Asphalt fractions in airborne particles from highway traffic and the accumulation in plants

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Abstract—— With reference to ASTM D4124, asphalt fractions, including polar aromatics (polars), naphthene aromatics (aromatics) and saturates, were characterized both in airborne particles collected in the distances of 2. 0—83. 6m from the highway and in the plant samples (including grass, leaves and wheat straw) collected in the distance of 2. 0—10. 0m from the highway. In comparison to the results of diesel particulate, background plant samples and asphalt cement samples from highway surface, it is concluded that there could be asphalt matters in airborne particles and asphalt makes the main contributions to the accumulation of the three factions mentioned above in plant species. In the ambient air, the concentrations of the three asphalt fractions are 0. 54—3. 06× 10^{-3} mg polars, 1. 77—9. 50× 10^{-4} mg aromatics and 0. 21—1. 23× 10^{-4} mg saturates for per cubic meter air. The percentage of bitumen in airborne particles is 1. 61%—11. 02%. In the plant samples, the concentrations are 0. 29—3. 07 mg polars, 0. 89—3. 89 aromatics and 0. 37—1. 53 mg saturates for per gram dry plant materials.

Keywords: asphalt; airborne particle; traffic pollution; HPLC.

1　Introduction

Asphalt concrete has been used as the predominant road surface material. Fourteen out of every 15 miles of surfaced road in the United States are topped with asphalt. The United States spends more than US $ 10 billion per year on asphalt pavements, about US $ 3 billion of which is for asphalt itself (Bishara, 1990). It is estimated that the asphalt consumption are 1400 kg/(person. a) in the United States and 600 kg/(person. a) in western European countries. Most of them have been used for road pavement.

The abrasion of tar-containing or bituminous road surface is one of the important sources of particulate air pollutants from traffic. It was determined that for a mean traffic load of 9000 vehicles per day abrasion liberated asphalt particles which contain 15 mg benzene(a) pyrene per month in winter and in summer 10 mg benzene(a) pyrene per month and per 1 meter length of a two-lances highway (Waibel, 1976).

For particulate air pollution problems caused by traffic, a lot of work has been done on diesel particulate from tailpipes and rubber debris from tire wear (Advances in Diesel particulate Control, 1990; Pierson, 1974; Dannis, 1974; Cadle, 1978). Very little has been published on asphalt particles from road surface abrasion. Considering the carcinophilia compositions contained in asphalt, it was felt that the investigation of asphalt fractions in airborne particles from highway traffic and the plant uptake of them would be a valuable addition to our knowledge of this subject.

2   Experimental methods

2.1   Sample collection

Asphalt concrete sample was taken from the top-layer (maximum 1 mm in thickness) of Helsingφr highway in Denmark. Airborne particles were collected by using ASI/GMW High Volume PM 10 Sampler and 20.3 × 25.4 cm quartz microfibre filters in the distances of 2.0, 7.8, 9.5, 13.5, 18.5, 29.1, 40.0, 48.6, 60.0, and 83.6 meters from the highway. The sampling period and air volume for each sample were 44—142.5 hours and 3068—9935 cubic meters, respectively. Plant sample collection was performed in August and September 1993. Grass samples and three kinds of leave samples were collected both in the close vicinity of Helsingφr highway and in Lyngby park about 1.25 km from the highway (as the background). Wheat samples were collected in the distance of 5 and 10 meters from the highway and about 1.0 km from the highway (as the background).

2.2   Sample extraction

Asphalt concrete sample (500 mg) and the filters with airborne particles (divided into small pieces) were boiled with 200 ml dichloromethane for 24 hour. The extract was filtered and evaporated to dryness at room temperature. 150 ml n-heptane was added and boiled for two hours. The extract was filtered and evaporated to the required volume of solution (50 ml for asphalt cement sample and 4—5 ml for airborne particles).

4—6g dry plant materials (divided into small pieces) were extracted 24 hour with 150 ml dichlormethane and 20 ml 5 mol/L NaOH by Soxhlet extraction. After finishing the alkaline part was removed by vacuum and the extract was carefully washed with redistilled water. 20 ml 2 mol/L sulphuric-acid was added and the extract boiled with the acid for half an hour. The acid part was removed by vacuum. The extract was washed by redistilled water and evaporated to dryness at room temperature. The sample was dissolved in 100 ml n-heptane by boiling two hours and filtered and evaporated to 2—4 ml.

