Applied Occupational and Environmental Hygiene
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uaoh20

Determination of Total Sulfur Compounds and Benzothiazole in Asphalt Fume Samples by Gas Chromatography with Sulfur Chemiluminescence Detection

Larry B. Jaycox [a] & Larry D. Olsen [a]
[a] Division of Applied Research and Technology , National Institute for Occupational Safety and Health , Cincinnati, Ohio
Published online: 30 Nov 2010.

To cite this article: Larry B. Jaycox & Larry D. Olsen (2000) Determination of Total Sulfur Compounds and Benzothiazole in Asphalt Fume Samples by Gas Chromatography with Sulfur Chemiluminescence Detection, Applied Occupational and Environmental Hygiene, 15:9, 695-704

To link to this article: http://dx.doi.org/10.1080/10473220050110112

Applied Occupational and Environmental Hygiene
Volume 15(9): 695–704, 2000
1047-322X/00 $12.00 + .00

Determination of Total Sulfur Compounds and Benzothiazole in Asphalt Fume Samples by Gas Chromatography with Sulfur Chemiluminescence Detection

Larry B. Jaycox and Larry D. Olsen
Division of Applied Research and Technology, National Institute for Occupational Safety and Health, Cincinnati, Ohio

As part of a collaborative project between the National Institute for Occupational Safety and Health and the Federal Highway Administration to evaluate asphalt pavers' exposures to asphalt fume and their potential health effects, a method was developed for the determination of total sulfur compounds and benzothiazole in asphalt fume samples. Asphalt fume samples were collected from asphalt mixtures with and without the addition of ground-up rubber tires. The asphalt fume samples were collected with sampling trains that consisted of a Teflon membrane filter and an XAD-2 adsorbent tube. Filter and sampling tube media were extracted with hexane and subsequently analyzed by gas chromatography with a sulfur chemiluminescence detector. Separation was achieved with a 100 percent dimethyl polysiloxane fused silica column. Typical calibration curves had linear correlation coefficients of 0.99 or better with a relative standard deviation (RSD) of 5 percent. Benzothiazole desorption efficiency (DE) determined using spiked sampling tubes ranged from 96.5 percent at 5.0 μg to 89.4 percent at 40 μg with RSD values from 0.9 to 4.0 percent. Benzothiazole storage recovery determined using sampling tubes spiked at 20 μg and refrigerated for 30 days at 4°C was 89.8 percent when corrected for the DE with an RSD of 1.1 percent. The limit of detection for the method determined using spiked sampling tubes was 0.30 μg. Quantitation for total sulfur compounds and benzothiazole was against benzothiazole standards in hexane. Because of detector selectivity, sample preparation consisted of a simple hexane extraction even when samples had a high background due to hydrocarbon overload. Detector sensitivity provided quantitation in the sub-microgram region. Because of the sample preparation step and because benzothiazole was determined during the same analysis run, this method is straightforward and analytically efficient. The method has been used to analyze asphalt fume samples collected at several asphalt paving and roof operations.

Keywords Benzothiazole, Organic Sulfur-Containing Compounds, Gas Chromatography, Chemiluminescence, Asphalt Fume, Construction, Analytical Methods Development

In 1994, the Federal Highway Administration (FHWA) and the National Institute for Occupational Safety and Health (NIOSH) entered into an interagency agreement to study the exposure of asphalt paving workers to asphalt fume. A prelude to this agreement was the fact that the FHWA was supporting a program to evaluate the use of ground-up rubber tires (a.k.a. crumb rubber) in asphalt mixes used for paving highways.[1] In 1991, the U.S. Congress passed the Intermodal Surface Transportation Efficiency Act that required each state to use crumb-rubber modified (CRM) asphalt starting at 5 percent of all asphalt laid and increasing to 20 percent by 1997. The emphasis for this is the use of CRM asphalt has the potential of reducing the disposal problem of used automotive rubber tires (285 million tires are discarded in the United States each year).

The role of NIOSH in the interagency agreement was to investigate paving worker exposures to the same asphalt mixture with and without the addition of ground-up rubber tires and compare potential health effects from these exposures. The individual features of this project included health hazard evaluations, health symptom assessments, a biomarker study, an engineering control study, and the development of sampling and analytical methods for the materials of interest in the asphalt fume. These studies are reported separately. This article focuses on the development of a sampling and analytical method for the measurement of sulfur-containing compounds in asphalt fume. The method, as

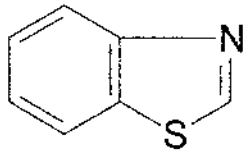
Mention of company name or product does not constitute endorsement by the Centers for Disease Control and Prevention.

described here, was used to provide data for the health hazard evaluations and the health symptom assessments.

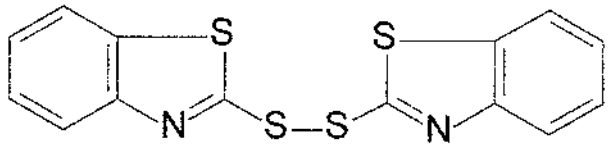
Sulfur and sulfur-containing compounds are irritants to the respiratory tract and skin.[2–6] Often, petroleum products and asphalt contain low levels of sulfur compounds, with the quantity of these compounds being mainly dependent upon the source of crude oil used in the petroleum or asphalt production.[7–9] Asphalt is a complex mixture of paraffinic, aromatic hydrocarbons, and heterocyclic compounds containing nitrogen, oxygen, and sulfur.[10] The addition of 12 to 20 percent crumb rubber to the asphalt mix only magnifies the chemical complexity of the fume by the addition of numerous organic compounds many of which contain sulfur. The main purpose of this project was to develop a method that would provide a total sulfur analysis to be used in epidemiological studies. A second objective was to investigate a means of analytically differentiating between the unmodified asphalt and the CRM asphalt.

