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Heritage Research Group

7901 W. Morris Street • Indianapolis, IN 46231 U.S.A.
317-243-0811 • 486-2985 (FAX)

FINAL RESEARCH SUMMARY

CHEMICAL COMPARISON OF LABORATORY GENERATED FUMES FROM STRAIGHT RUN VACUUM DISTILLED AND TWO DIFFERENT CRUMB RUBBER MODIFIED BITUMENS

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Anthony J. Kriech
Director of Research

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1. Objective and Background

The goal of this research was to compare bitumen fumes from unmodified bitumen versus two different formulations of crumb rubber modified bitumens. Sponsored by the Swedish Road Administration, three samples were submitted for investigation using the Heritage Research Group proposal dated October 31, 2006. These samples are described as follows:

1. B 70/100, 2006-11-30
2. B 70/100 83%, + gummi 0.0-0.8 17%, 2006-11-30
3. B 70/100 83% + 17% ROAD⁺, 2006-11-30

Since personal exposures in the paving industry while using hot bitumen can be influenced by many uncontrollable variables, laboratory fume generations were used for this study. This was accomplished using a modified Brandt (1) laboratory scale fume generation rig as pictured on the cover page and Figure 1. Modifications for this study included the use of a reaction flask head with four 25-mm openings used for the stirring rod, thermocouple, vent and collection tubes. Each opening, except for the vent, was sealed to improve reproducibility. Also, the collection of the fumes occurred using XAD-2 only, to allow collection of the total fume (vapor and aerosol phases) instead of just the aerosol fraction using filters.

Field validation has not been performed using this laboratory fume generation procedure in the exact manner in which these fumes were tested. The goal of this study was to determine the *relative* differences in the fumes released from the following test materials: straight run vacuum distilled and two different crumb rubber modified bitumens. In the preparation stage, the same base bitumen was used for all three materials. Through the elucidation of the chemistry of the resultant fumes, this study will help predict differences between these materials that mimic worst-case scenarios of potential exposures.

2. Fume Generation Procedure

Figure 1 shows a schematic of the modified Brandt laboratory fume generation rig proposed for use in this study. The system was designed to heat the bitumen to the desired temperature (in this case 160°C) while stirring the bitumen at a controlled rate (300-400 rev/min). When the bitumen reached the desired temperature, fumes released were captured on XAD-2 resin.

Certificates of fume generation outlining specific parameters of the fume generations are shown in Appendix A and include exact vessel temperature; stir rate, collection media quantities and sampling duration. Using XAD-2 tube collection systems, fumes emitted in the generator vessel were drawn through the resin with a pump calibrated to a flow rate of 2.0 liters per minute (lpm).

