyl ketone) and total hydrocarbons (as Stoddard solvent). Elemental carbon was measured to determine if diesel exhaust could have contributed to the air contaminants measured at the paving site. The airborne particulate at the paving site was analyzed to determine the fraction of particles which were respirable. Air samples were collected for 28 different metals and minerals and direct-reading instruments were used to measure carbon monoxide, hydrogen sulfide, sulfur dioxide, and ozone. Bulk air samples of asphalt fume were collected at the asphalt cement storage tank located at the hot mix asphalt plant and submitted for mutagenicity testing.

Weather Information

Meteorological conditions were recorded at regular intervals to allow comparison among survey days. The meteorological data included dry bulb and wet bulb temperatures (for subsequent calculation of relative humidity), wind speed and direction, and wet bulb globe temperature (WBGT). Wind speed and direction were measured with a Climatronics® cup anemometer equipped with a strip chart recorder. Environmental measurements were obtained at 15-minute intervals using a Reuter Stokes RSS 214 Wibget® heat stress meter.

Process Information

Process information and operational details were recorded daily by FHWA, State Department of Transportation (DOT), contractors, or NIOSH investigators. This information included the asphalt grade, type of application, crude source, percent rubber, additives, production quantities, application temperature, paving depth, average application rate, site description, and traffic density.

Area Air Samples

To evaluate worst-case conditions and characterize the asphalt fume, area air samples were collected above the screed auger of the paving vehicle and adjacent to the paver hopper. Background area air samples were collected in the construction trailer yard and in the highway median to evaluate the ambient air and possible impact from vehicle emissions. Area samples were collected for total and respirable particulate, PACs, sulfur-containing compounds (including benzothiazole), benzene soluble fraction (BSF), aromatic and aliphatic solvents (based on the qualitative identification of volatile organic compounds via mass spectroscopy), elemental and organic carbon, and elemental metals. Direct reading instruments were used to measure carbon monoxide, hydrogen sulfide, sulfur dioxide, and ozone.

Except for the samples obtained with direct-reading instruments, air samples were collected using calibrated battery-operated sampling pumps with the appropriate sorbent tube or filter media connected via Tygon® tubing. The area and personal breathing-zone (PBZ) sample concentrations were calculated based on the actual monitoring time (time-weighted average [TWA-actual] concentrations) instead of calculating an 8-hour TWA concentration so that the sampling data could be compared between days that had unequal monitoring durations. Calibration of the air sampling pumps with the appropriate sampling media was performed daily, before and after each monitoring period. Field blanks were collected and submitted to the laboratory for each analytical method.

High volume air samples of the asphalt fume were collected above an open hatch on the asphalt cement storage tank at the HMA plant and are being evaluated at various concentrations for mutagenic activity via a modified Ames testing protocol. The basic analytical procedure has been described by Maron and Ames [1983], except a spiral plater device described by Houk et al. [1989, 1991] is used. The results from these modified Ames tests of asphalt fume will be discussed in a separate NIOSH report.

Personal Breathing-Zone Air Samples

Personal breathing-zone monitoring was conducted on all ten members of the paving crew and one state highway employee (a density checker who was assigned to this paving operation). Total particulate samples were collected on all workers. Air samples for benzene soluble particulate, PACs, and sulfur-containing compounds (including benzothiazole) were also collected on some workers.

Air Sampling Methods

Table 2 summarizes all of the air sampling methods used in this evaluation. Since sampling for PACs involved a new analytical technique, Appendix A is included to provide additional detail on this method. Appendix B is the draft NIOSH Sampling and Analytical Method No. 5040 for elemental carbon.

MEDICAL EVALUATION DESIGN

On August 29th, NIOSH investigators began recruiting workers to participate in the health assessment, which included a general health and occupational history questionnaire, serial acute symptom questionnaires, and serial peak expiratory flow rate (PEFR) testing. PEFR testing was conducted to evaluate acute changes in lung function. Peak flow rate refers to the amount of air in liters per minute that can be exhaled through the flow meter in one complete breath.

All ten pavers were asked to participate in the study. Seven pavers volunteered and were included in the health assessment. With the assistance of Spartan Paving management, NIOSH investigators also recruited five non-pavers working at the same construction site, but not in proximity to the asphalt paving operation, to participate in the health assessment for comparison purposes.

A general health questionnaire was privately administered to each health assessment participant once during the study. Each worker was asked about the presence of chronic respiratory, eye, nose, throat, and skin symptoms. Additionally, information concerning smoking history and work history was solicited.

Acute symptom questionnaires were periodically administered to all study participants during their workshift to determine if eye, nose, throat, skin, or respiratory symptoms (including cough, chest tightness, or wheezing) were associated with their job. Whenever possible, the acute symptom questionnaires were administered before and after each work shift and three times during the work shift, at approximately two-hour intervals during each survey day.

PEFR measurements were made using Wrights portable peak flow meters just prior to the administration of the acute symptom questionnaire. Three exhalations were recorded each time, and the highest of the three recordings was accepted as the PEFR determination. Participants were considered to have significant bronchial lability if the difference between the minimum and the maximum PEFR on at least one day exceeded 20% of that day's maximum PEFR.

EVALUATION CRITERIA

To assess the hazards posed by workplace exposures, NIOSH investigators use a variety of environmental evaluation criteria. These criteria are exposure limits to which most workers may be exposed for a working lifetime without experiencing adverse health effects. However, because of the wide variation in individual susceptibility, some workers may experience occupational illness even if exposures are maintained below these limits. The evaluation criteria do not take into account individual sensitivity, preexisting medical conditions, medicines taken by the worker, possible interactions with other workplace agents, or environmental conditions.

The primary sources of evaluation criteria for the workplace are NIOSH criteria documents and recommended exposure limits (RELs) [NIOSH 1994], the Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) [OSHA 1993], and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs®) [ACGIH 1995]. These occupational health criteria are based on the available scientific information provided by industrial experience, animal or human experiments, or epidemiologic studies. It should be noted that RELs and TLVs are guidelines, whereas PELs are legally enforceable standards. The NIOSH RELs are primarily based upon the prevention of occupational disease without assessing the economic feasibility of the affected industries and, as such, tend to be conservative. The OSHA PELs are required to take into account the technical and economical feasibility of controlling exposures in various industries where the agents are present. A Court of Appeals decision vacated the OSHA 1989 Air Contaminants Standard in *AFL-CIO v OSHA*, 965F.2d 962 (11th cir., 1992); and OSHA is now enforcing the previous standards (listed as Transitional Limits in 29 CFR 1910.1000, Table Z-1-A), which were originally promulgated in 1971. However, some states with OSHA-approved state plans continue to enforce the more protective ("final rule") limits promulgated in 1989. For exposures with evaluation criteria, NIOSH encourages employers to use the 1989 OSHA PEL or the NIOSH REL, whichever is lower.

Evaluation criteria for chemical substances are usually based on the average PBZ exposure to the airborne substance over an entire 8- to 10-hour workday, expressed as a time-weighted average (TWA). Personal exposures are usually expressed in parts per million (ppm), milligrams per cubic meter (mg/m^3), or micrograms per cubic meter ($\mu g/m^3$). To supplement the TWA where adverse effects from short-term exposures are recognized, some substances have a short-term exposure limit (STEL) for 15-minute periods; or a ceiling limit, which is not to be exceeded at any time. Additionally, some chemicals have a "skin" notation to indicate that the substance may be appreciably absorbed through direct contact of the material or its vapor with the skin and mucous membranes.

It is important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these occupational health exposure criteria. A small percentage may experience adverse health effects because of individual susceptibility, preexisting medical conditions, previous exposures, or hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, or with medications or personal habits of the worker (such as smoking) to produce health effects even if the occupational exposures are controlled to the limit set by the evaluation criterion. These combined effects are often not considered by the chemical-specific evaluation criteria. Furthermore, many substances are appreciably absorbed by direct contact with the skin and thus potentially increase the overall exposure and biologic response beyond that expected from inhalation alone. Finally, evaluation criteria may change over time as new information on the toxic effects of an agent becomes available. Because of these reasons, it is prudent for an employer to maintain worker exposures well below established occupational health criteria.

Asphalt Fumes (Petroleum)

Asphalt, produced from refining crude petroleum, is commercially valuable for pavement construction because of its adhesive properties, flexibility, durability, water and acid resistance, and its ability to form strong cohesive mixtures with mineral aggregates. Asphalt pavement is the major paving product in commercial use and accounts for 85% of the total asphalt usage (and over 90% of the roadway paving) in the United States [AI 1990]. About 4,000 HMA facilities and 7,000 paving contractors employ nearly 300,000 workers in the United States [AI 1990].

The specific chemical content of asphalt, a brown or black solid or viscous liquid at room temperature, is difficult to characterize because it is extremely complex and variable. In general, asphalt primarily contains high molecular weight cyclic hydrocarbon compounds as well as saturated organics. The chemical composition and physical properties of the asphalt products are influenced by the original crude petroleum and the manufacturing processes. The basic chemical components of asphalt include paraffinic, naphthenic, cyclic, and aromatic hydrocarbons as well as heteroatomic molecules containing sulfur, oxygen, and nitrogen [AI 1990].

Petroleum based asphalt and coal tar pitch are often considered to be equivalent materials because of their similar physical appearance and construction applications. However, these materials are quite different chemically as a result of raw material origin and manufacturing processes. Approximately 80% of the carbon in coal tar is associated with the aromatic ring structures, whereas less than 40% of the carbon in asphalt is present in aromatic rings [Puzinauskas 1978]. Furthermore, analysis by nuclear magnetic resonance indicated that an asphalt fume condensate was <1% aromatic and >99%aliphatic, whereas a coal tar pitch condensate was >90% aromatic [Niemeier et al. 1988]. Coal tar has a greater reported carcinogenic activity than asphalt and is considered an occupational carcinogen by NIOSH [1992] and ACGIH [1995].

In a 1977 criteria document, NIOSH established a REL of 5 mg/m^3 (as a 15-minute ceiling limit) for asphalt fumes, measured as a total particulate. This level was intended to protect against acute effects, including irritation of the serous membranes of the conjunctivae and the mucous membranes of the respiratory tract [NIOSH 1977a]. Asphalt fumes can be absorbed through the lungs or the skin. Hansen [1991] and Maizlish et al. [1988] indicated that nonmalignant lung diseases such as bronchitis, emphysema, and asthma were also among the toxic effects of exposure to asphalt fumes. Norseth et al. [1991] reported that during road repair and construction, three groups of asphalt workers experienced abnormal fatigue, reduced appetite, eye irritation, and laryngeal/pharyngeal irritation.

Since publication of the criteria document [NIOSH 1977a], data have become available indicating that exposure to roofing asphalt fume condensates, raw roofing asphalt, and asphalt-based paints may pose a risk of cancer to workers occupationally exposed. In 1988, NIOSH recommended that asphalt fumes be considered a potential occupational carcinogen [NIOSH 1988]. This recommendation was based on information presented in the 1977 criteria document [NIOSH 1977a] and a study by Niemeier et al. [1988] showing that exposure to condensates of asphalt fumes caused skin tumors in mice. Several epidemiologic studies concerning workers exposed to asphalt fumes have indicated a potential excess in mortality from cancer [Hansen 1989a,b, 1991; Maizlish et al. 1988; Engholm et al. 1991; Wilson

1984; Bender et al. 1989; Mommsen et al. 1983; Risch et al. 1988; Bonassi et al. 1989].

Currently there is no OSHA PEL for asphalt fume. In 1992, OSHA published a proposed rule for asphalt fumes that included a PEL of 5 mg/m^3 (total particulate) for general industry as well as for the maritime, construction, and agricultural industries [OSHA 1992]. OSHA is presently reviewing public comments. The current ACGIH TLV® for asphalt fumes is 5 mg/m^3 as an 8-hour TWA [ACGIH 1995]. This TLV was recommended to "maintain good housekeeping conditions and reduce the risk of possible carcinogenicity" [ACGIH 1992].