The vulcanization process in tire manufacturing is the major source of sulfur compounds in CRM asphalt, but it does not seem to generate a specific sulfur entity needed as a CRM asphalt marker compound. However, benzothiazole accelerants used to speed the curing process during manufacture appeared to produce a specific moiety that could serve as an analytical marker. Two such accelerants are major curing agents used in the tire industry; these accelerants are 2,2′-Dithiobis[benzothiazole] and N-t-butyl-2-benzothiazole sulfenamide.[10,11] Figure 1 depicts the structure of both benzothiazole and these accelerants. These accelerants decompose both chemically and thermally during the curing process to produce benzothiazole. Moreover, benzothiazole has been found in the ambient air and in waste streams from plants where rubber tires are produced.[12] Also, in preliminary gas chromatography/mass spectrometry (GC/MS) studies of CRM asphalt in NIOSH laboratories, benzothiazole was identified as a component in the fume.[13]

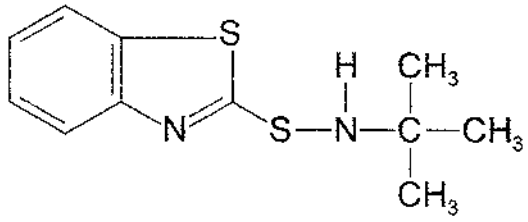
Several analytical techniques can be used to determine organic sulfur compounds. Gas chromatography with a variety of detectors: flame ionization, flame photometry, atomic emission, sulfur chemiluminescence (SCLD), and mass spectrometry (MS) has been used, as has liquid chromatography (LC) utilizing ultraviolet (UV) detection.[8,9,12,14–17] Although most of these detection techniques would have provided the necessary data, the complex matrix of asphalt fume dictated the need for a detection technique that was both selective and sensitive. A preliminary evaluation of gas chromatography with chemiluminescence detection indicated that the sensitivity required for the low sulfur levels and the selectivity needed to detect the sulfur compounds in the organic rich matrix of the fume could be achieved. Based on these preliminary findings, the method development proceeded in this direction.



Benzothiazole



2,2'-Dithiobis[benzothiazole]



N-t-butyl-2-benzothiazole sulfenamide

FIGURE 1
Structure of benzothiazole and accelerant sources.

EXPERIMENTAL

Chemicals and Solutions

Benzothiazole calibration standards were prepared from a chemical standard purchased from TCI Chemicals (Portland, OR), lot #FBRO-1, and assayed at 99+% pure by gas chromatography. Stock solutions, 10 mg/mL and 5 mg/mL, of benzothiazole in hexane were prepared and subsequently used to prepare calibration standards by serial dilution. Additionally, nominal 10 mg/mL and 5 mg/mL stock solutions were used to prepare samples for recovery and storage studies and quality assurance. LC and/or GC grade hexane (Burdick & Jackson, Muskegon, MI) was used in all sample preparation. Benzothiophene and dibenzothiophene were obtained from the Aldrich Chemical Company (Milwaukee, WI) and were used without further purification.

Sampling and Extraction Procedure

Field samples were collected at asphalt paving sites using a personal sampling pump with a two-section air sampling train. The first section consisted of a 37-mm Teflon membrane filter (Zefluor, Pall Gelman Sciences, Ann Arbor, MI) mounted between two cellulose spacer rings in a two-piece clear polystyrene cassette (SKC, Inc., Eighty Four, PA). The second section was an adsorbent sampling tube containing XAD-2 porous polymer

(ORBO-43 or ORBO-42 Large (LG), both: front = 100 mg, back = 50 mg, Supelco, Bellefonte, PA). This sampling train is described in NIOSH methods 5515[18] and 2550, 5506, and 5800.[19] The asphalt fume was drawn through the sampling train at a sampling rate of 1.0 to 2.0 L/min for an eight-hour shift giving a total volume of 480 to 960 liters.

In preparation for analysis, the membrane filter and the sampling tube were extracted as follows: The membrane filter was removed from the cassette, discarding the spacer rings, and placed in a 16 × 100 mm threaded test tube. The front media bed and the front glass wool plug from the sampling tube were removed and placed in another 16 × 100 mm threaded test tube. The rear media bed and the separating glass wool plug were placed in an additional 16 × 100 mm threaded test tube. Four mL of hexane were added to each test tube, capped with Teflon lined caps, and placed on a 360° rotating shaker for an overnight extraction (minimum 12 hours). (Note: overnight extraction was a matter of convenience to the sample preparation process.[20]) An aliquot of approximately 1 mL of the hexane extract was then removed for subsequent analysis for total sulfur compounds and benzothiazole.

Laboratory-spiked membrane filters and sampling tubes were prepared for analysis in a similar manner. Spiked membrane filters were prepared by adding 1.2 to 7.2-μL aliquots of a 4.16 mg/mL benzothiazole standard in hexane to each filter in a cassette. The filters were allowed to air dry for a minimum of 60 minutes before extraction and analysis. To prepare the sampling tubes for spiking, the end of the tube was scored, broken open, and spiked with an appropriate benzothiazole calibration solution on the front media bed of each tube. When spiking the sampling tube media bed with the same 4.16 mg/mL benzothiazole liquid standard, care was taken to make certain that the spiking syringe needle passed through the front glass wool plug and into the approximate center of the media bed before the sample was applied. After inoculation, the tube was capped and allowed to sit at room temperature for 24 hours before extraction and analysis.

Extraction of spiked membrane filters was accomplished by carefully removing the dry filter from the sampling cassette and placing the filter in a 5-mL or larger screw cap vial, and 4 mL hexane were added to each vial. The vial was capped with a Teflon-lined screw cap and shaken. Each vial was set aside for a minimum of 30 minutes with occasional agitation. Extraction of spiked sampling tubes was accomplished by carefully removing the front glass wool plug from the sampling tube and placing it in a 5-mL screw cap vial and pouring the front media bed into the same vial. Next, the middle glass wool plug was removed from the sampling tube and placed in a second 5-mL screw cap vial and the rear media bed was poured into the vial. The last glass wool plug was removed and also placed in the vial. Four mL hexane were added and the vials were capped with a Teflon-lined screw cap and agitated. Each vial was allowed to stand for a minimum of 30 minutes with occasional agitation. After the minimum stand time, an aliquot of approximately 1 mL was removed for subsequent analysis for benzothiazole.