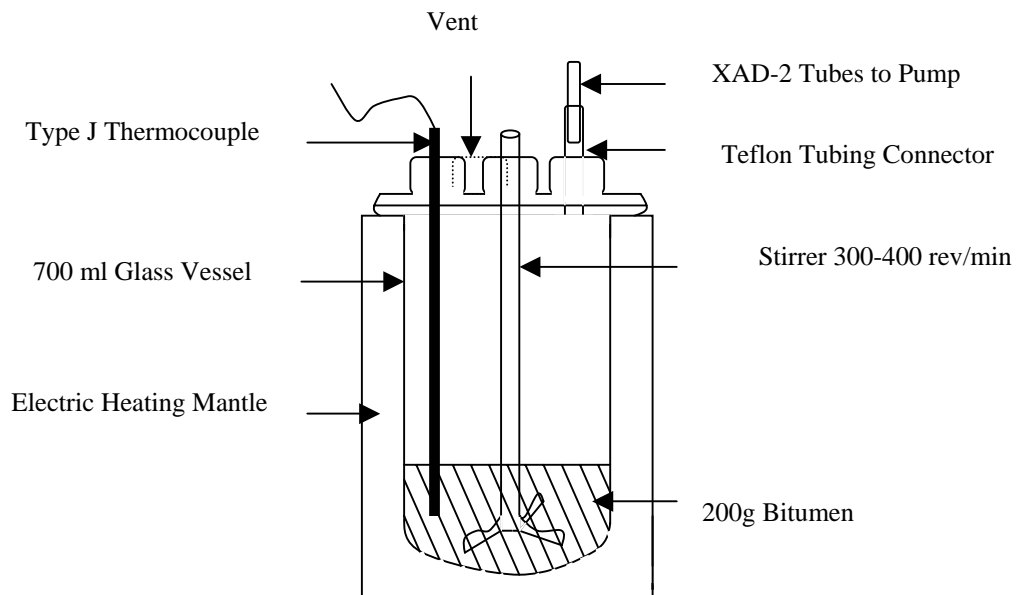


Figure 1. Modified Brandt laboratory fume generator schematic.

3. Bitumen Fume Analysis & Results

3 A. Gas Chromatography/ Flame Ionization Detection (GC/FID)

3 A i. Total Organic Matter (TOM)

Using gas chromatography with flame ionization detection (GC/FID), the amount of fume collected was determined, referred to as total organic matter (TOM) (SW 846-8015 mod) (2). TOM results are shown in Table 1. GC/FID Chromatograms are presented in Appendix B.

Table 1. TOM, Fluorescence and Sim-Dis Results on Laboratory-Generated Fumes

	2006-11-30 Source of Bitumen Fume	Total Organic Matter mg/m ³	Fluorescence Emission Units/gram (EU/g)	10% Distilled (°C)	50% Distilled (°C)	90% Distilled (°C)
1	B 70/100	752	191	250	362	535
2	B 70/100 83%, + gummi 0.0-0.8 17%	494	190	242	393	534
3	B 70/100 83% + 17% ROAD ⁺	451	193	244	398	540

3 A ii. Simulated Distillation (Sim-Dis)

Using GC/FID, the boiling point profile of each fume was determined using a simulated distillation method ASTM D-2887 (3). Results for the 10, 50 and 90 percent distilled are shown in Table 1 and the comparative boiling point distributions are shown in Figure 2.

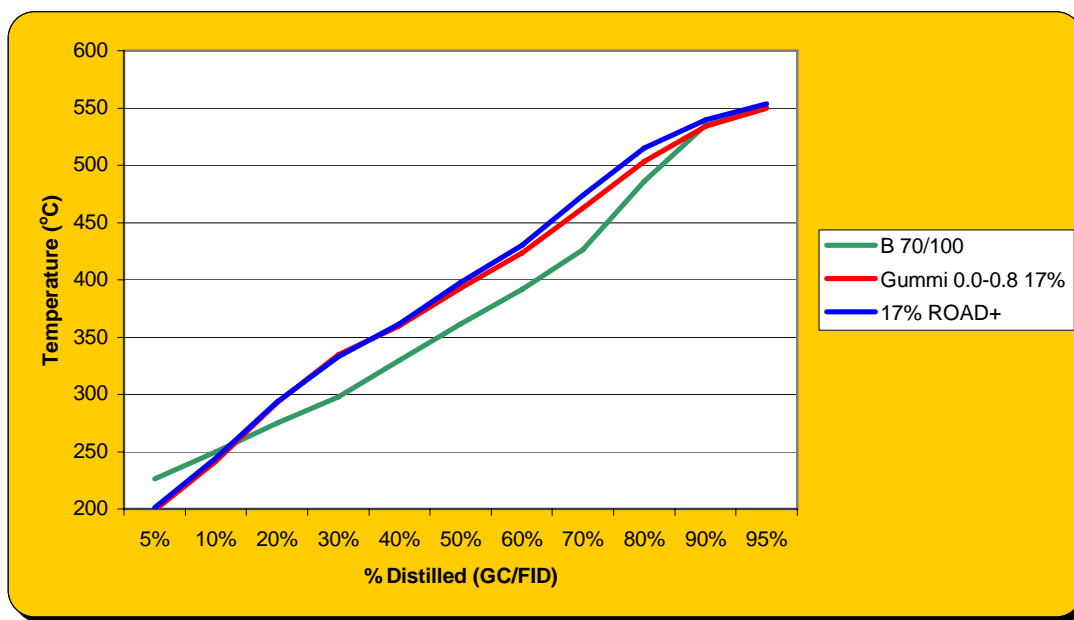


Figure 2. Simulated distillation comparison of parent bitumen fumes versus fumes generated from two modified bitumens. The parent bitumen fume boiling point range is lower for most of the curve. The two modified bitumen fumes almost overlap.