Table 3 summarizes the toxicity and exposure criteria information for asphalt fume and the other contaminants evaluated during this study, including total particulate, respirable particulate, benzene soluble particulate fraction, PACs, elemental carbon, and selected organic solvents.

INDUSTRIAL HYGIENE RESULTS

Weather

A daily description of the weather is extremely important since the outdoor conditions directly impact the construction process and air sampling results. Table 4 summarizes the weather data recorded for each survey day. Both of the conventional asphalt paving days were cloudy and overcast, while the CRM asphalt paving days were predominantly clear and sunny. The high temperatures recorded for all 4 days ranged from 19 to 23°C (67 to 74°F), and the average temperatures ranged from 15 to 20°C (59 to 68°F).

Wind speed and direction are particularly important factors that may influence the air sampling results. As shown in Table 4, the wind velocity and direction pattern differed each day. The strongest winds were observed on August 31 and on September 1. For the first three sampling days, the wind directions were somewhat consistent throughout the day but not between days. In contrast, the wind direction was variable on the last day, September 2.

Process Information

When reviewing the industrial hygiene results, it is important to note that mainline traffic lanes and shoulders were paved using conventional asphalt, whereas CRM asphalt was used mostly for ramps and ramp shoulders. This resulted in less paving time and lower production quantities for CRM asphalt compared to conventional asphalt. Furthermore, a windrow conveyor was used to load the paver hopper only on conventional asphalt paving days, a procedure which caused more agitation of the mix.

Area Air Samples

Total Particulate and Respirable Particulate

Tables 5 and 6 present results for the total and respirable particulate sampling, respectively. Total particulate concentrations were all below the 5 mg/m^3 exposure criteria. For each day, the total particulate concentrations measured at the paver screed were higher than those collected near the hopper. The two highest total particulate area concentrations (2.5 and 1.0 mg/m^3) were measured above the screed during CRM asphalt paving. The highest total particulate background concentration measured during this survey (0.36 mg/m^3) was collected in the construction trailer yard. However, this concentration may have included road dust generated by vehicle traffic on a nearby dirt road. In comparison, other total particulate background samples were $\leq$0.07 mg/m^3.

As shown in Table 6, the highest respirable dust concentrations were also measured over the screed, ranging from 0.08 to 0.52 mg/m^3. All of the remaining respirable dust concentrations were either non-detected (ND) or detected in very low concentrations.

Benzene Soluble Particulate Fraction (BSF)

As summarized in Table 7, the highest BSF concentrations (regardless of the hot mix asphalt composition) were measured over the screed. Overall, higher concentrations were measured during CRM asphalt paving (range: Traces to 0.97 mg/m^3) than during the conventional asphalt paving periods (range: Traces to 0.22 mg/m^3). There are no occupational exposure criteria for the benzene soluble particulate fraction (of asphalt fume) from NIOSH, OSHA, or ACGIH.

Polycyclic Aromatic Compounds (PACs), Sulfur-containing Compounds, and Benzothiazole

Several asphalt fume source samples from this study were analyzed by high pressure liquid chromatography (HPLC). The chromatograms obtained from these samples demonstrated the typical pattern associated with asphalt fume which prevented quantitation. Hence, NIOSH method 5506 was modified to quantitate total PACs, as a class, via a flow injection technique with spectrofluorometric detection using emission wavelengths of 370 and 400 nanometers (nm). The 370 nm emission wavelength provides greater sensitivity to 2-3 ring PACs and the 400 nm wavelength is more sensitive to 4-7 ring PACs.

Table 8 summarizes the total PAC area concentrations collected at emission locations as well as the background locations. The concentration for the total PAC_{370} at emission sources ranged from 1.9 to 14 $\mu g/m^3$ for conventional and from 1.4 to 33 $\mu g/m^3$ for CRM asphalts. The total PAC_{400} concentrations from these same samples ranged from 1.2 to 3.1 and from traces to 12 $\mu g/m^3$, respectively, for conventional and CRM asphalt paving. In every sample, the PAC_{370} concentrations were greater than the PAC_{400}, implying that the 2-3 ring PACs may be more abundant. The smaller ring number PACs are believed to be associated with more irritative effects, whereas more concern exists for suspect carcinogenicity of the 4-7 ring PACs. Occupational exposure criteria for total PACs, as a class, are presently unavailable from either NIOSH, OSHA, or ACGIH.

Table 8 also presents the sulfur compounds and benzothiazole concentrations obtained from hexane extracts of PAC samples which were analyzed by gas chromatography with sulfur chemiluminescence detection. Only trace levels of benzothiazole were detected during conventional asphalt paving; benzothiazole concentrations at the screed during CRM asphalt paving, however, ranged from 26 to 59 micrograms per cubic meter ($\mu g/m^3$). The highest concentrations detected for other sulfur compounds during conventional and CRM asphalt paving were 5.6 and 37 $\mu g/m^3$, respectively.

Elemental (EC) and Organic Carbon (OC)

Elemental and organic carbon analytical results are provided in Table 9. In general, a high elemental carbon (EC) to total carbon (TC) ratio and EC concentrations above background levels suggest that diesel engine exhaust may be contributing to other exposure measurements made in this study (such as the PAC results). All of the EC concentrations collected on the paver vehicle were above the background concentrations, suggesting that some diesel exhaust was present. The EC:TC ratio ranged from 0.07 to 0.11 near the hopper (which is adjacent to the paver engine) and from 0.02 to 0.06 above the screed. Since diesel exhaust has been reported to contain EC levels between 0.6 to 0.8 of the TC [Blade 1989], these ratios imply that diesel exhaust was not excessively contributing to these air sampling results.

Volatile Organic Compounds (VOCs) and Elements

Table 10 summarizes the predominant VOC concentrations detected during conventional and CRM asphalt paving periods. The qualitative GC/MS analysis identified over 50 VOCs. However, only the most significant peaks (benzene, toluene, methyl isobutyl ketone [MIBK], and total other hydrocarbons resembling a Stoddard solvent chromatogram pattern) were quantitatively analyzed by GC/FID. The quantities of these VOCs were orders of magnitudes below their respective occupational exposure criteria published by NIOSH, OSHA, or ACGIH.

Trace quantities or extremely low concentrations were observed for aluminum, calcium, iron, magnesium, manganese, and titanium. All other elements were not detected.

Hydrogen Sulfide (H_2S), Sulfur Dioxide (SO_2), Carbon Monoxide (CO), and Ozone (O_3)

Hydrogen sulfide, SO_2, CO, and O_3 were present in very low concentrations and were well below their respective occupational exposure criteria. Hydrogen sulfide and SO_2 concentrations near the screed were usually ND (with a few readings of 1 ppm); the highest CO concentration on the paver deck was 4 ppm; and the background O_3 concentrations ranged from 0.01 to 0.012 ppm.

Personal Breathing–Zone Air Samples

Table 11 presents the PBZ monitoring results for total particulate collected during conventional and CRM asphalt paving operations. The PBZ exposure to total particulate ranged from 0.01 to 1.2 mg/m^3 and from 0.06 to 1.2 mg/m^3 during conventional and CRM asphalt paving, respectively.

One of the highest recorded exposures was obtained on the finish roller operator. Most of this exposure is presumably due to general road dirt and dust since this roller operator was remote from the asphalt fume generation. The laborer's exposure was often higher than the other employees' exposure. However, this job had tasks that generated dust, including the occasional operation of a front end loader and a pavement saw. Total particulate PBZ exposure of the paver and screed operators (jobs in close proximity to asphalt fume emissions) ranged from 0.1 to 0.2 mg/m^3 during conventional asphalt paving and from 0.2 to 0.36 mg/m^3 during CRM asphalt paving.

Table 12 contains the PBZ results for PACs, benzothiazole, and sulfur compounds for the operator trainee and raker. The concentrations of PAC_{370} and PAC_{400} for these jobs ranged from 2.0 to 16 µg/m^3 and from <0.1 to 4.2 µg/m^3, respectively. The PBZ exposure to benzothiazole ranged from <0.38 to 13 µg/m^3, while exposures to other sulfur compounds ranged from <0.41 to 12 µg/m^3. Benzothiazole PBZ concentrations were either ND or detected in trace quantities during conventional asphalt paving. Due to the limited number of PBZ samples collected and the variable nature of the job tasks, it is not possible to determine from these PBZ exposures whether higher exposure occurred during the CRM asphalt paving.

A limited number of PBZ samples were collected for BSF particulate during this survey. The only PBZ sample that measured detectable BSF particulate occurred on the roller operator on the last CRM asphalt paving day. This operator also had one of the highest total particulate PBZ exposures recorded during this survey, implying that most of this exposure was not due to asphalt fume since the BSF concentration (0.13 mg/m^3) was substantially less than the total particulate exposure (1.2 mg/m^3).

MEDICAL RESULTS

The seven pavers participating in the health assessment included one paver operator, one screed operator, two roller operators, one raker, one laborer, and one tackman. The tackman also performed asphalt raking on occasion. The five non-pavers included one crew foreman, one laborer, two heavy equipment operators, and one road surveyor. All twelve workers participated in the study for all four survey days.

Six of the seven pavers were male and the average age of this group was 43 years (range 35 to 49 years). All of the non-pavers were male and the average age of this group was 41 years (range 22 to 61 years). Five (71%) of the pavers currently smoked cigarettes (all except one of these workers smoked during work), one was a former smoker, and one never smoked. Only one (20%) of the non-pavers currently smoked cigarettes (and smoked during work), one was a former smoker, and three never smoked.

The number of acute symptom questionnaires completed (i.e., the number of opportunities a worker had to report a health symptom) varied between survey days and among the pavers and non-pavers (Table 13). For each survey day, a maximum of 35 (seven pavers times five questionnaires/day) and 25 questionnaires (five non-pavers times five questionnaires/day) could have been completed for the pavers and non-pavers, respectively. About 25% more acute symptom questionnaires were completed during the CRM asphalt paving period (102 questionnaires) as compared to the conventional asphalt paving period (81 questionnaires).

Responses to the acute health questionnaires were evaluated for symptoms potentially associated with worker tasks and exposures. A worker could report seven different types of symptoms during each survey time (see Table 14); each such symptom report will be referred to as a "symptom occurrence." Thus, if a worker completed all five daily acute health questionnaires and reported all seven symptoms during each survey, he/she would have 35 symptom occurrences for that survey day.

Table 14 shows the number of workers reporting a health symptom at any time during a survey day. Also shown are the number of symptom occurrences reported during the survey day. Among non-pavers, all five symptom occurrences were reported by one worker on the two survey days. Among pavers, three workers reported symptoms on the first conventional asphalt paving day; two reported three occurrences of nasal symptoms and one worker reported four occurrences of wheezing. None of the pavers reported symptoms on the second conventional asphalt paving day. All seven pavers reported symptoms on both CRM asphalt paving days, with 67 symptom occurrences reported on these two days. Among pavers, the most frequently reported symptoms (as a percentage of occurrences on all four days) were throat irritation (43%) and nasal irritation (22%). Most of these reports (94%) occurred during the CRM asphalt paving period. Lower airway symptoms of chest tightness (12%) and cough (11%) were only reported during the CRM asphalt paving period. A total of 74 symptom occurrences were reported by pavers during the entire survey. Eighty-one percent (60/74) of the symptoms were reported during ongoing or recent exposure to asphalt fumes. Seven symptom occurrences (10%) were reported during the conventional asphalt paving period, as compared to 67 symptom occurrences (90%) reported during the CRM asphalt paving period. Ninety-three percent (69/74) of the symptoms reported by the pavers were rated as “mild” in severity (the choices were “mild,” “moderate,” or “severe”).