2.3   Sample analysis

With reference to ASTM D4124 and the method described by S. W. Bishara *et al.* (Bishara, 1990; Standard, 1986), all of the extract were analyzed on a high-pressure liquid chromatography system equipped with a LKB 2152 LC controller, a LKB 2150 HPLC pump, a LKB 11300 ultrograd mixer driver, a LKB 2151 variable wavelength monitor, a LKB 2144 fluorescence detector and a Milton Roy CI-4100 recorder. Samples were chromatographed on a chromspher C-18 column with typical particle size 5 μm, 3.0 mm i.d ×100mm, using gra-

dient elution. From 0 to 15 min, the solvent composition was changes linearly from 100% ethanol to 100% n-heptane and held there for 5min. From 20 to 30min, the solvent composition was changed linearly from 100% n-heptane back to 100% ethanol. Flow rate through the column was 0. 7 ml/min. The absorbance wavelength used for detection was 280 nm. 5 μm of the sample solution was injected into the system for every chromatogram.

3 Results and discussion

3. 1 Qualitative results

According to ASTM D4124 and the method described by S. W. Bishara *et al.* (Bishara, 1990; Standard, 1986), there should be three fractions which including polars, aromatics and saturates in the extract of asphalt cement sample after the extraction procedure described above. Fig. 1a gives out the chromatogram for one of the asphalt cement sample and there are very obvious three peaks in it. The retention times for the three peaks are about 1. 00, 2. 10 and 7. 20 min, respectively. From the gradient program, it is determined that the solvent compositions (ethanol/n-heptane) for the three peaks are 93. 9%/6. 7%, 86. 0%/14. 0% and 52. 0%/48. 0% in proper order. Considering the polarity index of ethanol and n-hepane, these three peaks should represent polars, aromatics and saturates respectively, as shown in Fig. 1a.

Diesel particulate collected from a laboratory device have been extracted and analyzed by the same procedures for asphalt cement and airborne particles and Fig. 1b gives out the result. One of the results for airborne particles is shown in Fig. 1c. Table 1 presents the percentage composition of peak areas of the three fractions for various samples. From the data for asphalt cement and airborne particle in Table 1 and the comparison between Fig. 1a and 1c, it is clear that airborne particles have similar composition of the three fractions as that of asphalt cement. The airborne particles have a little higher percentage for polars and a little lower percentage for saturates than those for asphalt cement. In addition, there are several small peaks in the

Fig. 1 HPLC chromatogram for asphalt cement, diesel particulates and airborne particles

chromatogram of airborne particles. It could be taken as the influence from the diesel particulate if Fig. 1b and the data for diesel particulate in Table 1 are taken into account. Therefore, it is sure that there could be asphalt compositions in airborne particles collected from ambient air relatively near to the highway.
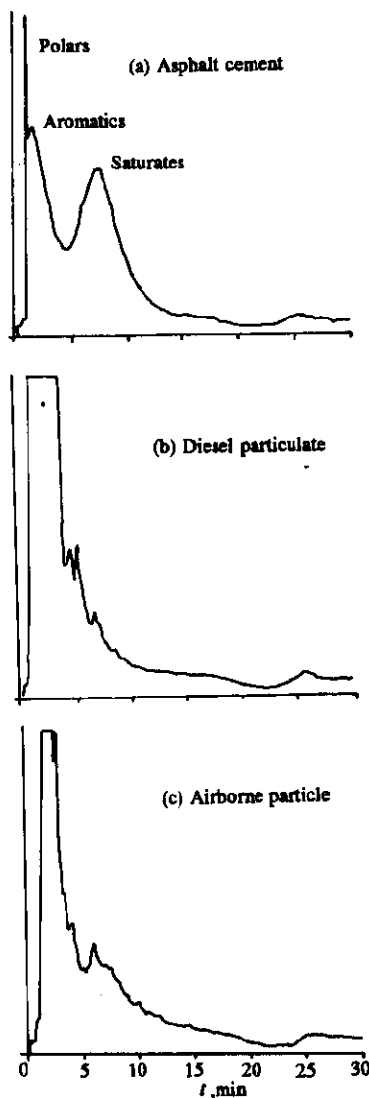
Table 1   Percentage composition of asphalt fractions in various samples   Unit: %

Sample	Polars	Aromatics	Saturates
Asphalt cement	1. 31—2. 34	31. 85—36. 93	61. 01—66. 08
Diesel particulate	32. 02	24. 21	43. 76
Airborne particle	4. 97	38. 29	56. 73
Grass	2. 60	30. 48	66. 91
Leave 1	0. 76	29. 82	69. 43
Leave 2	0. 99	33. 16	65. 85
Leave 3	1. 99	31. 74	66. 25
Wheat straw (5m)	1. 82	28. 84	69. 34
Wheat straw (10m)	0. 53	30. 24	69. 23