3 B. Fluorescence

An aliquot of the fume extract was also exchanged into cyclohexane for fluorescence analysis. These analyses were performed using a Perkin Elmer Luminescence Spectrometer LS50B following the asphalt fume fluorescence (AFF) test protocol outlined in a separate publication (4). This fluorescence test method is designed to optimize response to potentially carcinogenic compounds in bitumen fumes. Results are listed in Table 1 and show almost identical results for all three samples.

3 C. Gas Chromatography/Mass Spectroscopy (GC/MS)

Two different types of mass spectrometers were employed for analyses of these fume samples. Gas chromatography with a time of flight mass spectrometer (GC/TOFMS) was used for the speciation of polycyclic aromatic compounds (PACs). For fingerprinting various extracted ions, an Agilent GC with a quadrupole mass spectrometer was used.

3 C i. Polycyclic Aromatic Compounds

To investigate compounds of regulatory concern, these fume condensates were extracted with DMSO using modified IP-346 methodology and analyzed by GC/TOFMS for 35 PACs following the guidelines of EPA SW-846 8270 (5) and the method published by Heritage (6) for the Emergency Planning and Community Right to Know Act (EPCRA) list of compounds. These results are compiled in Table 2.

Figure 2 displays only the detectable results and the data is flagged with stars for those compounds that appear to be slightly higher for the gummi modified bitumen fume. Since crumb rubber modified bitumen is a part of this study, other compounds investigated via library searching included carbazoles and benzothiazoles. Benzothiazole (see structure in Figure 3) was detected at extremely high concentrations (% levels), whereas the parent bitumen concentration was ≤ 18 ppm.

3 C ii. Extracted Ion Fingerprints

To further characterize compounds in the fumes of these three bitumen materials, GC/MS was also used to create fingerprints of extracted ions. This takes advantage of collecting the three dimensional GC/MS data. Two of these dimensions are the mass versus intensity of the normal mass spectrum; the third dimension is the GC retention time over which the mass spectral data are acquired. Basically, it is a plot of the intensity of one selected mass as a function of time. Instead of plotting the *total* ion current vs. time, this extracted ion chromatogram allows the mass spectrometer to be used as a selective detector, displaying individual ions (m/z) of interest.

Table 2. Polycyclic Aromatic Compounds Concentrations (mg/kg)

	mg/kg (11-30-06)	1	2	3
	Polycyclic Aromatic Compounds	70/100	70/100 + Gummi 0.0-0.8 17%	70/100 + 17% ROAD ⁺
1	Naphthalene	350	385	178
2	Acenaphthene	43.3	118	31.0
3	Acenaphthylene	≤3	52.9	14.7
4	Anthracene	12.8	≤4	≤2
5	Fluoranthene	≤3	27.0	19.2
6	Fluorene	39.1	169	38.6
7	Benzo[a]anthracene	≤3	≤4	≤2
8	Chrysene	10.5	12.3	12.6
9	5-Methylchrysene	≤3	≤4	≤2
10	1-Nitropyrene	≤3	≤4	≤2
11	Pyrene	23.8	66.4	52.3
12	Phenanthrene	84.9	325	94.6
13	Benzo[b]fluoranthene	≤3	4.7	3.8
14	Benzo[j]fluoranthene	≤3	≤4	≤2
15	Benzo[k]fluoranthene	≤3	≤4	≤2
16	7,12-Dimethylbenz[a]anthrene	≤3	≤4	≤2
17	Benzo[a]pyrene	≤3	≤4	≤2
18	Benzo[e]pyrene	≤3	6.0	4.7
19	3-Methylcholanthrene	≤3	≤4	≤2
20	Dibenz[a,h]acridine	≤3	≤4	≤2
21	Dibenz[a,j]acridine	≤3	≤4	≤2
22	Indeno[1,2,3-cd]pyrene	≤3	≤4	≤2
23	Dibenz[a,h]anthracene	≤3	≤4	≤2
24	7H-Dibenzo[c,g]carbazole	≤3	≤4	≤2
25	Benzo[g,h,i]perylene	4.8	8.0	4.2
26	Dibenzo[a,e]fluoranthene	≤3	≤4	≤2
27	Dibenzo[a,e]pyrene	≤3	≤4	≤2
28	Benzo[r,s,t]pentaphene	≤3	≤4	≤2
29	Dibenzo[a,h]pyrene	≤3	≤4	≤2
30	Dibenzo[a,l]pyrene	≤3	≤4	≤2
31	Benzo[b]naphtho[2,1-d]thiophene	9.3	15.8	12.2
32	Cyclopenta[cd]pyrene	≤3	≤4	≤2
33	Triphenylene	≤3	≤4	≤2
34	Carbazole	≤3	≤4	≤2
35	Benzothiazole	≤18	254993	92413