Instrumental Setup

A Hewlett-Packard (Palo Alto, CA) 5890 Series II Gas Chromatograph, a Hewlett-Packard 7673 Auto injector, and an Antek (Houston, TX) 704E Sulfur Chemiluminescence Detector (SCLD) were used for the analysis of total sulfur compounds and benzothiazole. The analog signal from the SCLD was processed by Dionex (Sunnyvale, CA) AI-450 software running on a standard laboratory PC.

The GC analytical conditions were as follows: Several 100 percent dimethyl polysiloxane-bonded phase fused silica GC columns were surveyed. These GC columns included a Restek Rtx-1 (Bellefonte, PA), a Hewlett-Packard HP-1 (Palo Alto, CA), and a Supelco SPB-1 Sulfur (Bellefonte, PA). The column parameters for these columns were all 30 meters long with an i.d. of 0.32 mm and a film thickness of 1.0 μm, except the Supelco SPB-1 Sulfur that had a film thickness of 4.0 μm. For reasons to be discussed later, the Rtx-1 GC column was used for method development and sample analyses. Column carrier gas was helium set at a constant flow rate of 2.4 mL/min. The injection port temperature was 250°C. Interface heater temperature for the transfer interface between the GC and the SCLD was set at 280°C. Two GC oven temperature programs were used. The temperature program used most often started with the GC at 50°C for 1.0 minute; next, the GC was ramped at 6°C/minute to 225°C and held at 225°C for 15 minutes; then, the GC was ramped at 15°C/minute to 320°C. The other temperature program started with the GC at 50°C for 1.0 minute; next, the GC was ramped at 5°C/minute to 225°C and held at 225°C for 20 minutes; then, the GC was ramped at 10°C/minute to 320°C and held for 5 minutes. The total run times were 51.5 minutes and 70.5 minutes, respectively. A sample injection volume of 1.0 μL was used and was injected in the splitless mode of operation.

Operational parameters for the SCLD were set to Antek's recommended initial settings for the detector. Combustion furnace temperature was set to 1000°C. Rotameter settings for the three gases were: O_2 = 3.0, O_3 = 2.5, and H_2 = 4.0. Detector sensitivity was maximized by adjusting the oxygen and hydrogen flow to the combustion furnace, and the oxygen flow to the ozone generator as a benzothiazole standard solution of 1.0 μg/mL was repeatedly injected. Because flow characteristics are dependent on the furnace ceramic combustion tube dynamics, the oxygen and hydrogen flows must be maximized with each new set of ceramic combustion tubes. (Note: experience has shown that the ceramic combustion tubes will give roughly 9 to 12 months of continuous service before they need to be replaced because of coking.) Optimized rotameter settings for the gases to the original set of combustion tubes were: O_2 = 2.5, O_3 = 5.0, and H_2 = 4.0. These settings correspond to approximate flow rates of 6 mL/min, 75 mL/min, and 300 mL/min respectively. The furnace temperature also was lowered to 900°C for optimal performance.

RESULTS AND DISCUSSION

Initial GC/MS investigative work[13] on the asphalt fume indicated that the CRM asphalt fume had a higher level of sulfur-containing compounds when compared to the unmodified asphalt fume. This same investigative work showed that benzothiazole was the most predominant component in the CRM asphalt fume extract and should serve well as a marker compound for the CRM asphalt. Although there were a significant number of other sulfur-containing compounds in the asphalt fume samples and their summed mass was often greater than the benzothiazole, none occurred with a predominance that even approached benzothiazole. Consequently, benzothiazole was chosen as the marker compound for CRM asphalt. Additionally, benzothiazole became the surrogate compound for quantitating the other sulfur-containing compounds in the asphalt fume and was used in the recovery and storage studies without regard for any of the other sulfur-containing compounds.

Several drawbacks result from the use of benzothiazole as a surrogate quantitation standard. Compounds containing more than one sulfur atom will be overestimated. Overestimation of the "total" sulfur compounds provides a conservative approach when looking for correlations between these results and the health symptoms assessment. Also, benzothiazole is not expected to correlate with the total sulfur compounds in the sample because there is more than one source for benzothiazole and the other sulfur compounds. Additionally, any synergistic effects of these other sulfur-containing compounds on the desorption of benzothiazole would not be known. Consequently, quantitative recovery of benzothiazole from the solid sorbent became the major analytical issue.

Benzothiazole volatility is sufficiently high to keep it in the vapor phase; therefore, it is not retained on the membrane filter but passes through and is adsorbed on the media of the sampling tube. During the initial development work, however, both the filters and sampling tubes were extracted separately and the solutions analyzed to ascertain the efficiency of the sampling train. Although benzothiazole was not expected to be found on the filter, during field testing of the method some benzothiazole was found on some of the filters. Typically, only trace levels were found but several filters from CRM asphalt sampling sites were as high as 37 micrograms. The presence of benzothiazole on the filters is thought to be the result of adsorption to particulate matter on the filter although no definitive work was performed to determine this supposition. Furthermore, the field samples taken for the development work showed only trace levels or no benzothiazole on the backup section of the sampling tube and therefore, a breakthrough study was not performed.

One indirect means to evaluate the possible adsorption of benzothiazole on particulate matter and to demonstrate benzothiazole volatility was to perform a recovery study of liquid benzothiazole solutions from membrane filters. Filters were spiked with benzothiazole in hexane solution at levels equivalent to 5.0 to 40 μg and allowed to dry at room conditions overnight. When these filters were extracted and analyzed, no peaks were seen at the retention time for benzothiazole nor at other times in the chromatographic run. These results indicate that under normal air sampling conditions without a high particulate background, membrane filters will not retain benzothiazole.

Several capillary GC columns were surveyed for this method development which included a Hewlett-Packard HP-1, a Supelco SPB-1 Sulfur, and a Restek Rtx-1. Any one of the columns evaluated could have been used for this work because the selectivity, sensitivity, and retention times were nearly the same for each of the columns. Benzothiazole standards run on each column showed only minor variations in retention time and resolution. However, the Restek Rtx-1 column was selected because it produced a less noisy baseline and the retention times for most compounds were shorter without any loss of resolution under the same oven temperature conditions.