Because of differences in the number of completed questionnaires, the *number* of symptom occurrences may not be the best measure for comparing health effects between CRM and conventional asphalt paving exposures. A more appropriate measure is the *rate* of symptom occurrences per completed questionnaire (defined as the *number of symptom occurrences* divided by the *number of completed questionnaires*). The rates of reported symptom occurrences among pavers by survey day are presented in Table 15. Although there was about a 25% increase in the number of completed acute symptom questionnaires for pavers during the CRM asphalt paving period, this increase does not appear to account for the observed change in symptom rate during the CRM asphalt paving period. The symptom reporting rate increased from 0.14 symptoms per completed questionnaire during the conventional asphalt paving period to 1.10 symptoms per completed questionnaire during the CRM asphalt paving period, an almost 8-fold increase.

The number of hours the road crew performed paving operations, and thus, were potentially exposed to asphalt fumes, varied between survey days. Each paver estimated his or her own exposure time to the paving operation (typically in 15-minute increments) and this information was collected with each acute symptom questionnaire. Table 16 shows each pavers' estimated exposure time to asphalt paving for each survey day. The average estimated hours of exposure to asphalt paving noticeably decreased over the survey period. Workers had a combined average of 6.2 hours of exposure/day to the paving operation during the conventional asphalt paving period, compared to a combined average exposure of 4.2 hours/day during the CRM asphalt paving period. All non-pavers denied any exposure to asphalt paving at any time during the survey period.

The *rate* of reported symptom occurrences per hour of estimated exposure to asphalt fume (defined as the *number of symptom occurrences* divided by the *number of hours of estimated exposure*) was calculated for the pavers for each survey day (Table 17). The rate of symptom occurrences per hour of exposure increased about 14-fold, from 0.08 during the conventional asphalt paving period to 1.10 during the CRM asphalt paving period. Of note, one paver reported no exposure to asphalt paving operations during the conventional asphalt paving period but had exposure during the CRM asphalt paving period. Recalculation of the *number* of reported symptom occurrences, *rate* of symptom occurrences per completed questionnaire, and *rate* of symptom occurrences per hour of asphalt paving exposure among pavers, excluding this worker, had no appreciable effect on the results.

The PEFR measurements revealed that only one worker, a paver, demonstrated a change consistent with significant bronchial lability (i.e., difference between a day's minimum and maximum PEFR exceeding 20% of that day's maximum PEFR). However, this worker showed an improvement in PEFR over the course of the workday, a pattern not typical of work-related bronchoreactivity.

DISCUSSION

Weather

The weather, especially wind conditions, could affect air sampling measurements obtained outdoors during this construction project. Based on observations of the paver and the movement of the asphalt plume, it appears that the wind could impact the area air samples collected near the paver hopper more than those collected above the screed auger. (The paver hopper was more open and emissions were more prone to effects from wind speed and direction than at the more enclosed screed auger area.) Therefore, the screed sample results may be more useful than the hopper sample results for comparison between conventional and CRM asphalt paving.

Process Information

The most significant difference between conventional and CRM asphalt paving on the I-96 construction project during this survey was the scope of each project. For example, mainline traffic lanes and mainline shoulders were paved using conventional asphalt. Since CRM asphalt was used mostly for ramps and ramp shoulders, less asphalt mix and less paving time was required. In addition, on the first CRM asphalt paving day, this problem was accentuated because only five dump trucks were dispatched to haul the CRM asphalt to the paving site. This truck shortage resulted in periods of work stoppage and a reduced average production rate. Finally, the use of the windrow conveyor only on conventional asphalt paving days is another factor that could influence asphalt fume exposures.

Air Sampling

The current occupational criterion for asphalt fume is 5 mg/m^3 (for total particulate). All of the PBZ and area samples collected adjacent to emission sources were well below this concentration. Concentrations of other compounds that were detected above the screed (i.e., benzene, MIBK, petroleum distillates, etc.) were also well below any existing occupational exposure criteria. However, exposure criteria are presently unavailable for several groups of compounds (such as total PACs, other sulfur compounds, and benzothiazole) which are present in asphalt fume.

Comparison of the paver operator and screed operator PBZ exposures between days is shown in Table 11. The PBZ total particulate exposure of these operators showed a similar pattern as the area screed samples; exposure during the conventional asphalt paving period was slightly lower than during the CRM paving period (0.1 to 0.2 mg/m^3 versus 0.2 to 0.36 mg/m^3, respectively).

Total particulate PBZ concentrations for the paver operator, screed operator, and raker were similar with those for employees working away from the paver (such as the tackman, foreman, and roller operators). The jobs that cause the worker to be in closer proximity to HMA (and thus have greater exposure to asphalt fume) were also jobs that were less likely to generate dust. In this regard, the paver and screed operators' PBZ exposure probably represents the highest asphalt fume exposure. Total particulate PBZ exposure for these job titles ranged from 0.1 to 0.36 mg/m^3.

Table 18 contains the results from the area air samples, arranged by location. Although there were many inconsistent factors that could affect results, the following descriptive observations are presented.

- Total particulate, respirable particulate, and BSF concentrations were higher during CRM asphalt paving, despite the lower production quantities.

- Two detector emission wavelengths were used to provide greater sensitivity either to 2-3 ring PACs (370 nm) or to 4+ ring PACs (400 nm). Greater PAC concentrations were detected using the 370 nm wavelength, implying that the 2-3 ring PACs may be more abundant.

- Total PAC concentrations above the screed were higher on CRM asphalt paving days than on conventional asphalt paving days. Furthermore, the CRM asphalt paving generated more benzothiazole and other sulfur containing compounds than the conventional asphalt paving at this site.

Medical

The results of the acute symptom survey revealed approximately an 8-fold increase in the *rate* of symptom occurrences *per completed questionnaire* and about a 14-fold increase in the *rate* of symptom occurrences *per self-reported hour of asphalt paving exposure* during the CRM asphalt paving period as compared to the conventional asphalt paving period. The observed increase in symptom occurrences was primarily due to increased reporting of mild nose and throat symptoms among pavers during the CRM asphalt paving period. Additionally, almost half (3/7) of the pavers reported lower airway symptoms (cough and shortness of breath) during the CRM asphalt paving period as compared to no reports of these symptoms during the conventional asphalt paving period.

Evaluation of acute symptoms in combination with peak flow testing was performed to determine whether acute irritant effects of the airways (as measured by symptom reporting) were associated with intermittent or reversible bronchospastic responses. While acute irritant symptoms, including lower airway symptoms, were reported by a number of workers in association with worksite exposures, none of the reported symptoms were accompanied by significant bronchial lability. The inability to detect an association, if truly present, between reported symptoms and/or exposures and PEFR results at this study site may be due to the small number of workers tested and/or variability between worker exposures and individual responses to those exposures. Also, the two-hour PEFR testing interval may not be of sufficient frequency to detect intermittently occurring transient bronchospastic effects. Continued evaluation of the relationship between reported symptoms, bronchoreactivity, and environmental measurements indicative of workers' asphalt fume exposure will be conducted as additional data become available from other study sites.

CONCLUSIONS

Results presented here only apply to this survey and cannot be generalized to indicate the exposures or health effects associated with CRM asphalt paving. This study showed that asphalt fume emissions, as well as other exposure measurements, were below current NIOSH RELs or other relevant exposure limits (for those substances with established occupational exposure criteria). Acute symptoms were reported by workers in association with asphalt paving exposures, with higher symptom responses associated with CRM asphalt paving.

Presently, it is premature to draw definitive conclusions from this single site evaluation. Data provided from this evaluation are based on a very small sample size and may reflect production and weather conditions specific to this site. Additional site evaluations will increase our ability to understand and interpret observations made at this site and should lead to more definitive conclusions.

RECOMMENDATIONS

The following recommendations are based on observations made during the survey and are intended to help ensure the safety and health of paving crew workers. These recommendations stem from our present understanding of the workers' occupational exposures and potential health effects associated with these exposures.

1. To minimize asphalt fume generation, the hot mix should be applied at the lowest temperature possible that can maintain quality control specifications.

2. To avoid contamination and possible ingestion of potentially harmful substances, workers should be prohibited from consuming food and beverages and from using tobacco products in close proximity to asphalt fume emissions.

3. Workers should be provided with adequate washing facilities for use prior to eating and leaving the worksite.

4. In order to reduce potential contamination of workers' cars and homes, workers should be encouraged to change clothing prior to leaving the worksite and should be provided with adequate facilities for changing.

5. All workers should wear protective clothing or appropriate sunscreen to shield exposed skin surfaces from the harmful ultraviolet component of sunlight.

6. In this survey workers were observed performing a number of job tasks which could potentially lead to musculoskeletal injury. Employees performing manual lifting and shoveling should be taught appropriate lifting techniques and be provided with the appropriate equipment to minimize musculoskeletal strain.

ABBREVIATIONS AND TERMS

ACGIH	American Conference of Governmental Industrial Hygienists
BSF	Benzene soluble (particulate) fraction
C	Ceiling, an exposure that shall not be exceeded during any part of the workday
CFR	Code of Federal Regulations
cm^2	Square centimeters
CO	Carbon monoxide
Control	A person working in road construction but not exposed to hot asphalt fume.
CRM	Crumb rubber modifier
DOT	Department of Transportation
EC	Elemental carbon
EPA	Environmental Protection Agency
FHWA	Federal Highway Administration
FID	Flame ionization detector
GC-MS	Gas chromatography-Mass Spectrometry
H_2S	Hydrogen sulfide
HHE	Health hazard evaluation
HMA	Hot mix asphalt
IARC	International Agency for Research on Cancer
ICP-AES	Inductively coupled (argon) plasma-atomic emission spectroscopy
IH	Industrial hygiene
ISTEA	Intermodal Surface Transportation Efficiency Act
LC	Liquid chromatography
LOD	Limit of detection (analytical method)
LOQ	Limit of quantitation (analytical method)
Lpm	Liters per minute
MCE	Mixed cellulose-ester filter
MDC	Minimum detectable concentration (the smallest amount of a material which can be reliably detected). The MDC is calculated by dividing the analytical LOD by a representative air volume.
mg	Milligrams
mg/m^3	Milligrams per cubic meter of air
MIBK	Methyl isobutyl ketone
mL	Milliliter
mm	Millimeter
MQC	Minimum quantifiable concentration (the smallest amount of a material which can be reliably measured). The MQC is calculated by dividing the analytical LOQ by a representative air volume.
ND	Not detected
NIOSH	National Institute for Occupational Safety and Health

nm	Nanometer
OC	Organic carbon
OSHA	U.S. Occupational Safety and Health Administration
PAC_{370}	PACs monitored at an emission wavelength of 370 nanometers (representative of 2-ring and 3-ring compounds)
PAC_{400}	PACs monitored at an emission wavelength of 400 nanometers (representative of 4-ring and higher compounds)
PACs	Polycyclic aromatic compounds
PAHs	Polynuclear aromatic hydrocarbons
PBZ	Personal breathing-zone air sample
PEFR	Peak expiratory flow rate
PEL	Permissible exposure limit (OSHA)
ppm	Parts (of a contaminant) per million parts of air
REL	Recommended exposure limit (NIOSH exposure criteria)
RP	Respirable particulate
SCLD	Sulfur chemiluminescent detector
Screed	During road paving, the screed levels the hot-mix asphalt to the desired thickness and slope as the paving vehicle moves forward
SO_2	Sulfur dioxide
STEL	Short-term exposure limit
TC	Total carbon (elemental + organic)
TLV®	Threshold limit value (ACGIH exposure criteria)
TWA	Time-weighted average
VOCs	Volatile organic compounds
WBGT	Wet bulb globe temperature
°C &°F	Degrees Celsius and Degrees Fahrenheit
µg	Microgram (10^{-6}), a unit of weight
µg/m^3	Micrograms of contaminant per cubic meter of air (a unit of concentration)

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APPENDIX A

MODIFIED ANALYTICAL METHOD FOR POLYCYCLIC AROMATIC COMPOUNDS

Historically, attempts to characterize asphalt fume have focused on the analysis of 16 standard unsubstituted polynuclear aromatic hydrocarbons (parent PAHs). This approach has been successful in most of the other matrices where PAH exposure occurs; however, asphalt fume is composed of a multitude of aliphatic and alkylated PAC compounds that is so complex that the mixture cannot be separated into discrete compounds. The analytical results obtained from analyzing asphalt fume samples by simply monitoring the 16 parent PAHs typically does not yield useful information regarding worker exposure.