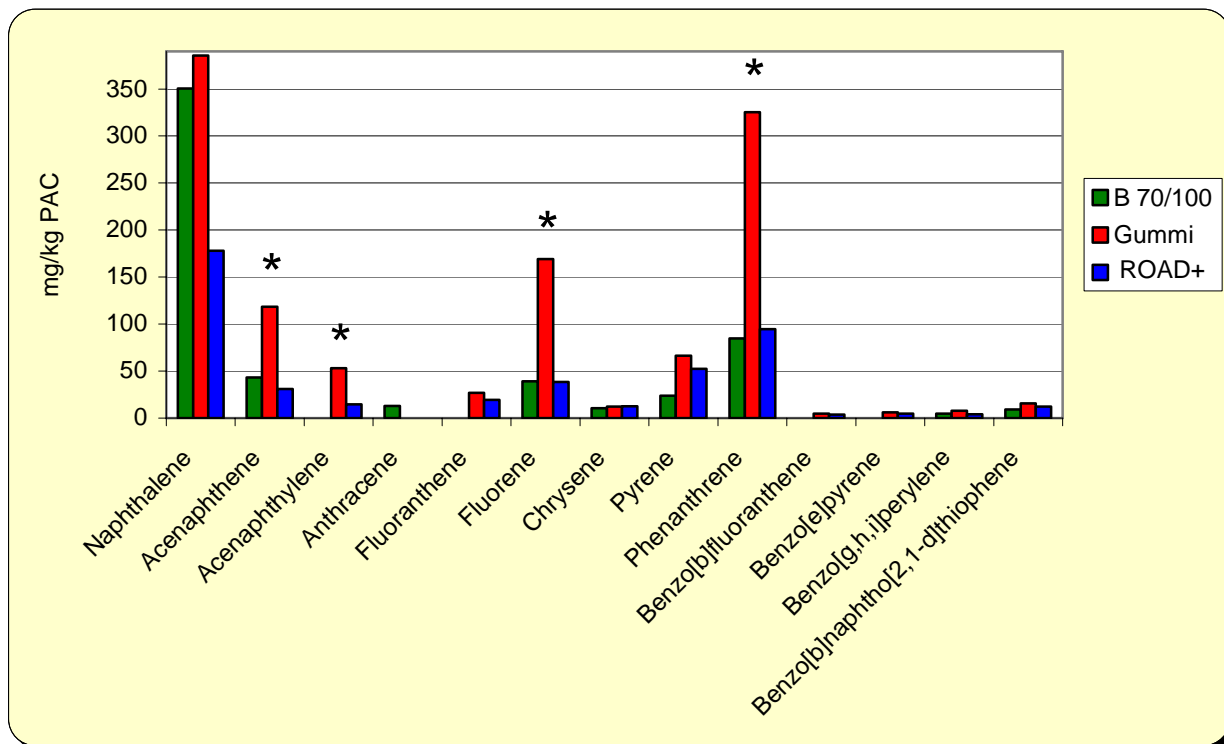


Figure 2. Detectable PACs in the fumes of the parent bitumen and the two modified bitumens. This does not include benzothiazole, which is present in the modified bitumens at percent levels. The starred compounds appear to be higher in the gummi sample than the other two fumes.