Fig. 2, 3 and 4 show the chromatograms both for highway sample and for background sample of various plant species. In these figures, it is very obvious that there are large differences between the results of highway sample and background sample. Because the same weight of plant material and the same volume of the final extract are used for both of them, the differences must be caused by the highway traffic. From the comparisons between Fig. 1a
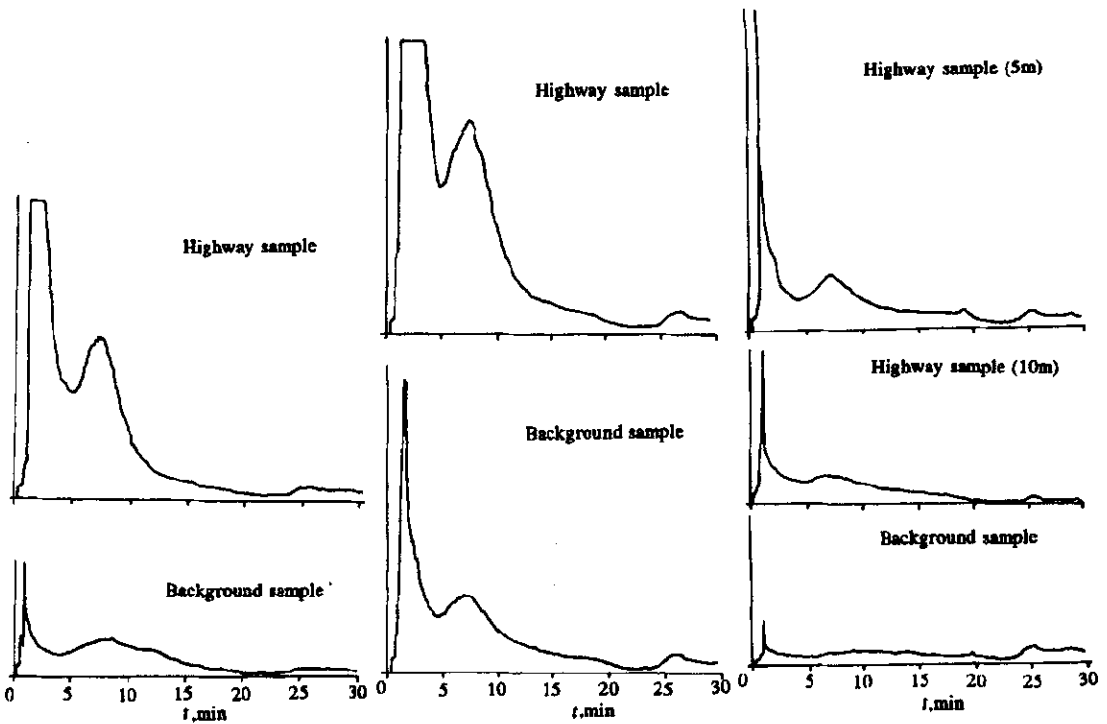

Fig. 2   HPLC chromatograms for highway sample and background sample of grass

Fig. 3   HPLC chromatograms for highway sample and background sample of leave 3

Fig. 4   HPLC chromatograms for highway sample and background sample of wheat straw

and Fig. 2a, 3a, 4a, and 4b and the data for asphalt cement and plant samples in Table 1, it

is found that the plant samples have nearly the same percentage composition of the three fraction as that for asphalt cement sample. It could be concluded that asphalt makes the main contribution to the accumulation of three fractions in plant species.

3.2 Quantitative results

S. W. Bishara *et al.* separated the asphalt cement into three fractions using HPLC following removal of asphaltenes by filtration and presented the percentages by weight of the four fractions. The average value of the percentages from three samples are 12.7 for asphaltenes, 15.5 for saturates, 42.4 for aromatics and 29.4 for polars. These data are employed to be the basis of the calculation for quantitative results. For example, for the asphalt cement sample with the result shown in Fig. 1a, 60.6 mg bitumen was obtained after the extract of dichloromethane was evaporated to dryness. Therefore, the weight of the three fractions in 50 ml final extract are 17.82 mg for polars, 25.69 mg for aromatics and 9.39 mg for saturates. On the basis of areas of the three peaks in Fig. 1a and $5\mu m$ sample used for each injection, the index of the peak area for per mg asphalt fraction (K) can be calculated by following equation:

$$K = [\text{peak area/weight of fraction (mg)}] \times [50(\text{ml})/0.005(\text{ml})].$$

Six asphalt cement samples have been analyzed and used for the calculation of index K. The average results of index K are employed in the calculation of the weight of asphalt fractions in airborne particles and plant samples (M) by following equation:

$$M = [\text{peak area}/K] \times [\text{volume of final extract(ml)}/0.005(\text{ml})].$$

The concentrations of asphalt fraction in ambient air and plants can be calculated depending on the air volume of sampling and the weight of dry plant materials used for extraction.