Individual PACs typically are not quantifiable from asphalt fume if the current NIOSH liquid chromatography (LC) and gas chromatography (GC) methods (NIOSH methods 5506 and 5515) for PACs are used. This is due to the enormous number of substituted PACs in asphalt fume that are present in minute quantities which create signal interference from compounds that chromatographically co-elute at the same retention time. This has been previously shown in conventional asphalt fume studies when only the standard 16 unsubstituted PACs were evaluated.

Furthermore, the current method for detecting PACs does not evaluate the asphalt fumes for the compounds believed to be the most likely human health hazards. The health hazards associated with asphalt fume exposure are usually attributed to polycyclic aromatic compounds (PACs) that contain three to seven annulated rings with side chains of one to two carbons in length (with a maximum of four saturated carbons), or to PACs containing nitrogen, oxygen, and sulfur. For these reasons, a new method has been developed to separate the asphalt fume samples into aliphatic, aromatic, and polar fractions.

Since the published NIOSH methods do not account for all of these different compound types, the current methods were modified to provide a better indication of the total PAC content of the asphalt fumes. A new liquid chromatographic method was developed to give a better indication of the total PAC content in asphalt fume. This was achieved by adapting existing methods, reported in the literature, to initially remove the saturated compounds and the highly polar organic compounds. The remaining PACs can then be analyzed by LC with fluorescence detection. This modification should not only allow for the detection of the standard 16 PACs, that are usually analyzed, but should also allow measurement of the total PAC content present in each sample (i.e. sum of the peak areas). The total PAC content in the sample can then be compared to a PAH reference standard mixture to determine which fume samples have the most PACs. The total PAC content of the crumb rubber modified (CRM) asphalt fume can be compared to the total PAC content of the conventional asphalt collected from each sample location.

A commercially available standard mixture of 16 PACs was used in a recovery study to show that these compounds are not lost during sample preparation and that the remaining materials can be analyzed. Asphalt fume collected from an earlier pilot investigation has been used to test the possible methods. The sample preparation used solid phase extraction columns and solvent extraction steps. The material remaining after the sample preparation (PACs) was analyzed by means of a reversed-phase high performance liquid chromatographic column with fluorescence detection. After this study was successfully accomplished, the asphalt fume samples collected from paving construction sites were analyzed.

The air sampling collection methods for PACs are very similar to those published in NIOSH method 5506, Polynuclear Aromatic Hydrocarbons. The sampling train consisted of 37-mm, 2 µm pore size, Teflon® filter to collect particulate PACs, connected in series with an ORBO 43 sorbent tube to collect volatile or semi-volatile PACs. Air was sampled at a pump flow rate of 2 liters per minute (lpm). Opaque filter cassettes and sorbent tube holders were used to prevent the degradation of PACs by ultraviolet light.

After collection, the asphalt fume sample was extracted from the sampling filter with hexane. The hexane extract was then eluted through a cyano solid phase extraction column. The polar material will be retained on the column, and the aliphatic and the aromatic compounds will elute with hexane. Dimethyl sulfoxide (DMSO) is added to the hexane solution; the aromatic compounds will partition into the DMSO layer while the aliphatics will remain in the hexane layer. Next, the polar compounds are eluted from the column with methanol. The aromatic compounds in the DMSO fraction are analyzed by means of reversed-phase liquid chromatography with fluorescence detection. Since the excitation and emission wavelengths are not the same for all PACs, two sets of excitation and emission wavelengths were utilized. One set of wavelengths is more sensitive for the 2-ring and 3-ring compounds (254 nm excitation, 370 nm emission), and the other set of wavelengths is more sensitive for the 4-ring and higher compounds (254 nm excitation, 400 nm emission). Finally, the total fluorescent response was normalized with a commercially available standard of 16 unsubstituted PAHs.

This methodology was applied to a representative number of CRM and conventional asphalt samples that were obtained from emission locations. The results obtained from this procedure confirmed that the chromatograms were due to widespread signal responses, elapsing over 20 minutes of column retention time indicative of co-elution interference. Upon completion of the chromatography, the samples were analyzed with a flow injection (FI) technique where the LC column was bypassed; an aliquot of the DMSO/asphalt fume extract was injected directly into the fluorescence detection system. The advantage of this modification is that it is a much quicker procedure and the signal response is a single, reproducible peak due to all PAC compounds that fluoresce at the selected wavelength producing a more sensitive and precise signal. The total fluorescent response was also normalized with the same commercially available standard of 16 unsubstituted PAHs that was used in the chromatography methods.

Furthermore, an investigation of the compounds that contain sulfur was conducted. If a significant difference exists between conventional and CRM asphalt, it may be evident in the number and type of sulfur compounds in each asphalt formulation because of the vulcanizing process used during rubber tire production. Preliminary analyses by GC/MS have indicated that the CRM asphalt does contain more sulfur-containing compounds than the conventional asphalt mix. Additionally, higher levels of benzothiazole was present in the CRM asphalt samples. To exploit this potential difference in the asphalt compounds, a sulfur chemiluminescent detector (SCLD) was used in conjunction with a gas chromatograph (GC). This detector is sulfur specific and enables the analysis of sulfur in the low picogram range. The GC/SCLD system was used to analyze hexane extracted sample aliquots prepared from each asphalt fume sample.

Larry Olsen, Charles Neumeister, and Larry Jaycox

APPENDIX B

ELEMENTAL CARBON (DIESEL EXHAUST) 5040

C MW: 12.01 CAS: none RTECS: none

METHOD: 5040, Issue 1 **EVALUATION:** PARTIAL **Issue 1:** 15 March 1996

OSHA :
NIOSH: see APPENDIX A
ACGIH:

PROPERTIES: nonvolatile solid; MP >350 °C

SYNONYMS (related terms): soot, black carbon, diesel emissions, diesel exhaust particles, diesel particulate matter

SAMPLING

SAMPLER: FILTER (quartz fiber, 37-mm; size-selective impactor may be required, see INTERFERENCES)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 106 L @ 40 µg/m^3
-MAX: 4300 L (for filter load ~ 20 µg/cm^2)

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 4.0 mg/m^3 (60-L sample) [1]

BIAS: none [1]

OVERALL PRECISION ($\hat{S}_{rT}$): see EVALUATION OF METHOD

ACCURACY: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: EVOLVED GAS ANALYSIS (EGA) by thermal-optical analyzer

ANALYTE: elemental carbon (EC)

FILTER PUNCH SIZE: 1.54 cm^2

CALIBRATION: methane injection [1]

RANGE: 0.76 to 54 µg per filter portion

ESTIMATED LOD: 0.2 µg per filter portion

PRECISION ($\bar{S}_r$): 0.10 @ 1 µg C, 0.01 @ 10 - 72 µg C

APPLICABILITY: The working range is 4.4 to 312 µg/m^3 with an LOD of ~1.3 µg/m^3 for a 960-L air sample collected on a 37-mm filter with a 1.54 cm^2 punch from the sample filter. If a lower LOD is desired, a larger sample volume and 25-mm filter may be used (e.g., a 1920-L sample on 25-mm filter gives an LOD of 0.3 µg/m^3) [1]. The split between organic-based carbon (OC) and EC may be affected at higher EC loadings (e.g., >30 µg/cm^2 of filter), depending on type and amount of OC present. If pyrolysis correction is not required, an upper limit of ~800 µg/m^3 (90 µg/cm^2) can be determined, but post-analysis designation of OC-EC split may be necessary [1].

INTERFERENCES: As defined by the thermal-optical method, EC is the carbon determined during the second stage of the analysis (after pyrolytic correction). If the sample contains no pyrolyzable material, all the carbon evolved during this stage is considered elemental. Carbonate and cigarette smoke do not interfere. Various EC sources (diesel engines, carbon black, coal dust, and humic acid) may be present [1]. For measurement of diesel-source EC in coal mines, an impactor with submicrometer cutpoint [2,3] must be used to minimize collection of coal dust.

OTHER METHODS: Other methods for determination of EC and OC are described in the literature [4].

REAGENTS:

1. Aqueous organic carbon solutions (e.g., sucrose), 0.10 to 2.4 mg C per mL solution.
2. Helium, prepurified.
3. Hydrogen, purified.
4. Oxygen (10%) in helium, premixed, purified.
5. Methane (5%) in helium, premixed, purified.

EQUIPMENT:

1. Sampler: Quartz fiber filter, precleaned (clean in low temperature asher 2 to 3 h, or muffle furnace at ~ 800 °C), 37-mm, in a 3-piece, 37-mm cassette with support pad (stainless steel or cellulose).
2. Personal sampling pump, 1 to 4 L/min, with flexible tubing.
3. Thermal-optical analyzer, or other analyzer capable of EC speciation (see APPENDIX B).
4. Punch (e.g., cork borer) for removal of filter sample portion.
   NOTE: Portion $\geq$0.5 cm^2 with diameter or width of $\leq$ 1 cm is recommended.
5. Syringe, 10-µL

SPECIAL PRECAUTIONS: None

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
   NOTE: Sampler should be used in open-face configuration.
2. Attach sampler outlet to personal sampling pump with flexible tubing. Remove top piece of cassette.
3. Sample at an accurately known flow rate between 1 and 4 L/min.
4. After sampling, replace top piece of cassette and pack securely for shipment to laboratory.
   NOTE: If the EC in the sample is more difficult to oxidize (e.g., graphite) than typical black carbon (e.g., soot), notify the laboratory of this fact.

SAMPLE PREPARATION:

5. Use punch to cut out a representative portion of the sample filter for analysis. Take care not to disturb deposited material and avoid hand contact with sample.

CALIBRATION AND QUALITY CONTROL:

6. Perform CH_4 calibration injection at end of each sample analysis.
7. If a particular sample filter deposit appears uneven, take a duplicate portion (step 5) for analysis to check evenness of deposition. Analyze at least one duplicate and others as required to replicate 10% of the samples for sets of up to 50 samples and 5% of the samples over 50.
   NOTE: Precision in duplicate analyses of a filter is usually better than 2%.
8. Analyze three quality control blind spikes and three analyst spikes to ensure that instrument calibration is in control. Prepare spike as follows:
   a. Using a microliter syringe, apply known volume of OC standard solution directly onto portion taken (step 5) from a precleaned blank filter.
   b.. Allow H_2O to evaporate and analyze with samples and blanks (steps 10 and 11).
9. Determine instrument blank (results of analysis with no sample present) for each sample set.

MEASUREMENT:

10. Set analyzer according to manufacturer's recommendations (see APPENDIX B). Place sample portion into sample oven.
    NOTE: Forms of carbon that are difficult to oxidize (e.g., graphite) may require increased analysis time to ensure that all EC in the sample is quantified.
11. Determine EC (and OC) mass, µg, as provided by analyzer and divide by sample punch area, cm^2, to report result in terms of µg C per cm^2 of filter.

CALCULATIONS:

12. Multiply the reported EC value by filter deposit area, cm^2, (typically 8.55 cm^2 for a 37-mm filter) to calculate total mass, µg, of EC on each sample (W_{EC}). Do the same for the blanks and calculate the mass found in the average field blank (W_b). (OC masses may be calculated similarly.)
13. . Calculate EC concentration (C_{EC}) in the air volume sampled, V (L):

$$C_{EC} = \frac{W_{EC} - W_b}{V}, \text{ mg/m}^3$$

EVALUATION OF METHOD:

Currently, a suitable EC standard reference material is not available for verification of the accuracy of the method in the determination of EC. For this reason, only the accuracy of the method in the analysis of various OC standards and carbonaceous dusts for total carbon could be examined [1]. A commercial instrument was used for method evaluation [5]. No discernable differences in the responses of five different compounds were noted. Linear regression of the data for all five compounds gave a slope and correlation coefficient near unity [**m** = 0.99 (± 0.01), r^2 = 0.999, n = 43]. Based on results for individual compounds, reported carbon values are expected to be from 98 to 100% of the actual amount present. In addition, results (total carbon) of analysis of different carbonaceous materials were in good agreement with those reported by two other independent laboratories. These findings indicate that instrumental response appears to be compound- and matrix-independent (i.e., carbon is accurately quantified irrespective of compound and matrix type). Such a response is required for accurate carbon determination.