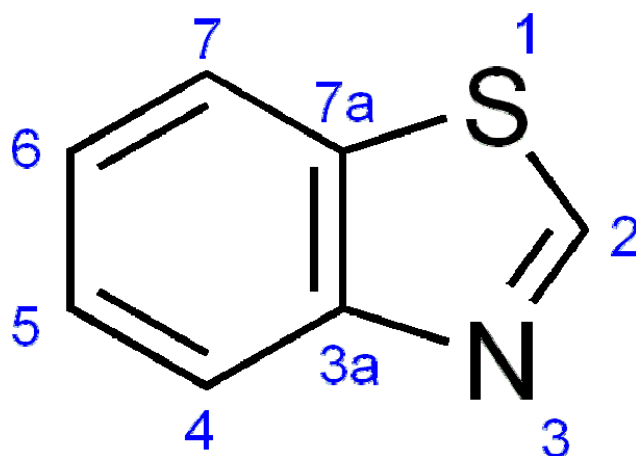


Figure 3. Structure and numbering system for Benzothiazole.

Examination of these extracted ion fingerprints (listed in Table 3), provided additional means of comparing the fume composition between these three materials. Recommended by Dr. Larry Olsen of NIOSH (National Institute of Occupational Safety and Health) for other studies, this list is based on work done on the original NIOSH fumes (7) and his own research. (The carbazoles and benzothiazoles were added to this table for the crumb rubber modified bitumen). Figure 4 shows the extracted ion 85 for the three test materials compared to the straight run bitumen. All of the ion fingerprints are shown in Appendix C. A summary of qualitative difference after examination of all of these extracted ions is presented in Table 4.

Table 3. List of Extracted Ions (m/z) for Validation and Characterization

<u>Compounds</u>	<u>Extracted Ions (m/z)</u>
n-alkanes	85
Naphthalene	128
alkylated naphthalenes	142,156,170
Monocycloalkanes	69
Benzothiophene	134
alkylated benzothiophenes	148,162,176
Dibenzothiophene	184
alkylated dibenzothiophenes	198,212
Benzofuran	118
alkylated benzofurans	132,146
Dibenzofuran	168
alkylated dibenzofurans	182,196
benzothiozoles	108, 135
carbozoles	211, 139, 167