A typical calibration curve for benzothiazole covered a working range of 4.0 to 80.0 μg/sample. Linear regression analysis of peak areas for each injected standard versus the standard concentration showed linearity for the concentration range and was demonstrated by a coefficient of determination (R^2) value equal to 0.99 or greater. Based on the regression results for the low-level liquid standards, the limit of detection (LOD) [$3s_y$/slope] and the limit of quantitation (LOQ) [$10s_y$/slope] of the method were determined to be 0.3 and 1.0 μg/sample, respectively,[21,22] where, by definition, low-level liquid standards have concentrations ranging from the estimated LOD to 10 times the estimated LOD and the s_y = standard error of Y (approximates the standard error of regression), and the slope = slope of regression analysis. Linearity of the analyte response is very good as the calibration curve has been extended to 800 μg/sample without any loss of linearity or change of slope. Application of this method to the analysis of field samples from industrial hygiene studies typically used a calibration curve made from a low range (4.0 to 80.0 μg/sample) of standards to fit the analyte range of the samples.

Calibration and analysis for total sulfur compounds were performed using the benzothiazole standards and calibration data. No effort was made specifically to identify any of the other sulfur-containing compounds, although retention times provided some clues to their identities. Because the SCLD totally combusts the organic matrix and releases the sulfur and is responsive almost exclusively to the sulfur moiety, responses for all sulfur compounds should be the same. As a result, the remaining peak areas for all compounds except benzothiazole were totaled and reported as one total sulfur compound value.

For the first three asphalt paving sites, media standards, and spiked sampling tubes, the ORBO-43 sampling tubes were used. However, many battery-operated sampling pumps were failing at the field sites presumably because of a large pressure drop across the sampling train. The pump failure problem was either minimized or eliminated altogether when the sampling train was modified to include the ORBO-42 LG sampling tube presumably because the ORBO-42 LG sampling tube has a larger diameter (10 mm) than the ORBO-43 sampling tube (8 mm). Both sampling tubes contain 100 mg XAD-2 in the front media bed

TABLE I
Desorption efficiency and storage studies

Amount spiked	% Recovered	% RSD
5.0 μg	96.5	3.7
10.0 μg	90.1	4.0
20.0 μg	90.5	0.9
40.0 μg	89.4	3.0
30-Day storage on ORBO-43 sampling tubes containing XAD-2 Resin (n = 6)		
20 μg	81.3[A] (16.3 μg)	1.1

[A]Correction of the storage recovery for 90.5 percent DE at 20 μg gives a result of 89.8 percent recovery for the 30-day samples.

and 50 mg XAD-2 in the back media bed.[23] Manufacturer's literature[23] indicates that the difference between the two sampling tube media is in the type of cleanup given the XAD-2 resin. No effort was undertaken to determine if recovery would be affected by the two different media cleanup steps.

Recovery of benzothiazole from spiked ORBO-43 sampling tubes was determined at four levels of 5.0, 10, 20, and 40 μg/sample. Six tubes were prepared at each fortification level for analysis. Results of this study are tabulated in Table I. In addition, six tubes were spiked at the 20 μg level for use in a 30-day storage stability study. After spiking, the tubes were capped and stored in a refrigerator at 4°C. Results of the 30-day storage study are also summarized in Table I.

Once the conditions for analysis had been established, the technique was applied to asphalt fume samples collected by NIOSH industrial hygienists. These samples included both area and personal breathing zone (PBZ) samples from several paving sites in different parts of the continental United States. Samples from these sites were analyzed by this method to verify the original goals of the method development program—to provide data for an epidemiological irritancy study and to differentiate unmodified (non-rubber-containing) asphalt from crumb-rubber-modified (CRM) asphalt.

Extracted asphalt fume samples are complex in nature because they have a broad spectrum of aliphatic, aromatic, and heteroatom compounds. Fractionation of the extract by liquid/liquid extraction or solid-phase extraction could have been performed, but at the possible expense of a loss of a portion of the sulfur containing compounds. Because one objective of this work was to obtain a quantitative value of the total sulfur compounds in the asphalt fume to correlate with the health symptom assessments, sample handling was kept to a minimum. The consequence of this was that the full hydrocarbon load of the asphalt fume extract was injected into the GC for analysis of the sulfur-containing compounds. The Antek SCLD has a sulfur-to-hydrocarbon response factor of 10^7 and under normal circumstances this is sufficient to eliminate nearly all hydrocarbon interference, including the solvent response, and still give baseline resolution for all the sulfur peaks. However, some of the asphalt fume extracts overloaded the hydrocarbon response of the SCLD because of the amount of hydrocarbons in the sample. The effect was a chromatogram that had a large "hump" in the baseline from about 20 minutes up to about 45 minutes of the chromatographic run. This effect is demonstrated by the chromatogram shown in Figure 2.