To calculate the estimated LOD of the method (i.e., ≈ 0.24 µg C or 0.15 µg C/cm^2), ethylenediaminetetraacetic acid (EDTA) calibration standards covering a range from 0.23 to 2.82 µg C (or from 0.15 to 1.83 µg C per cm^2 of filter) were analyzed. Results of linear regression of the low-level calibration data (i.e., µg C reported vs. actual) were then used to calculate the LOD as 3 σ_y/**m** (where σ_y is the standard error of the regression and **m** is the slope of the regression line). The calculated LOD shows good agreement with that estimated as LOD = (blank + $3\sigma_{blank}$), which gives a value of ≈ 0.22 µg C. The mean (n = 40) instrumental blank was ≈ .02 (± 0.07) µg C.

Because the split between EC and OC is method-dependent [1,4], and no suitable EC standard exists for assessment of a particular method's accuracy, various methods can be compared on a relative basis only. At present, the thermal-optical method is considered unbiased (i.e., it is the reference method), and the overall precision reflects the method accuracy. The S_r of the mean EC concentration (4 mg/m^3) found using fourteen samplers (two each of seven types) for collection of diesel exhaust was 5.6%. Although pumps were used for sample collection, a 5% pump error was added in the calculation of the overall precision of the method because of the relatively small sample taken (0.5 h, 60 L). Based on the 95% confidence limit (19%; 13 degrees of freedom, n =14) on the accuracy, results of this experiment indicate that the NIOSH accuracy criterion [6] is fulfilled. The amount of EC collected (240 µg per sample) would be equivalent to sampling an EC level of 250 µg/m^3 for 8 h at 2 L/min.

The thermal-optical method is applicable to nonvolatile, carbon-containing species only. The method is not appropriate for volatile or semivolatiles, which require sorbents for efficient collection. A complete discussion on the evaluation of this method for monitoring occupational exposures to particulate diesel exhaust in general industry can be found in the literature [1]. Application of the method for monitoring exposures to diesel particulate matter in the mining industry may require use of a size-selective sampling strategy in some situations [11]. In coal mines, a specialized impactor [2,3] with a sub-μm cutpoint is required to minimize the contribution of coal-source EC [2].

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METHOD WRITTEN BY:

M. Eileen Birch, Ph.D., NIOSH/DPSE.

APPENDIX A.

Diesel exhaust has been classified by IARC as a probable human carcinogen [8]. NIOSH has recommended "...that whole diesel exhaust be regarded as a potential occupational carcinogen..." and that workers' exposures be reduced[9,10]. The American Conference of Governmental Hygienists (ACGIH) has proposed a TWA of 0.15 mg/m^3 for diesel particulate (see Notice of Intended Changes for 1995-1996) [12]. The TLV applies to submicrometer particulate matter, which includes the solid carbon particle core and particulate-adsorbed components. A submicrometer size fraction was selected so that interference of other larger dusts is minimized. If other submicrometer particulate (e.g., cigarette smoke, fumes, oil mists) is present, it will interfere in the gravimetric determination of diesel particulate.

APPENDIX B. THERMAL-OPTICAL ANALYZER DESIGN AND OPERATION:

In the thermal-optical analysis of carbonaceous aerosols, speciation of various carbon types (organic, carbonate, and elemental) is accomplished through temperature and atmosphere control, and by continuous monitoring of filter transmittance. A schematic of the instrument is given below. The instrument is a modified version of a design previously described in the literature [11]. An optical feature corrects for pyrolytically generated elemental carbon (EC), or "char," which is formed during the analysis of some materials (e.g., cigarette smoke, pollen). He-Ne laser light passed through the filter allows continuous monitoring of filter transmittance. Because temperatures in excess of 850°C are employed during the analysis, quartz-fiber filters are required for sample collection. A punch from the sample filter is taken for analysis, and organic carbon (OC) and elemental carbon are reported in terms of µg/cm^2 of filter area. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. In this approach, a homogeneous sample deposit is assumed. At the end of the analysis (after the EC is evolved), calibration is achieved through injection of a known volume of methane into the sample oven.

Thermal-optical analysis proceeds essentially in two stages. In the first, organic and carbonate carbon (if present) are evolved in an inert helium atmosphere as the temperature is raised (stepped) to about 850 °C. Evolved carbon is catalytically oxidized to CO_2 in a bed of granular MnO_2 (at 950°C), CO_2 is reduced to CH_4 in a Ni/firebrick methanator (at 450°C), and CH_4 is quantified by an FID. In the second stage of the analysis, the oven temperature is reduced, an oxygen-helium mix (2% O_2 in He) is introduced into the sample oven, and the oven temperature is again raised to about 850°C. As oxygen enters the oven, pyrolytically generated EC is oxidized and a concurrent increase in filter transmittance occurs. The point at which the filter transmittance reaches its initial value is defined as the "split" between EC and OC. Carbon evolved prior to the split is considered OC (or carbonate), and carbon volatilized after the split (excluding that from the CH_4 standard) is considered elemental. The presence of carbonate can be verified through analysis of a second portion (punch) of the filter after its exposure to HCl vapor. In the second analysis, the absence of the suspect peak is indicative of carbonate carbon in the original sample.

Currently, only one commercial laboratory (Sunset Laboratory) performs thermal-optical analyses. To support the new method, a collaborative effort between NIOSH researchers and the instrument's developer is underway. During 1996, a thermal-optical instrument will be constructed and evaluated. This effort will assist in the transfer of this technology to other interested parties.

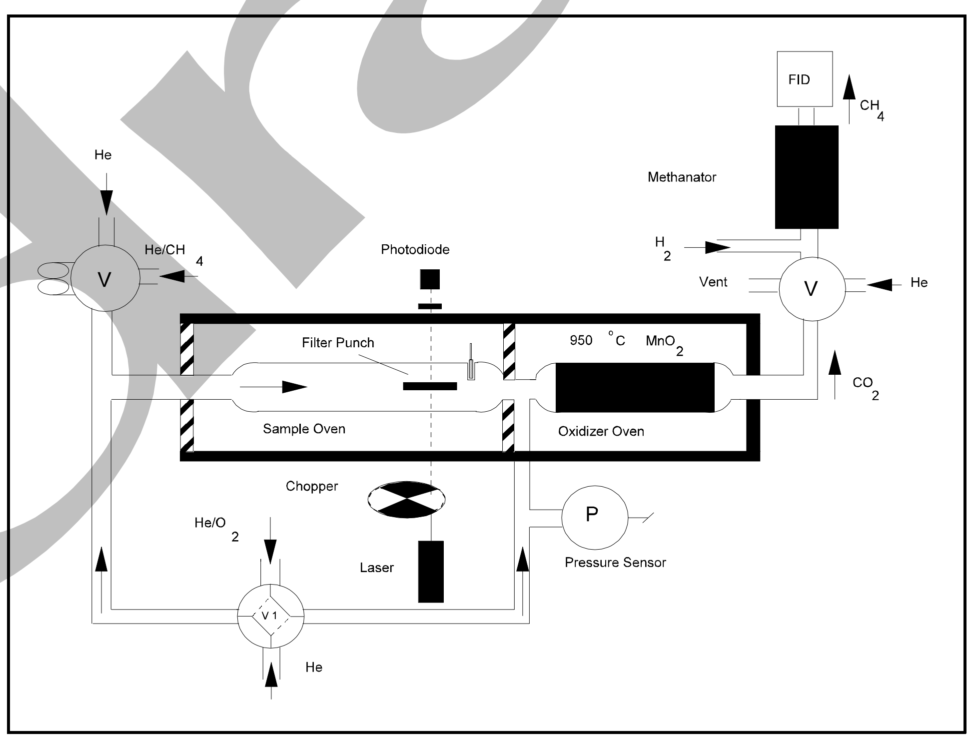

Figure 1. Schematic of Thermal-Optical Analyzer.

Table 1
Production and Equipment Information for I–96 Project
Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)

Description	8/30/94 Conventional[1]	8/31/94 Conventional	9/1/94 Rubber[2]	9/2/94 Rubber
Pavement Function	Traffic Lanes ‘2C’ Base Course	Traffic Lanes and Shoulders ‘2C’ Base Course	Ramps and Ramp Shoulders ‘2C’ Base Course	Ramps and Shoulders ‘2C’ Base Course
Hot Mix Asphalt Type	Conventional (dense)	Conventional (dense)	Rubber (dense)	Rubber (dense)
Crude Supplier	Thompson McCulley	Thompson McCulley	Thompson McCulley	Thompson McCulley
AC Grade[3]	85/100 penetration	85/100 penetration	200/250 penetration	200/250 penetration
% Rubber (by weight)[4]	0	0	15	15
Production Quantity	1340 metric tons (1477 short tons)	1155 metric tons (1273 short tons)	869 metric tons (958 short tons)	918 metric tons (1012 short tons)
Mean Application Temperature	142°C (287°F)	147°C (296°F)	134°C (273°F)	147°C (296°F)
Laydown Depth	8–10 cm (3–4")	8–10 cm (3–4")	8–10 cm (3–4")	8–10 cm (3–4")
Laydown Width	3 meters (≈10')	3 meters (≈10')	2–3.7 meters (≈7–12')	3 meters (≈10')
Hot Mix Asphalt Conveyance	FlowBoy trailer; windrow pick–up into hopper	FlowBoy trailer; windrow pick–up into hopper	Double dump trucks; dump directly into hopper	FlowBoy trailer; conveyor directly into hopper
Job Duration	7 hours	7.5 hours	8 hours	5.5 hours
Transportation	8 “FlowBoy” trailers 45 metric tons each (50 short tons each)	8 “FlowBoy” trailers 45 metric tons each (50 short tons each)	5 double dump trucks 18 metric tons each (2 x 20 short tons each)	8 “FlowBoy” trailers 45 metric tons each (50 short tons each)
Windrower Pick–up	yes	yes	no	no
Paver	2 (one w/windrower; one w/screed)	2 (one w/windrower one w/screed)	1 (only w/screed)	1 (only w/screed)
Roller (joint pinch)	yes	yes	yes	yes
Roller (breakdown)	yes	yes	yes	yes
Roller (finishing)	yes	yes	part–time	part–time
Average Production Rate	191 metric tons/hr (211 short tons/hr)	154 metric tons/hr (170 short tons/hr)	109 metric tons/hr (120 short tons/hr)	167 metric tons/hr (184 short tons/hr)

1 Conventional hot mix asphalt
2 Rubber = Crumb rubber modified hot mix asphalt
3 Asphalt cement
4 By weight of asphalt cement

Table 2
Summary of Sampling and Analytical Methods
Spartan Paving Company, Lansing, Michigan (HETA 94-0365)