Tables 2 and 3 present the quantitative results of the three asphalt fractions in ambient air and plant materials. It is shown that the concentrations of three asphalt fractions in ambi-

Table 2 Concentrations of asphalt fractins in ambient air (mg/m³ air) and the percentage of bitumen in airborne particles

Distance from highway, m	Polars	Aromatic	Saturates	Bitumen(except asphaltene)	Bitumen in airborne particle, %
2.0	7.09×10^{-4}	2.37×10^{-4}	0.63×10^{-4}	1.01×10^{-3}	1.61
7.8	1.18×10^{-3}	2.86×10^{-4}	0.23×10^{-4}	1.49×10^{-3}	3.32
9.5	2.63×10^{-3}	9.50×10^{-4}	1.23×10^{-4}	3.70×10^{-4}	10.4
13.5	1.22×10^{-3}	3.54×10^{-4}	3.41×10^{-5}	1.61×10^{-3}	3.07
18.5	5.40×10^{-4}	1.89×10^{-4}	4.14×10^{-5}	0.77×10^{-3}	2.26
29.1	3.06×10^{-3}	8.61×10^{-4}	1.10×10^{-4}	4.03×10^{-3}	11.02
40.0	6.02×10^{-4}	1.77×10^{-4}	3.78×10^{-5}	8.17×10^{-4}	1.77
48.6	1.97×10^{-3}	6.36×10^{-4}	5.62×10^{-5}	2.66×10^{-3}	6.95
60.0	9.83×10^{-4}	3.08×10^{-4}	5.62×10^{-5}	1.35×10^{-3}	1.89
83.6	9.64×10^{-4}	2.44×10^{-4}	2.11×10^{-5}	1.23×10^{-3}	5.31

ent air in the range of 0. 54—3. 06×10^{-3} mg polars, 1. 77—9. 50 ×10^{-4} mg aromatics and 0. 21—1. 23 ×10^{-4} mg saturates for per cubic meter ambient air. Relatively high concentration of bitumen has been found in the distance of about 30 meters from the highway. The percentage of bitumen in airborne particles is 1. 61%—11. 02%. The concentrations of the three asphalt fraction in plant samples are 0. 29—3. 07 mg polars, 0. 89—3. 89 mg aromatics and 0. 37—1. 53 mg saturates for per mg dry plant material. It is found that the leave samples have relatively higher concentrations of asphalt fractions than those for grass and wheat samples. The results for wheat straw samples show the trend that the concentrations of the asphalt fractions decrease as the distance from the highway increases.

Table 3   Concentrations of asphalt fractions in various plant species

Unit: mg/g dry plant material

Sample	Polars	Aromatics	Saturates
Grass	0. 9608	0. 8928	0. 3708
Leave 1	3. 0708	3. 8762	1. 5312
Leave 2	1. 4629	3. 8927	1. 4630
Leave 3	0. 9263	2. 9097	1. 2825
Wheat straw (5m)	1. 0975	1. 3756	0. 6261
Wheat straw (10m)	0. 2869	1. 2957	0. 5616

4   Conclusions

From the experimental results, it is sure that there could be asphalt compositions in airborne particles collected from ambient air relatively near to the highway. The percentage of bitumen in airborne particles is 1. 61%—11. 02%. The concentrations of asphalt fractions in ambient air are 0. 54—3. 06×10^{-3} mg polar, 1. 77—9. 50 ×10^{-4} mg aromatics and 0. 21—1. 23 ×10^{-4} mg saturates for per cubic meter air. Asphalt particles from highway traffic make the main contributions to the accumulation of the three fractions in various plant species. Relatively higher concentrations of asphalt fractions have been found in leave samples than those in other plant species. The concentrations of the three fractions in plant samples are 0. 29—3. 07 mg polars, 0. 89—3. 89 mg aromatics and 0. 37—1. 52 mg saturates for per gram dry plant materials.

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