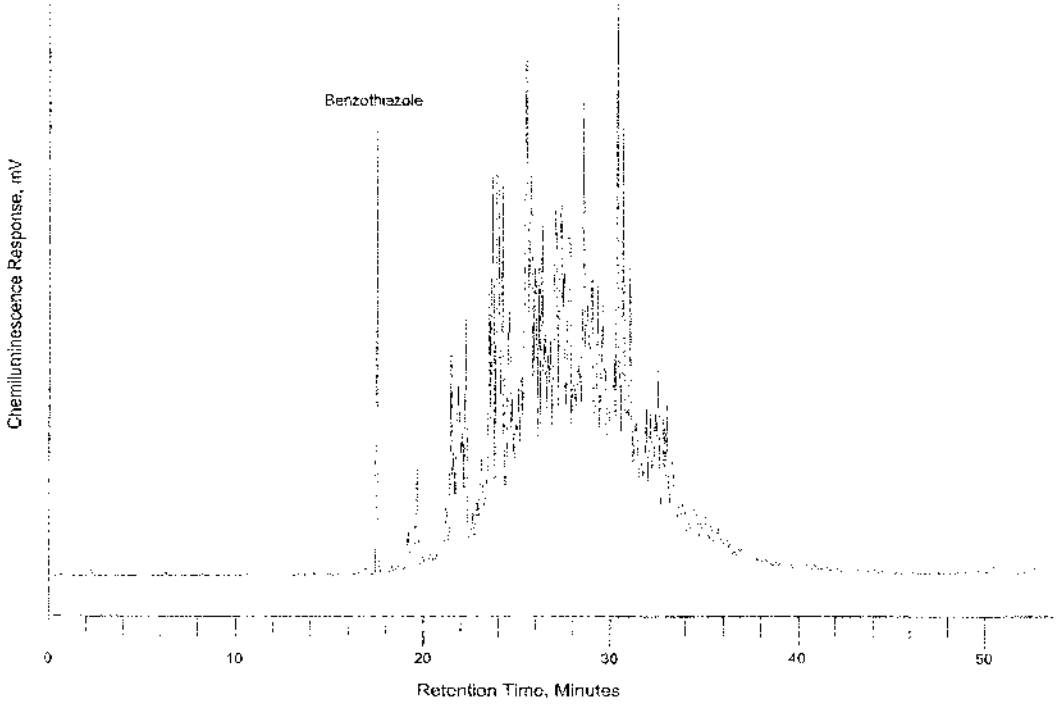


FIGURE 2
Chromatogram of an asphalt fume sample with high hydrocarbon content.

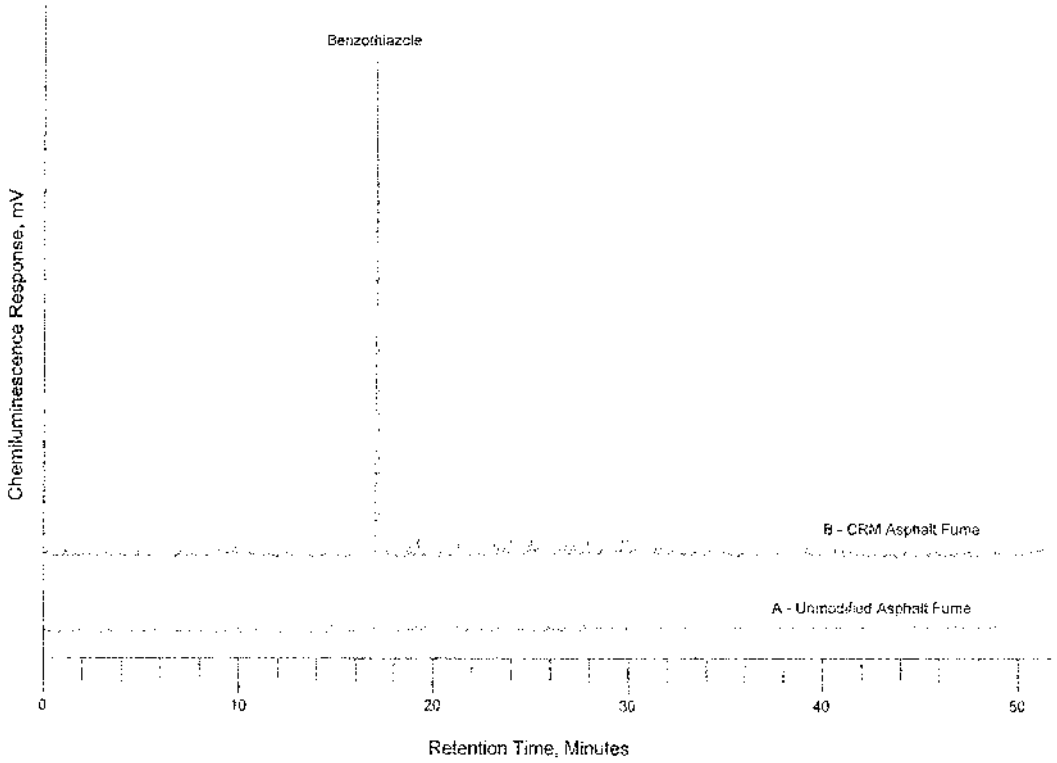


FIGURE 3
Chromatograms of a worker personal breathing-zone sample taken during the application of (A) unmodified asphalt and (B) CRM asphalt.

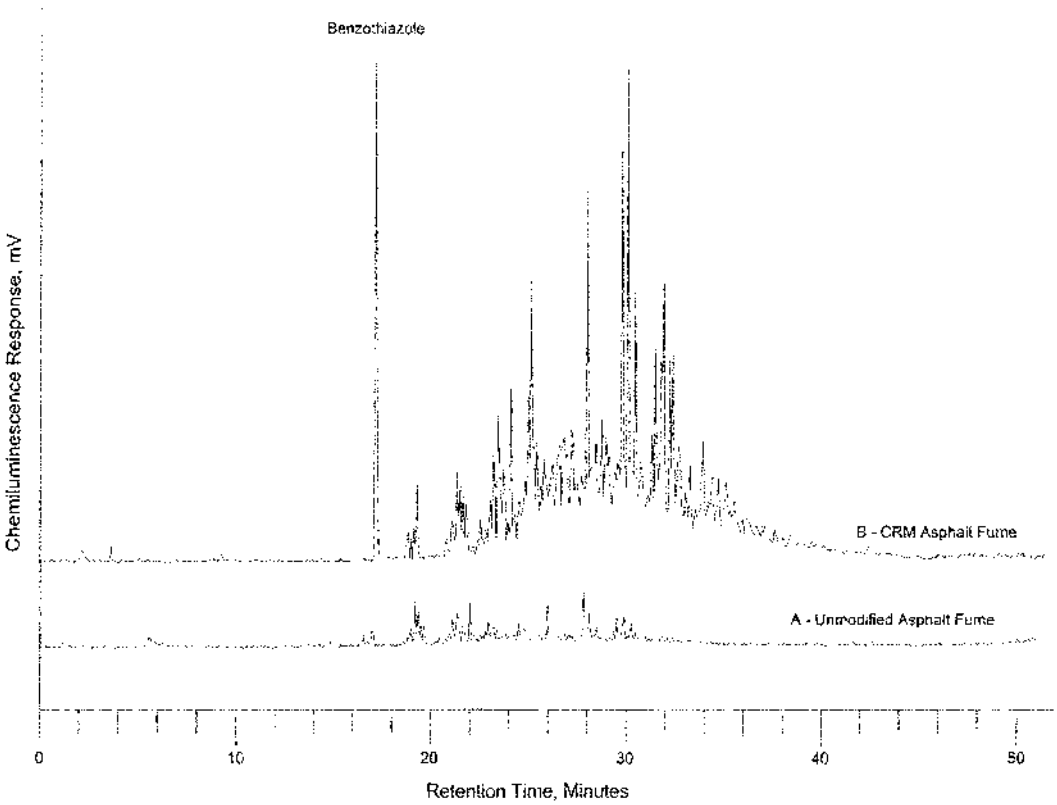


FIGURE 4
Chromatograms of a highway background sample taken during the application of (A) unmodified asphalt and (B) CRM asphalt.