Substance	Flow Rate (Lpm)	Sample Media	Analytical Method	Comments
Total Particulate	2.0	Tared PVC filter (37 mm diameter, 0.8µm pore size)	NIOSH Method No. 0500, Gravimetric analysis	Both personal breathing-zone and area samples collected
Respirable Particulate	1.7	Tared PVC filter (37 mm diameter, 0.8µm pore size)	NIOSH Method No. 0600, Gravimetric analysis	Dorr-Oliver nylon cyclone used as particle size selector
Polycyclic Aromatic Compounds (PACs) and Sulfur Compounds	2.0	Zefluor filter (37 mm diameter, 2µm pore size), followed by an ORBO 43 sorbent tube *(Note: an ORBO 42 sorbent tube was used in subsequent evaluations to reduce the pressure drop and pump failures.*	NIOSH 5506, modified to quantitate PACs via HPLC and a flow injection technique with spectrofluorometric detection. Two detector emission wavelengths were used: 370 nm (more sensitive to 2-3 ring PACs); and 400 nm (more sensitive to 4+ ring PACs). Sulfur compounds were analyzed by gas chromatography with sulfur chemiluminescence detection. This method may be found in Appendix A.	The collection method is similar to NIOSH method 5506, Polynuclear Aromatic Hydrocarbons. Opaque filter cassettes and sorbent tube holders were used to prevent the degradation of PACs by ultraviolet light. A detailed description of this method may be found in Appendix A.
Benzene Soluble Particulate	2.0	Glass fiber filter (37 mm diameter)	OSHA Method No. 58. The filters were rinsed with benzene, the leachate collected and evaporated, and the residue weighed to report the *benzene soluble fraction*. Organic compounds are generally soluble in benzene, whereas inorganic compounds are not benzene soluble. This method has been applied as an indirect measure of exposure to polynuclear aromatic hydrocarbons (PAHs) to evaluate a variety of exposure matrices including asphalt fume.	Because the method is nonspecific, the results are not necessarily due to PAH compounds. This method was used since it has been reported in many asphalt investigations and will also allow comparison of the conventional and CRM asphalt paving operations.
Elemental/Organic Carbon	2.0	Quartz-fiber filters (37 mm diameter, open face)	A rectangular punch (1.54 cm^2) is taken from the quartz filter for a three stage thermal-optical analysis.	A draft copy of NIOSH Method 5040 is provided as Appendix B.
Metals	2.5	Mixed cellulose ester (MCE) membrane filters (37 mm diameter)	NIOSH Method No. 7300. The samples were wet-ashed with concentrated nitric and perchloric acids. The residues were dissolved in a dilute solution of the same acids and the resulting solutions were analyzed for metals and minerals via Inductively Coupled Argon Plasma, Atomic Emission Spectroscopy (ICP-AES).	Analyses included silver, aluminum, arsenic, barium, beryllium calcium, cadmium, cobalt, chromium, copper, iron, lithium, magnesium, manganese, molybdenum, sodium, nickel, phosphorous, lead, platinum, selenium, tellurium, thallium, titanium, vanadium, yttrium, zinc, and zirconium.

Table 2 Summary of Sampling and Analytical Methods Spartan Paving Company, Lansing, Michigan (HETA 94-0365)				
Substance	**Flow Rate (Lpm)**	**Sample Media**	**Analytical Method**	**Comments**
Qualitative Volatile Organic Compound (VOC) Screen	0.02	Thermal desorption tubes	Samples analyzed using the Tekmar thermal desorber interfaced directly to a gas chromatograph and a mass spectrometry detector (GC/MS).	Each thermal desorption (TD) tube contains three beds of sorbent materials: (1) a front layer of Carbotrap C; (2) a middle layer of Carbotrap; and (3) a back section of Carbosieve S-III.
Quantitative Analysis for Selected Solvents	0.2	Activated charcoal sorbent tubes (100 milligram front section/50 milligram back section)	Currently existing NIOSH methods were merged and modified (i.e. NIOSH Methods 1300 and 1301 for ketones, 1501 for aromatic hydrocarbons, and 1550 for petroleum distillates.) The activated charcoal was desorbed with carbon disulfide; an aliquot of this solution was analyzed using GC-FID.	Specific VOCs that were quantified included benzene, toluene, MIBK, and petroleum distillates (other hydrocarbons with retention times greater than toluene).
H_2S, SO_2, CO, and Ozone	Diffusion	Toxilog® diffusion monitors for H_2S, SO_2, CO. CEA® TG-KA Portable Toxic Gas Detector for ozone	Toxilog® diffusion monitors use individual electrochemical sensors specific for H_2S, SO_2, CO. The CEA® TG-KA Portable Toxic Gas Detector for ozone uses an electrochemical galvanic cell method.	Spot measurements were made throughout the work day around the paving site.
Mutagenic Potential	≈10	Zefluor filter (37 mm diameter)	Mutagenic activity evaluated via a modified Ames testing protocol. The basic analytical procedure used has been described by Maron and Ames except it was to be conducted using a spiral plater device as described by Houk et al. (<u>Environ. Mol. Mut.</u> 1991, <u>17</u>, 112-121; and <u>Mut. Res.</u> 1989, <u>223</u>, 49-64).	Area samples were collected in the plume over an open port of a heated asphalt cement storage tank at the hot mix plant. The results of this modified Ames testing will be discussed in a separate NIOSH report.

The following are abbreviations which were not spelled out in the table.

PVC	=	**Polyvinyl chloride sampling filter**	**SO_2**	=	**Sulfur dioxide**
mm	=	**millimeter**	**CO**	=	**Carbon monoxide**
µm	=	**micrometer**	**lpm**	=	**Liters per minute**
GC-FID	=	**Gas chromatography-flame ionization detector**	**MIBK**	=	**Methyl isobutyl ketone**
H_2S	=	**Hydrogen sulfide**	**Zefluor**	=	**Teflon® sampling filter**
HPLC	=	**High pressure liquid chromatography**	**nm**	=	**Nanometer**

Table 3 **Toxicity and Exposure Criteria Information** **Spartan Paving Company, Lansing, Michigan (HETA 94-0365)**		
Compound	**Toxicity Review**	**Exposure Criteria**
Asphalt Fume **(As Total Particulate)**	Although the composition of asphalt fume cannot be easily characterized, one evaluation technique has been to sample total particulate. Total particulate is a measure of all airborne particulate which was collected on the sample filter. Current occupational exposure criteria from NIOSH and ACGIH for asphalt fume are expressed as total particulate. Asphalt fume has also been measured as the benzene soluble particulate fraction (BSF), a surrogate of exposure to polynuclear aromatic hydrocarbons (PAHs, see discussion below). Asphalt consists primarily of polycyclic aromatic compounds (PACs), many of which are soluble in benzene. These substances are of concern due to their irritancy and cancer-causing potential.	The NIOSH REL is 5 mg/m^3 for a 15-minute ceiling exposure. There is no current OSHA PEL for asphalt fume. The ACGIH TLV® is 5 mg/m^3 as an 8-hour TWA to total particulate.
Respirable Particulate	In contrast to total particulate, a respirable particulate sample uses a selection device to obtain the fraction of the airborne particulate that is small enough to be retained in the respiratory system once inhaled. Any conclusions based on respirable (or total) particulate concentrations may be misleading since other potentially toxic substances may be present. These particulate concentrations, along with the results obtained from tests for individual components (such as polycyclic aromatic compounds [PACs], benzene solubles, and selected solvents) should be considered together when determining the degree of hazard.	No NIOSH REL The OSHA PEL is 5 mg/m^3, 8-hour TWA. The ACGIH TLV® for particulates not otherwise classified is 10 mg/m^3 for inhalable particulate and 3 mg/m^3 for respirable particulate. Both are 8-hour TWAs.
Benzene Soluble Particulate	The benzene soluble particulate fraction (BSF) is that portion of the total particulate that is soluble in benzene. Organic compounds are generally soluble in benzene, whereas inorganic compounds are not benzene soluble. Historically, the BSF concentrations were measured in asphalt studies in an attempt to differentiate exposure between the asphalt fume and dirt or other dust present at asphalt construction operations. However, this method is non-specific and the BSF results are not necessarily due to polycyclic aromatic compounds (PACs) or polynuclear aromatic hydrocarbons (PAHs).	None established for BSF associated with asphalt fume
Polynuclear Aromatic Hydrocarbons **and** **Polycyclic Aromatic Compounds**	Analysis for unsubstituted PAHs has been applied to evaluate asphalt fume exposure. However, this approach provides limited information because asphalt fume contains numerous alkylated PACs that coelute, causing chromatographic interference, which prevents quantitation of specific compounds. Polycyclic aromatic compounds refer to a set of cyclic organic compounds that includes PAHs and also includes compounds that may have sulfur, nitrogen, or oxygen in the ring structure and alkyl substituted cyclics. Hundreds of PACs with varying degrees of alkyl substitutions are typically associated with asphalt materials [Lunsford et al. 1989]. PAHs have received considerable attention since some have been shown to be carcinogenic in experimental animals. NIOSH investigators have hypothesized that PACs with 2 to 3 rings (referred to in this report as PAC_{370}) are associated with more irritative effects, while the 4 to 7 ring PACs (termed PAC_{400}) may have more carcinogenic and/or mutagenic effects. It is not currently posssible to definitively distinguish between these two PAC groups analytically; however, using two different spectrofluorometric detector wavelengths (370 nanometer [nm] and 400 nm) allows the detector to be more sensitive to PACs based on ring number. A more complete discussion of the NIOSH analytical method for PACs may be found in Appendix A.	None established for PAHs and PACs as a class.
Benzothiazole	In its pure form, benzothiazole is a yellow liquid with an unpleasant odor [Sax 1987]. It is used as a rubber vulcanization accelerator [ILO 1971], as an antimicrobial agent [ITO 1978], and in dyes [Kirk-Othmer 1978]. Benzothiazole was identified in the air during rubber vulcanization [Rappaport 1977]. Reports also indicate that benzothiazole is present in tires and CRM asphalt. Benzothiazole was selected for study since it may be useful as an indicator to represent the complex exposures resulting from CRM asphalt paving. It is not known if there are any health effects associated with benzothiazole at the air concentrations measured in this study.	None established

Table 3 Toxicity and Exposure Criteria Information Spartan Paving Company, Lansing, Michigan (HETA 94-0365)		
Compound	**Toxicity Review**	**Exposure Criteria**
Other Sulfur-Containing Compounds	The addition of tire rubber may increase sulfur compounds in asphalt. In this report "other sulfur-containing compounds" refer to aliphatic and aromatic organic compounds that contain sulfur. Although no specific occupational exposure limits exist for this group of sulfur compounds, it was hypothesized by NIOSH investigators that some of them may cause respiratory irritation.	None established
Organic and Elemental Carbon	Measuring organic, elemental, and total carbon concentrations (and determining a ratio between elemental and total carbon) provides an indication of diesel exhaust exposure. Any elemental carbon above background will most likely be from diesel exhaust. Unfortunately, this method cannot be used to specifically differentiate carbon sources (i.e., asphalt fume, diesel exhaust, cigarette smoke). There are no occupational exposure criteria for either elemental or organic carbon. This method was employed previously in several NIOSH trucking industry studies [Zaebst et al. 1991, Blade 1989]. A copy of the draft NIOSH Method 5040 is provided in Appendix B.	None established
MIBK	Tire rubber may be a source for methyl isobutyl ketone (MIBK) since this organic compound can be used as an antioxident in the tire manufacturing process. In its pure form, MIBK is a colorless, flammable organic solvent that is typically used as a solvent in the surface coating and synthetic resin industries [ACGIH 1992]. This solvent is absorbed primarily through inhalation and causes irritation of the eyes, mucous membranes, and skin [Proctor 1989]. At air concentrations much higher than were measured in this asphalt study, MIBK has caused central nervous system depression [Proctor 1989]. Continued or prolonged skin contact with the liquid can cause dermatitis [Proctor 1989].	The NIOSH REL and ACGIH TLV are 50 ppm, 8-hour TWA; and 75 ppm, 15 minute STEL. OSHA PEL is 100 ppm for an 8-hour TWA.
Benzene	Acute benzene overexposure can cause central nervous system depression with symptoms such as headache, nausea, and drowsiness. Chronic exposure to benzene has been associated with the depression of the hematopoietic system and is associated with an increased incidence of leukemia and possibly multiple myeloma [ACGIH 1992]. NIOSH classifies benzene as a human carcinogen [NIOSH 1992]. *Note: ACGIH has proposed to lower its TLV® for benzene to 0.3 ppm with a skin notation (indicating that skin exposure contributes to the overall absorbed inhalation dose and potential effects), and classify it as a proven human carcinogen [ACGIH 1995].	NIOSH REL is to reduce exposures to the lowest feasible level. OSHA PEL is 1 ppm for an 8-hour TWA. ACGIH TLV is 10 ppm* for an 8-hour TWA.
Toluene	Toluene can cause acute irritation of the eyes, respiratory tract, and skin. Since it is a defatting solvent, repeated or prolonged skin contact will remove the natural lipids from the skin which can cause drying, fissuring, and dermatitis [Proctor 1989, NIOSH 1973]. Studies have shown that subjects exposed to 100 ppm of toluene for six hours complained of eye and nose irritation, and in some cases, headache, dizziness, and a feeling of intoxication (narcosis) [WHO 1981]. No symptoms were noted below 100 ppm in other studies [Bruckner 1981a,b]. The ACGIH TLV® carries a skin notation, indicating that skin exposure contributes to the overall absorbed inhalation dose and potential effects [ACGIH 1995].	NIOSH REL is 100 ppm, 8-hour TWA (15-minute STEL of 150 ppm). OSHA PEL is 200 ppm, 8-hour TWA; 300 ppm for a ceiling limit. ACGIH TLV is 50 ppm, 8-hour TWA (skin).
Total Hydrocarbons (as Stoddard Solvent)	In this study, total hydrocarbons (HC) refer to Stoddard solvent, a petroleum distillate mixture. Effects from exposure to Stoddard solvent are primarily acute, unless significant amounts of substances that have chronic toxicity are present, such as benzene or glycol ethers. Epidemiologic studies have shown that exposure to similarly refined petroleum solvents (i.e.,Stoddard solvent, mineral spirits) can cause dry throat, burning or tearing of the eyes, mild headaches, dizziness, central nervous system depression, respiratory irritation, and dermatitis [NIOSH 1977b]. The evaluation criteria are based upon the similarity of the mixture composition in relation to the most commonly available products (in this case Stoddard solvent).	NIOSH REL is 350 mg/m^3, 10-hour TWA; the NIOSH ceiling limit is 1800 mg/m^3, 15 minutes. OSHA PEL is 2,900 mg/m^3, 8-hour TWA. ACGIH TLV is 525 mg/m^3, 8-hour TWA.