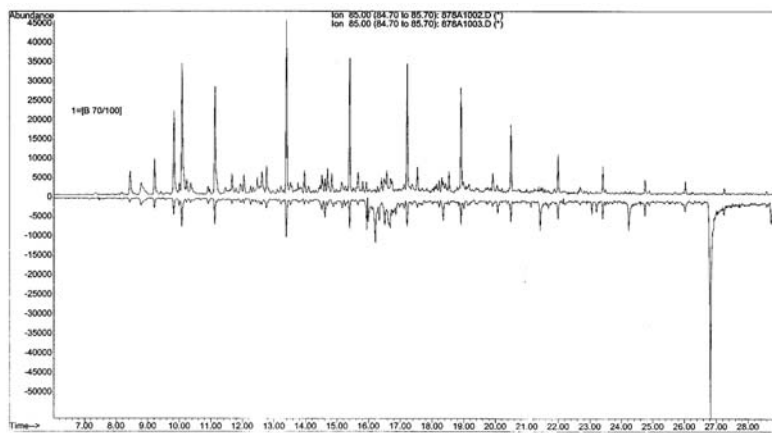
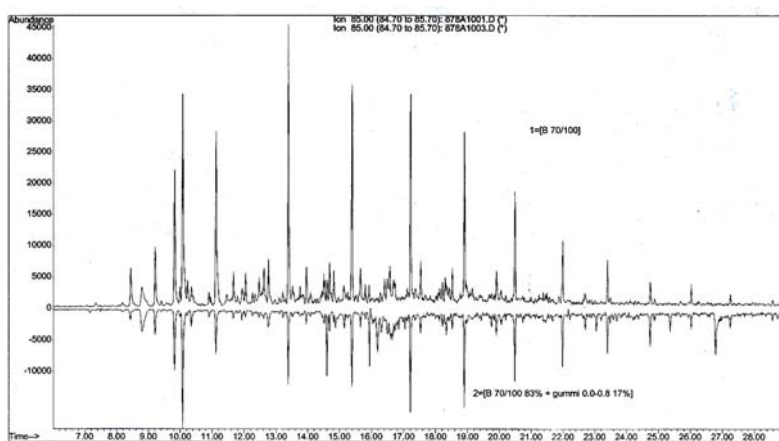
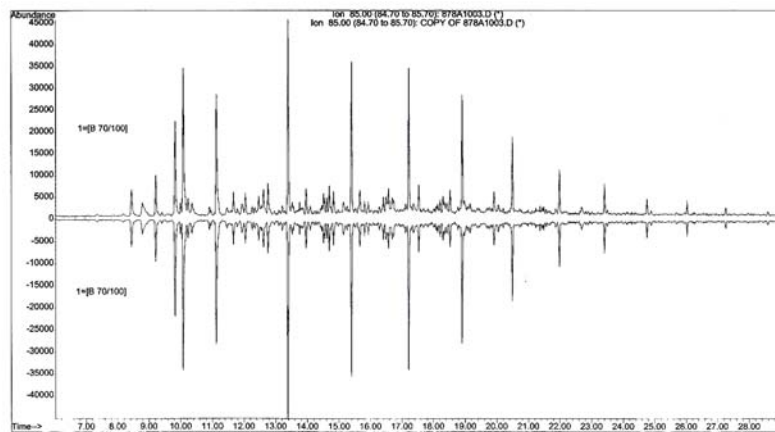


Figure 4. Extracted Ion 85, indicative of n alkanes, for fumes generated from all three test bitumens. The peak at ~27 minutes for sample 3 is tentatively identified as hexadecanoic acid.

Table 4. Extracted Ions-Description of Differences Relative to the Parent Bitumen Fumes

Class of Compounds	Extracted Ion	B 70/100 83%, + gummi 0.0-0.8 17% 2006-11-30	B 70/100 83% + 17% ROAD ⁺ , 2006-11-30
n-alkanes	85	very different ratios	very different ratios
naphthalene	128	small differences	small differences, extra peak at ~27 min.
alkylated naphthalenes	142	similar, 1 peak slightly higher at ~19.8 min.	similar, 1 peak slightly higher at ~19.8 min., extra peak at ~27 min.
alkylated naphthalenes	156	similar, 1 peak slightly higher at ~19.8 min.	similar, 1 peak slightly higher at ~19.8 min., extra peak at ~27 min.
alkylated naphthalenes	170	similar, 2 small peaks in front of alkylated series and slightly higher peaks at end	similar, 2 small peaks in front of alkylated series, extra peak at ~27 min.
monocycloalkanes	69	significantly different at ~16 min.	significantly different at ~16 min., extra peak at ~27 min.
benzothiophene	134	significantly different at ~16 min., slightly higher pk at 22 min.	significantly different at ~16 min., slightly higher pk at 22 min.
alkylated benzothiophenes	148	peak at ~17.5 ratio is different, extra peak at 25.5 min.	peak at ~17.5 ratio is different, extra peaks at ~22, 24.5, 25.5 and 27 min.
alkylated benzothiophenes	162	similar with extra peak at ~17 min.	similar with extra peak at ~17 min.
alkylated benzothiophenes	176	peak at ~24.9 slightly higher relative to other peaks	peak at ~24.9 slightly higher relative to other peaks
dibenzothiophene	184	similar with some slight ratio variations	similar with some slight ratio variations plus extra group at end
alkylated dibenzothiophenes	198	similar-slight ratio variations, small extra peak at ~21.8 min.	similar-slight ratio variations, small extra peak at ~21.8 min.
alkylated dibenzothiophenes	212	similar	similar
benzofuran	118	many extra peaks especially from 22-26.5 min.	many extra peaks especially from 22-26.5 min.
alkylated benzofurans	132	similar	similar
alkylated benzofurans	146	similar with some small extra peaks	similar with some small extra peaks
dibenzofuran	168	similar except for 1 peak at ~22.5 min.	similar except for 1 peak at ~22.5 min.
alkylated dibenzofurans	182	similar peaks but varying ratios	similar peaks but varying ratios
alkylated dibenzofurans	196	very different pattern	very different pattern
benzothiozoles	108	strong peak at ~16 min.	strong peak at ~16 min.
benzothiozoles	135	strong peak at ~16 min.	strong peak at ~16 min.
carbozoles	211	similar-some extra patterns ~23 min. + 32.5 min. strong peak (see separate extended chromatogram)	similar-some extra patterns ~23 min. + 32.5 min. strong peak (see separate extended chromatogram)
carbozoles	139	similar but varying ratios	similar but varying ratios, extra peak at ~27 min.
carbozoles	167	similar but varying ratios	similar but varying ratios