Two of the ways to correct for the large hydrocarbon content of the asphalt fume samples are: one, dilute the sample with additional hexane and rerun the sample and, two, change the temperature program of the oven to stretch out the chromatographic run. Both sample dilution and extended chromatographic run cause the instantaneous hydrocarbon mass flow through the detector to be lowered, resulting in an elimination of the "hump." Diluting the sample causes the hydrocarbon load to be reduced at constant injection volumes and, therefore, the elimination of hydrocarbon response is more effective. However, because of sample handling considerations, the second mode was selected as the most feasible way to achieve a lower baseline with improved resolution. An effective GC oven temperature program to reduce the "hump" was previously outlined. Extending the overall run time resulted in nearly reducing the large "hump" to the normal baseline.

Shown in Figure 3 are chromatograms of the sulfur-containing compounds from an asphalt fume sample of a unmodified (A) and CRM (B) asphalt mix. These samples were taken in the PBZ of a road-paving equipment operator whose station is at the rear of the paver that lays the asphalt on the road surface. The response factor for both A and B chromatograms is the same. Note that the number of sulfur-containing compounds is significantly increased in the CRM asphalt fume sample and peaks at the same retention time in both chromatograms are larger in the CRM asphalt fume sample. The peak with the greatest height in Figure 3, at approximately 17.5 minutes, is benzothiazole as confirmed by calibration standards and GC/MS. Paving site area (background) samples, taken over an eight-hour work shift, also show the same correspondence between a unmodified asphalt and a CRM asphalt sample. This is illustrated by the chromatograms A and B shown in Figure 4, which can be compared to the PBZ chromatograms A and B in Figure 3. Peak response factors for all these chromatograms are the same.

Results from the analysis of asphalt fume samples from four asphalt paving sites are compiled, tabulated and shown in Table II. These data demonstrate one of the initial premises that benzothiazole can be used to differentiate between unmodified asphalt mixes and CRM asphalt mixes. There is, however, a caveat to this statement in that a single sample taken at the asphalt paving work site will not necessarily be able to differentiate between the two types of asphalt. As seen in Table II, both asphalt mixes had benzothiazole and total sulfur compound data that were below the LOD; nearly all these results were from samples taken as background samples, such as in a highway median or in a construction trailer at the asphalt paving site. Some unmodified asphalt mixes have been shown to contain very small quantities of benzothiazole or a compound that elutes at the benzothiazole retention time. However, it is typically seen at or below the calculated LOD of the method. On the other hand, all the CRM asphalt fume mix samples which were taken at the same asphalt paving site location as the previous unmodified asphalt fume samples showed a range of results where the upper values were all well above the LOD of the method. The one exception was asphalt paving site #2 where benzothiazole was found at a level well above the LOD for unmodified asphalt fume. No apparent reason for this anomaly was determined. Total sulfur compound data reported in Table II were calculated by subtracting the peak areas for benzothiazole from the summed peak areas in the chromatogram report.

TABLE II
Paving site results

	Concentration range	
	Benzothiazole ($\mu g/m^3$)	Total sulfur[A] ($\mu g/m^3$)
Site #1		
Area samples		
Unmodified asphalt	<0.5–≤1.6[B]	<0.5–5.6
CRM[C] asphalt	<0.5–59	<0.5–37
PBZ[D] samples		
Unmodified asphalt	<0.5–≤1.6[B]	<0.5–11
CRM asphalt	<0.5–13	<0.5–12
Site #2		
Area samples		
Unmodified asphalt	<0.5–24	<0.5–750
CRM asphalt	<0.5–120	<0.5–186
PBZ samples		
Unmodified asphalt	<0.5–≤1.6[B]	<0.5–≤1.6[B]
CRM asphalt	<0.5–68	<0.5–14
Site #3		
Area samples		
Unmodified asphalt	<0.5–≤1.6[B]	<0.5–31
CRM asphalt	<0.5–20	<0.5–270
PBZ samples		
Unmodified asphalt	<0.5–≤1.6[B]	<0.5–12
CRM asphalt	<0.5–17	<0.5–85
Site #4		
Area samples		
Unmodified asphalt	<0.5–≤1.6[B]	<0.5–105
CRM asphalt	<0.5–127	<0.5–790
PBZ samples		
Unmodified asphalt	<0.5–≤1.6[B]	<0.5–≤1.6[B]
CRM asphalt	<0.5–58	<0.5–135

[A]Total sulfur value = Total sulfur found minus the benzothiazole amount found.
[B]<0.5 = < limit of detection (LOD), ≤1.6 = equal to or below limit of quantitation (LOQ).
[C]CRM = crumb-rubber-modified.
[D]PBZ = personal breathing-zone.