Abbreviations:
REL = Recommended Exposure Limit (NIOSH)
TLV = Threshold Limit Value (ACGIH)
STEL = Short-term exposure limit
µm = micrometers
PEL = Permissible Exposure Limit (OSHA)
TWA = Time-weighted average
ppm = parts per million
mg/m^3 = milligrams per cubic meter

Table 4
Environmental Conditions
Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)

Description	**8/30/94 Conventional**	**8/31/94 Conventional**	**9/1/94 Crumb Rubber**	**9/2/94 Crumb Rubber**
Summary	Cloudy	Overcast	Clear	Sunny
Minimum Temperature	16°C (60°F)	17°C (62°F)	11°C (51°F)	7°C (45°F)
Maximum Temperature	23°C (73°F)	23°C (74°F)	19°C (67°F)	20°C (68°F)
Average Temperature	20°C (68°F)	19°C (67°F)	16°C (61°F)	15°C (68°F)
Average Humidity	58%	67%	55%	72%
Minimum WBGT	58.1°F	61.0°F	49.2°F	44.4°F
Maximum WBGT	68.0°F	70.3°F	62.3°F	69.0°F
Wind Speed	Slight breeze	Windy	Breezy	Slight Breeze
Wind Direction	S–SE	W	N	Variable N–NW
Traffic Density	Low	Low	Low	Low

WBGT = Wet bulb globe temperature, a heat stress index

Other comments:

Conventional = Non-rubber hot mix asphalt
Crumb Rubber = Crumb rubber modified hot mix asphalt

Table 5
Total Particulate Concentrations: Area Samples
Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m^3)
Conventional Asphalt 8/30/94	Paver Hopper	427	855	0.08
	Screed	434	870	0.19
	Ambient Background	463	928	0.36
	Highway Background	490	982	ND (<0.02)
Conventional Asphalt 8/31/94	Paver Hopper	417	838	0.38
	Screed	423	840	0.45
	Ambient Background	442	901	0.05
	Highway Background	443	915	ND (<0.02)
Crumb Rubber Asphalt 9/1/94	Paver Hopper	479	967	0.17
	Screed	433	871	2.49
	Ambient Background	500	1009	0.06
	Highway Background	495	993	0.03
Crumb Rubber Asphalt 9/2/94	Paver Hopper	302	609	0.22
	Screed	310	623	1.05
	Ambient Background	336	676	0.04
	Highway Background	320	639	0.07

mg/m^3 = Air concentration, expressed in milligrams per cubic meter
ND = Not Detected (concentration is below the Minimum Detectable Concentration)
( ) = The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a "less than" (<) value.

Table 6
Respirable Particulate Concentrations: Area Samples
Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m^3)
Conventional Asphalt 8/30/94	Paver Hopper	425	727	0.05
	Screed	434	719	0.16
	Ambient Background	371	634	ND (<0.03)
	Highway Background	377	619	0.07
Conventional Asphalt 8/31/94	Paver Hopper	417	708	0.06
	Screed	423	717	0.08
	Ambient Background	442	741	ND (<0.03)
	Highway Background	443	753	ND (<0.03)
Crumb Rubber Asphalt 9/1/94	Paver Hopper	482	815	0.08
	Screed	177‡	299	0.52
	Ambient Background	494	842	0.04
	Highway Background	504	864	0.04
Crumb Rubber Asphalt 9/2/94	Paver Hopper	302	514	ND (<0.04)
	Screed	302	513	0.30
	Ambient Background	339	578	ND (<0.03)
	Highway Background‡	145	249	ND (<0.08)

mg/m^3 = Air concentration, expressed in milligrams per cubic meter
ND = Not Detected (concentration is below the Minimum Detectable Concentration)
( ) = The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a "less than" (<) value.
‡ = Pump failure. The Time Weighted Average is based on the actual sampling time which may be less than the workshift duration.

Table 7
Benzene Soluble Particulate Concentrations: Area and PBZ Samples
Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)

Area Air Samples

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m^3)
Conventional Asphalt 8/30/94	Paver Hopper	425	1059	Trace
	Screed	434	1088	0.09
	Ambient Background	499	1255	ND (<0.02)
	Highway Background	490	1224	ND (<0.02)
Conventional Asphalt 8/31/94	Paver Hopper	417	1043	0.09
	Screed	423	1068	0.22
	Ambient Background	442	1129	ND (<0.03)
	Highway Background	443	1126	ND (<0.03)
Crumb Rubber Asphalt 9/1/94	Paver Hopper	475	1195	Trace
	Screed	494	1239	0.38
	Ambient Background	495	1238	ND (<0.02)
	Highway Background	494	1232	ND (<0.02)
Crumb Rubber Asphalt 9/2/94	Paver Hopper	305	765	Trace
	Screed	312	778	0.97
	Ambient Background	338	850	ND (<0.04)
	Highway Background	318	795	ND (<0.04)

Personal Breathing-Zone Air Samples

Sampling Date	Job Activity	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m^3)
Conventional Asphalt 8/31/94	Roller Operator	461	1180	ND (<0.03)
Crumb Rubber Asphalt 9/1/94	Roller Operator	414‡	1033	Trace
Crumb Rubber Asphalt 9/2/94	Roller Operator	351	880	0.13

Comments:
mg/m^3 = Air concentration, expressed in milligrams per cubic meter
ND = Not Detected (below the Minimum Detectable Concentration)
( ) = The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a less than (<) value.
‡ = Pump failure. The Time Weighted Average is based on the actual sampling time which may be less than the workshift duration.

Table 8
Polycyclic Aromatic Compounds (PACs) Concentrations: Area Samples
Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, micrograms per cubic meter			
				PACs @ 370 nm	PACs @ 400 nm	Other SulCom‡	Benzothiazole
Conventional Asphalt 8/30/94	Paver Hopper	269‡	537	14	2.7	ND (<0.6)	Trace
	Screed	434	873	1.9	1.4	2.1	Trace
	Ambient Background	487‡	976	ND (<0.06)	ND (<0.1)	NA	NA
	Highway Background	490	982	0.31	ND (<0.1)	ND (<0.3)	ND (<0.3)
Conventional Asphalt 8/31/94	Paver Hopper	417	834	4.8	1.4	5.6	Trace
	Screed	410‡	808	9.8	3.1	Trace	Trace
	Ambient Background	340‡	673	Trace	ND (<0.2)	2.5	Trace
	Highway Background	432	871	Trace	ND (<0.1)	ND (<0.3)	ND (<0.3)
Crumb Rubber Asphalt 9/1/94	Paver Hopper	476	951	3.0	Trace	ND (<0.3)	5.6
	Screed	491‡	983	14	4.1	17	26
	Ambient Background	496	993	1.9	Trace	3.8	ND (<0.3)
	Highway Background	509‡	1016	0.27	ND (<0.1)	ND (<0.3)	ND (<0.3)
Crumb Rubber Asphalt 9/2/94	Paver Hopper	306	612	1.4	Trace	ND (<0.5)	11.4
	Screed	318	637	33	12	37	59
	Ambient Background	340	682	0.57	ND (<0.2)	ND (<0.4)	ND (<0.4)
	Highway Background	318	639	1.5	Trace	Trace	ND (<0.5)

‡ = Other sulfur-containing compounds
370 nm = 370 nanometers, spectrofluorometric detector wavelength (includes both vapor and particulate phase)
400 nm = 400 nanometers, spectrofluorometric detector wavelength (includes both vapor and particulate phase)
Trace = Concentration is between the Minimum Detectable and Minimum Quantifiable Concentrations
ND = Not Detected (below the Minimum Detectable Concentration)
NA = Not applicable.
( ) = The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a less than (<) value.
‡ = Pump failure. The Time Weighted Average is based on the actual sampling time which may be less than the workshift duration.

Comments:
1. Air samples were collected using 37 millimeter Zefluor® filters followed by an ORBO 43 sorbent tube.

Table 9
Elemental Carbon Concentrations: Area Samples
Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, micrograms per cubic meter			EC/TC
				Organic Carbon (OC)	Elemental Carbon (EC)	Total Carbon (TC)	
Conventional Asphalt 8/31/94	Paver Hopper	417	838	158	12	170	0.07
	Screed	423	845	250	15	265	0.06
	Ambient Background	442	883	11	ND (<1.9)	NA	NA
	Highway Background	443	882	12	ND (<1.9)	NA	NA
Crumb Rubber Asphalt 9/1/94	Paver Hopper	480	959	90	10	100	0.1
	Screed	490	988	419	7.7	427	0.02
	Ambient Background	502	1009	18	ND (<1.7)	NA	NA
	Highway Background	508	1012	8.1	2.6	11	0.24
Crumb Rubber Asphalt 9/2/94	Paver Hopper	305	609	90	11	101	0.11
	Screed	313	623	1006	Trace	NA	NA
	Ambient Background	339	679	ND (<2.5)	ND (<2.5)	NA	NA
	Highway Background	317	637	ND (<2.7)	Trace	NA	NA

NA = Not applicable since one or both analytes were not detected.
$\mu g/m^3$ = Micrograms per cubic meter.
EC/TC = Ratio of elemental carbon to total carbon.