4. Discussion

Rank ordering the amount of fumes as TOM generated from each bitumen show the the B 70/100 83% + 17% ROAD⁺ to yield the least amount of fumes (451 mg/m³), B 70/100 83%, + gummi 0.0-0.8 17% is next with a TOM of 494 mg/m³ and finally, the un-modified B 70/100 bitumen fume produced the highest amount of TOM (752 mg/m³).

Between about 15 and 85 percent distilled, the parent bitumen fumes appear to have a lower boiling point distribution than the modified bitumens. At the front end (between 5 and 15% distilled), the two modified bitumens appear to have a slightly lower boiling point than the un-modified bitumen, but not at a significant level. Then at the back end, all three end up at the same boiling point range (85-95% distilled). However, upon close examination of the chromatograms (Appendix B), there are two prominent peaks present in the modified bitumen fumes that influence these results, but do not appear to be hydrocarbon materials normally found in bitumen fume. Benzothiazole, which is found in crumb rubber, was one peak that was identified. The other peak was not definitively identified but likely comes from rubber or the process.

Fluorescence results show no change in response between all three bitumen fumes. This indicates that the addition of the modifiers and crumb rubber do not appear to increase the 4-6 ring PAC concentration.

Other than the large percentages of benzothiazole present in the two modified bitumen fumes, the other PAC concentration differences are not significantly prominent. Benzothiazole is added to crumb rubber, so its presence at percent levels is not surprising. Acenaphthylene is detected in the modified bitumen fumes, but is not detected in the parent fumes. This compound is not typically seen in bitumen fumes (8). Acenaphthene, fluorene and phenanthrene are present

at slightly higher concentrations in the B 70/100 83%, + gummi 0.0-0.8 17% fume than in the other two fumes.

As compared to the B 70/100 bitumen fumes, examination of the extracted ion fingerprints from the modified bitumen fumes show strong ratio variations for the n-alkanes, a prominent peak at ~16 minutes that show up on the 69, 134, 108 and 135 mass to charge ions which is identified as benzothiazole, many extra peaks at the benzofuran ion (118), a very different pattern for the alkylated dibenzofurans, and a strong peak at 32 minutes corresponding to the 211 ion. It appears that the strong peak at 32 minutes may be within the benzothiazole family, but the identification is unknown. It was not seen after extraction on the GC/TOFMS analyses.

It is important while reviewing this data to consider that these results represent a worst case scenario under the laboratory conditions by which the condensates were generated. Because real world field conditions are complicated by many variables which can not be accounted for in a controlled laboratory setting it is recommended that industrial hygiene exposure measurements be made to obtain information about actual worker exposures.

5. Conclusions

Within this laboratory study, it would appear that the modified bitumen test materials generated less fumes as compared with the unmodified bitumen based on the TOM. Although benzothiazole is present in the modified bitumen fumes at % levels, the modification process does not appear to contribute to the 4-6 ring PAC concentration in the subsequent fumes based on both the fluorescence results and individual PAC calculations.

6. References

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