A further breakdown of PBZ samples for one of the asphalt paving sites is shown in Table III. This table shows the results for several workstation operators during both unmodified and CRM asphalt paving operations. As demonstrated by this data, benzothiazole and sulfur-containing compounds were not found in the unmodified asphalt PBZ samples. However, all the CRM

TABLE III
Personal breathing-zone analyte concentrations

	Concentration range	
	Benzothiazole ($\mu g/m^3$)	Total sulfur[A] ($\mu g/m^3$)
Unmodified asphalt		
Paver operator	<0.5–<1.6[B]	<0.5–<1.6[B]
Screed operator	<0.5–<1.6[B]	<0.5–<1.6[B]
Screed operator	<0.5–<1.6[B]	<0.5–<1.6[B]
Roller operator (front)	<0.5–<1.6[B]	<0.5–<1.6[B]
Roller operator (middle)	<0.5–<1.6[B]	<0.5–<1.6[B]
Roller operator (rear)	<0.5–<1.6[B]	<0.5–<1.6[B]
Laborer	<0.5–<1.6[B]	<0.5–<1.6[B]
State inspector	<0.5–<1.6[B]	<0.5–<1.6[B]
Crumb-rubber-modified asphalt		
Paver operator	33–58	8.9–16
Screed operator	33–41	1.0– 6.1
Screed operator	30–34	<0.5–<1.6[B]
Roller operator (front)	5.1	<0.5–<1.6[B]
Roller operator (rear)	2.0–7.8	<0.5–<1.6[B]
Laborer	19	<0.5–135
Laborer	38	<0.5–<1.6[B]
State inspector	15–18	<0.5–<1.6[B]

[A]Total sulfur value = Total sulfur found minus the benzothiazole amount found.

[B]<0.5 = <limit of detection (LOD), <1.6 = below limit of quantitation (LOQ).

asphalt samples showed benzothiazole present in the corresponding PBZ sample with varying levels of other sulfur-containing compounds.

Although the work described here concentrated on the identification and analysis of benzothiazole, additional work was performed in an effort to identify other compounds which appeared in the asphalt fume sulfur chromatograms. Only benzothiazole has been confirmed in the asphalt fume samples by GC/MS analysis from actual paving sites where CRM asphalt was being used.[13] As seen in Figures 3 and 4, most of the sulfur-containing compounds elute from the column between approximately 15 and 35 minutes. Figure 5 presents several chromatograms in which only the time span between 14 and 32 minutes is shown. Chromatograms A, B, and C are reference compounds—benzothiazole, benzothiophene, and dibenzothiophene, respectively—used as retention time markers for the other two chromatograms. Chromatograms D and E are of a unmodified asphalt fume and a CRM asphalt fume, respectively. Response factors for the five chromatograms are not all the same. As indicated by these chromatograms, it would appear that most of the sulfur compounds lie between benzothiazole and dibenzothiophene in terms of boiling point and/or molecular weight.

Two possible scenarios could account for the several peak groupings in the CRM fume sample based on the closeness of the peaks in each grouping. The first scenario is a homologous series of compounds with increasing single side chain length attached to the aromatic moiety. The second is geometric isomers of a compound with a side chain of constant length attached to the base aromatic moiety. The most likely base compound would

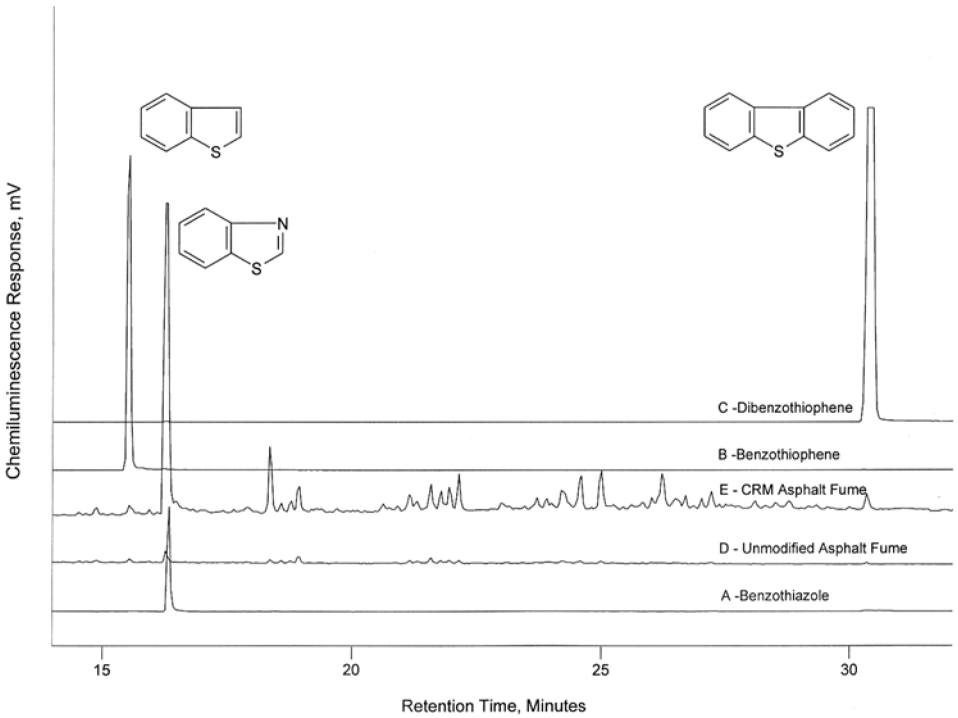


FIGURE 5
Overlay of chromatograms of heterogeneous sulfur compound standards, unmodified asphalt, and CRM asphalt.

be benzothiazole or a benzothiophene in these cases. None of these compounds or possible structures have been confirmed at this time by GC/MS with the exception of benzothiazole.

CONCLUSIONS

The purpose of the work described in this article was to develop a sampling and analytical method for total sulfur-containing organic compounds and benzothiazole in asphalt fume. These methods would provide support to an evaluation of the health effects of the asphalt fume on asphalt paving workers. There were two main objectives to this research effort. First, provide an analytical method of quantitation of total sulfur compounds and benzothiazole; and second, to develop a method to differentiate between asphalt fume generated by unmodified asphalt and those generated by crumb-rubber-modified asphalt. Analytical results shown in this research indicate that both objectives have been achieved.

The analytical technique described here has a linear response to benzothiazole over several orders of magnitude in concentration. Additionally, the same chromatographic analysis provides a total sulfur compound value for use in epidemiological studies on asphalt paving worker health. Data from the analysis of samples taken at four of the selected paving sites support the hypothesis that the method can be used to differentiate between unmodified asphalt and CRM asphalt mixtures. For the unmodified asphalts, levels of benzothiazole found were from none detected to levels below the limit of quantitation. For CRM asphalts, the levels found were from none detected to several hundred micrograms per cubic meter of the sampled air. All the none detected results were limited to the background samples. Total sulfur compound data were reported for all the asphalt fume samples and ranged from none detected to amounts well above the limit of quantitation. These data, as reported to the epidemiologists, are still being evaluated as to their correlation with any possible health effects related to the asphalt paving workers.