Other Comments:

1. **Some of the rows may not total to the exact amount shown due to rounding.**
2. **No elemental carbon samples were collected on 8/30/94 due to the unavailability of sampling media.**

Table 10
Selected Volatile Organic Compounds (VOCs) Concentrations: Area Samples
Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)

Sampling Date	Area	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, expressed in parts per million			Concentration, mg/m^3
				Benzene	Toluene	MIBK	Total HC > Toluene‡
Conventional Asphalt 8/30/94	Paver Hopper	426	85	ND	ND	ND	0.24
	Screed	434	87	ND	ND	ND	0.57
	Ambient Background	500	100	ND	ND	ND	ND
	Highway Background	490	100	ND	ND	ND	ND
Conventional Asphalt 8/31/94	Paver Hopper	417	86	ND	ND	ND	0.67
	Screed	423	85	ND	ND	ND	0.57
	Ambient Background	442	79	ND	ND	ND	ND
	Highway Background	443	90	ND	ND	ND	ND
Crumb Rubber Asphalt 9/1/94	Paver Hopper	483	95	ND	ND	ND	1.2
	Screed	496	99	ND	ND	0.15	5.6
	Ambient Background	497	100	ND	ND	ND	ND
	Highway Background	512	102	ND	ND	ND	ND
Crumb Rubber Asphalt 9/2/94	Paver Hopper	307	62	ND	ND	ND	0.75
	Screed	314	63	Trace	ND	0.28	3.4
	Ambient Background	337	67	ND	ND	ND	ND
	Highway Background	315	63	ND	ND	ND	ND

‡ = Total hydrocarbons with a gas chromatograph retention time greater than (>) toluene. Concentrations are expressed in milligrams per cubic meter (mg/m^3).
MIBK = Methyl isobutyl ketone
Trace = Concentration is between the Minimum Detectable and Minimum Quantifiable Concentrations
ND = Not Detected (below the Minimum Detectable Concentration)

Table 11 Total Particulate Concentrations: Personal Breathing Zone Samples Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)				
Sampling Date	**Job Title**	**Sampling Time (minutes)**	**Sample Volume (Liters)**	**Concentration (mg/m^3)**
Conventional Asphalt 8/30/94	Paver Operator	525	1050	0.15
	Operator Trainee	522	1045	0.17
	Screed Operator	512	1025	0.10
	Raker	485	968	0.17
	Laborer	513	1028	0.55
	Roller Operator	89‡	178	0.14
	Roller Operator	474	949	0.15
	Roller Operator	470	943	0.09
	Tackman	512	1025	0.16
	Foreman	467	936	0.10
	Density Checker	398‡	796	0.17
Conventional Asphalt 8/31/94	Paver Operator	513	1028	0.20
	Operator Trainee	543	1097	0.13
	Screed Operator	459	921	0.10
	Raker	518	1025	0.01
	Laborer	477	948	1.2
	Roller Operator	592	1156	0.08
	Roller Operator	459	906	0.14
	Roller Operator	579	1193	0.06
	Tackman	489	972	0.27
	Foreman	508	1002	0.11
	Density Checker	491	981	0.27

Table 11 (continued)
Total Particulate Concentrations: Personal Breathing Zone Samples
Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)

Sampling Date	Job Title	Sampling Time (minutes)	Sample Volume (Liters)	Concentration (mg/m^3)
Crumb Rubber Asphalt 9/1/94	Paver Operator	560	1129	0.28
	Operator Trainee	561	1136	0.25
	Screed Operator	548	1094	0.20
	Raker	535	1084	0.24
	Laborer	551	1110	0.33
	Roller Operator	543	1096	0.28
	Roller Operator	554	1093	0.16
	Roller Operator	429‡	859	0.11
	Tackman	542	1091	0.30
	Foreman	550	1095	0.16
	Density Checker	520	1033	0.13
Crumb Rubber Asphalt 9/2/94	Paver Operator	405	814	0.36
	Operator Trainee	396	797	1.0
	Screed Operator	368	742	0.21
	Raker	364	731	0.14
	Laborer	177	354	0.10
	Roller Operator	400	799	0.16
	Roller Operator	373	746	0.06
	Roller Operator	355	715	1.2
	Tackman	337‡	678	0.20
	Foreman	390	778	0.49
	Density Checker	354	707	0.15

Comments:

mg/m^3 = Concentration, milligrams per cubic meter
‡ = Pump failure. The Time Weighted Average is based on the actual sampling time which may be less than the workshift duration.

Table 12
Polycyclic Aromatic Compounds (PACs) Concentrations: Personal Breathing Zone Samples
Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)

Sampling Date	Job Title	Sampling Time (minutes)	Sample Volume (Liters)	Concentration, micrograms per cubic meter			
				PACs @ 370 nm	PACs @ 400 nm	Other SulCom†	Benzothiazole
Conventional Asphalt 8/30/94	Operator Trainee	367‡	733	3.9	1.2	Trace	ND (<0.4)
	Raker	232‡	463	7.1	2.1	ND (<0.7)	ND (<0.7)
Conventional Asphalt 8/31/94	Raker	246‡	483	16	4.2	11	Trace
Crumb Rubber Asphalt 9/1/94	Operator Trainee	505	1054	2.0	ND (<0.1)	Trace	2.5
	Raker	459	793	2.5	Trace	Trace	ND (<0.4)
Crumb Rubber Asphalt 9/2/94	Operator Trainee	313‡	627	7.7	1.2	12	13
	Raker	365	728	2.1	ND (<0.1)	ND (<0.4)	7.0

†SulCom = Other sulfur-containing compounds
370 nm = 370 nanometers, spectrofluorometric detector wavelength (includes both vapor and particulate phase)
400 nm = 400 nanometers, spectrofluorometric detector wavelength (includes both vapor and particulate phase)
ND = Not Detected (below the Minimum Detectable Concentration)
‡ = Pump failure. The Time Weighted Average is based on the actual sampling time which may be less than the workshift duration. Used pump timer for sampling time.

Comments:
1. **Air samples were collected using 37 millimeter Zefluor® filters followed by an ORBO 43 sorbent tube.**
2. **The PACs concentrations reported in this table include both the particulate phase (collected on the filter) and the vapor phase (from the sorbent tube).**

Table 13
Number of Acute Symptom Questionnaires Completed by Workers
Paving Site: Spartan Paving, Lansing, Michigan (HETA 94-0365)

Work Group		Acute Questionnaires Completed: Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Asphalt	Day 4 CRM Asphalt
Pavers (n= 7)		28/35‡	21/35	34/35	27/35
Non-pavers (n= 5)		17/25	15/25	23/25	18/25
Paving Period Totals	**Pavers**	49/70		61/70	
	Non-pavers	32/50		41/50	

‡ Number of completed questionnaires/potential number of questionnaires

Table 14
Number of Workers Reporting Symptoms and Number of Symptom Occurrences by Survey Day
Paving Site: Spartan Paving, Lansing, Michigan (HETA 94-0365)

Symptoms	Work groups	Number of workers reporting symptoms (Number of symptom occurrences reported): Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Asphalt	Day 4 CRM Asphalt
Dry, itching, or irritated eyes	Pavers Non-pavers	0 0	0 0	1 (2) 0	1 (3) 0
Stuffy, burning, or irritated nose	Pavers Non-pavers	2 (3) 0	0 0	5 (6) 1 (1)	4 (7) 1 (2)
Sore, dry, scratchy, or irritated throat	Pavers Non-pavers	0 0	0 0	6 (11) 1 (1)	7 (21) 0
Skin burning, rash, itching, or irritated	Pavers Non-pavers	0 0	0 0	0 0	0 0
Bothered by coughing	Pavers Non-pavers	0 0	0 0	1 (1) 1 (1)	3 (7) 0
Chest tightness or shortness of breath	Pavers Non-pavers	0 0	0 0	1 (2) 0	3 (7) 0
Wheezing or whistling in chest	Pavers Non-pavers	1 (4) 0	0 0	0 0	0 0
Totals	**Pavers** **Non-pavers**	**3 (7)** **0 (0)**	**0** **0**	**7 (22)** **1 (3)**	**7 (45)** **1 (2)**

Table 15
Rate of Symptoms Occurrence Per Questionnaire Among Pavers by Survey Day
Paving Site: Spartan Paving, Lansing, Michigan (HETA 94-0365)

Pavers (n=7)	Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Asphalt	Day 4 CRM Asphalt
Completed	28	21	34	27
Symptom Occurrences	7	0	22	45
Rate of symptom occurrence per questionnaire	0.25	0	0.65	1.7
	0.14		1.1	

Table 16
Estimated Hours of Exposure to Asphalt Fume Among Pavers by Job Title and Survey Day
Paving Site: Spartan Paving, Lansing, Michigan (HETA 94-0365)

Job Title (n=7)	Estimated hours exposure to asphalt fume			
	Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Asphalt	Day 4 CRM Asphalt
Paver Operator	8	7.5	6	4.5
Screedman	8.5	7.25	6	4.5
Raker	8.75	7	5.25	4.5
Roller	8.75	8.75	4	5.5
Roller	9	1.5	5	1
Laborer	5.5	6.75	3.5	4.75
Tack truck/raker	0	0	2.5	1.75
Daily Total Hours (Average)	48.5 (6.9)	38.75 (5.5)	32.25 (4.6)	26.5 (3.8)
Total Hours by Asphalt Paving Material (Average)	87.25 (6.2)		58.75 (4.2)	

Table 17
Rate of Symptoms Per Hour of Exposure Among Pavers by Survey Day
Paving Site: Spartan Paving, Lansing, Michigan (HETA 94-0365)

	Day 1 Conventional Asphalt	Day 2 Conventional Asphalt	Day 3 CRM Asphalt	Day 4 CRM Asphalt
Estimated Exposure to Asphalt (total hours)	48.5	38.75	32.25	26.5
Number Symptom Occurrences	7	0	22	45
Rate of symptom occurrence per hour of exposure	0.14	0	0.68	1.7
	0.08		1.1	

Table 18
Summary of Area Air Concentrations
Paving Site: Spartan Paving Company, Lansing, Michigan (HETA 94–0365)

Sampling Location	Analyte	TWA Concentration (micrograms per cubic meter)			
		8/30/94 Conventional	8/31/94 Conventional	9/1/94 CRM Asphalt	9/2/94 CRM Asphalt
Paver Hopper	Total Particulate	80	380	170	220
	Respirable Particulate	50	60	80	ND (<40)
	Benzene Soluble Particulate Fraction	Trace	90	Trace	Trace
	$PACs_{370}$ (vapor and particulate)	14	4.8	3.0	1.4
	$PACs_{400}$ (vapor and particulate)	2.7	1.4	Trace	Trace
	Benzothiazole	Trace	Trace	5.6	11.4
	Other Sulfur Compounds	ND (<0.6)	5.6	ND (<0.3)	ND (<0.5)
	Total Hydrocarbons w/a retention time >Toluene	240	670	1200	750
Paver Screed	Total Particulate	190	450	2490	1050
	Respirable Particulate	160	80	520	300
	Benzene Soluble Particulate Fraction	90	220	380	970
	$PACs_{370}$ (vapor and particulate)	1.9	9.8	14	33
	$PACs_{400}$ (vapor and particulate)	1.4	3.1	4.1	12
	Benzothiazole	Trace	Trace	26	59
	Other Sulfur Compounds	2.1	Trace	17	37
	Total Hydrocarbons w/a retention time >Toluene	570	570	5600	3400
Ambient Background	Total Particulate	360‡	50	60	40
	Respirable Particulate	ND (<30)	ND (<30)	40	ND (<30)
Highway Background	Total Particulate	ND (<20)	ND (<20)	30	70
	Respirable Particulate	70	ND (<30)	40	ND (<80)

Trace = Concentration is between the Minimum Detectable and Minimum Quantifiable Concentrations
ND = Not Detected (below the Minimum Detectable Concentration)
( ) = The value which is shown in brackets is the minimum detectable concentration (MDC) for this sample. The MDC is calculated by dividing the analytical Limit of Detection by the air sample volume and is reported as a less than (<) value.
PAC_{370} = Polycyclic aromatic compounds measured with 370 nanometer detector wavelength
PAC_{400} = Polycyclic aromatic compounds measured with 400 nanometer detector wavelength
‡ = Sample result may have been biased by excessive vehicle traffic on a nearby dirt road
Note = Highway background concentrations for benzene soluble fraction, PAC370 and PAC400 are not reported in this summary table. Please refer to the previous tables for these concentrations.