Future research related to this project would entail the identification and quantitation of the other sulfur compounds seen in the asphalt fume chromatograms. While retention time comparisons using a two-column confirmation technique will provide potential identification, mass spectral analysis would give positive identification. Additionally, mass spectral identification is a more reasonable approach to the identification of the many possible alkylated thiophenes suspected as the major contributors to the total sulfur compound spectrum.

ACKNOWLEDGMENTS

The authors wish to make a special acknowledgment to Donald D. Dollberg for valuable discussions during this development work, as well as the following for additional helpful discussions: Charles E. Neumeister and Dawn G. Tharr. The Federal Highway Administration is acknowledged for partial funding of this work.

The authors also wish to thank the following NIOSH industrial hygienists who collected and then supplied extra field samples used in the development of this method: Daniel Almaguer, Gregory A. Burr, and Kevin W. Hanley.

REFERENCES

1. State of the Practice: Design and Construction of Asphalt Paving Materials with Crumb Rubber Modifier. Report No. FHWA-SA-92-022; U.S. Department of Transportation, Federal Highway Administration (FHWA). U.S. Government Printing Office, Washington, D.C. (1992).
2. Rothe, A.: Contact Dermatitis from Chemicals Used in the Production of Photographic Emulsions. Cont Dermat 23(4):269 (1990).
3. Kraut, A.; Lilis, R.: Pulmonary Effects of Acute Exposure to Degradation Products of Sulfur Hexafluoride During Electrical Cable Repair Work. Br J Ind Med 47(12):829–832 (1990).
4. Lenga, R.E.; Votoupal, K.L.; eds.: The Sigma–Aldrich Library of Regulatory and Safety Data, Vol. 2. Sigma-Aldrich, Milwaukee (1993).
5. Sama, S.R.; Kriebel, D.; Woskie, S.; et al.: A Field Investigation of the Acute Respiratory Effects of Metal Working Fluids. II. Effects of Airborne Sulfur Exposures. Am J Ind Med 31(6):767–776 (1997).
6. Sun, C.-C.; Sue, M.-S.: Sulfur Springs Dermatitis. Cont Dermat 32(1):31–34 (1995).
7. Poirier, M.; Das, B.S.: Characterization of Polynuclear Aromatic Hydrocarbons in Bitumen, Heavy Oil Fractions Boiling Above 350 Degrees C by G.C.-M.S. Fuel 63(3):361–367 (1984).
8. Chawla, B.; Di Sanzo, F.: Determination of Sulfur Components in Light Petroleum Streams by High-Resolution Gas Chromatography with Chemiluminescence Detection. J Chromatogr 589:271–279 (1992).
9. Shearer, R.L.; Poole, E.B.; Nowalk, J.B.: Application of Gas Chromatography and Flameless Sulfur Chemiluminescence Detection to the Analysis of Petroleum Products. J Chromatogr Sci 31:82–87 (1993).
10. The Condensed Chemical Dictionary, 10th ed., G.G. Hawley, Ed., p. 119. Van Nostrand Reinhold Company, New York (1981).
11. Rappaport, S.M.; Fraser, D.A.: Air Sampling and Analysis in a Rubber Vulcanization Area. J Amer Ind Hyg Assoc 38(5):205–209 (1977).
12. Parsons, J.S.; Mitzner, S.: Gas Chromatographic Method for Concentration and Analysis of Traces of Industrial Organic Pollutants in Environmental Air and Stacks. Environ Sci Technol 9(12):1053–1058 (1975).
13. Grote, Ardith A.: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Physical Science and Engineering, 4676 Columbia Parkway, Cincinnati, Ohio 45226; personal communication on unpublished GC/MS laboratory evaluations of asphalt fume.
14. Berthou, F.; Dreano, Y.; Sandra, P.: Liquid and Gas Chromatographic Separation of Isomeric Methylated Dibenzothiophenes. J High Res Chrom 7(12):679–686 (1984).
15. Ojala, M.; Ketola, R.; Mansikka, T.; et al.: Detection of Volatile Organic Sulfur Compounds in Water by Headspace Gas Chromatography and Membrane Inlet Mass Spectrometry. J High Res Chrom 20(3):165–169 (1997).

16. Shearer, R.L.; O'Neal, D.L.; Rios, R.; et al.: Analysis of Sulfur Compounds by Capillary Column Gas Chromatography with Sulfur Chemiluminescence Detection. J Chromatogr Sci 28(1):24–28 (1990).
17. Scott, B.F.; Sverko, E.; Maguire, R.J.: Determination of Benzothiazole and Alkylphosphates in Water Samples from the Great Lakes Drainage Basin by Gas Chromatography/Atomic Emission Detection. Water Qual Res J Canada 31(2):341–360 (1996).
18. Eller, P.E.; Cassinelli, M.E.; eds.: NIOSH Manual of Analytical Methods, 4th ed., DHHS (NIOSH) Publication Number 94-113, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. U.S. Government Printing Office, Washington, D.C. (1994).
19. Eller, P.E.; Cassinelli, M.E.; eds.: NIOSH Manual of Analytical Methods, 4th ed., 2nd Supplement., DHHS (NIOSH) Publication Number 98-119; U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. U.S. Government Printing Office: Washington, D.C. (1998).
20. Neumeister, C.E.; Olsen, L.D.; Dollberg, D.D.: Development of Flow-Injection Spectrofluorometric Method for Determination of Total Polycyclic Aromatic Compounds in Asphalt Fume. Unpublished manuscript (1998).
21. Kennedy, E.R.; Fischbach, T.J.; Song, R.; et al.: Guidelines for Air Sampling and Analytical Method Development and Evaluation. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117. NIOSH, Cincinnati, OH (1995).
22. Keith, L.H.; Crummett, W.; Deegan, J., Jr.; et al.: Principles of Environmental Analysis. Anal Chem 55:2210–2218 (1983).
23. Supelco Chromatography Products for Analysis and Purification Catalog., 1998, Supelco Park, Bellefonte, PA 16823.