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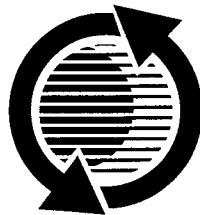
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ABSTRACT

Most countries consider it is harmful for humans to inhale SPM of fine organic particles and elemental carbon less than 2.5μ in diameter^{1,2)}. It is generally believed that organic matters in SPM are mainly composed of diesel exhaust particulate and soot from residential chimneys or industrial smokestacks^{3,4)}. To determine the contribution ratios of several organic substances to SPM, we characterized SPM, diesel exhaust particulate (DEP), powdered summer radial tire, and bitumen, using high performance liquid chromatography, field desorption mass spectrometry and linear theory.

INTRODUCTION

Most countries consider suspended particulate matter (SPM) to be a major concern not only regarding the health of humans but also regarding impact on the natural environment⁵⁾. SPM containing fine organic particles and elemental carbon less than 2.5μ in diameter is considered very harmful when inhaled by humans⁶⁾. It is generally believed that the organic matters in SPM are mainly composed of diesel exhaust particulate (DEP) and soot from residential chimneys and industrial smokestacks. Many researchers have pursued the sources of organic matters in SPM using various methods, most often the chemical mass balance (CMB) method^{7,8)}. However, the contribution ratio of those matters to SPM has not been found exactly, because these materials include with many types of complex organic matters⁹⁾.

We tried to determine the contribution ratio of organic matters to SPM using the HPLC method and linear model. This method was found to be very effective in obtaining contribution ratio to SPM for diesel exhaust particulate, bitumen and summer radial tire.

MATERIALS

We collected SPM samples using a high-volume sampler (HVC-1000N: Shibata Scientific Technology, Pallflex 2500QAT-UP, quartz fiber filter, 23.5 x 17.5 cm, 1000 l/min x 4 days, July 1-4, 2000) in Sapporo, at the top of the six-story building that houses our department. (Sapporo is a city in Northern Japan.) DEP samples were collected with air filter using dilution tunnel of Japan Automobile Research Institute in Tsukuba (Horiba, DLT-24150W). We collected bitumen (straight bitumen of penetration grade 80/100) used in Sapporo and abraded tire (summer radial tire). We prepared samples (SPM, DEP, bitumen, summer radial) for high-performance liquid chromatography (HPLC), as follows¹⁰⁾.

We weighed a glass beaker containing the sample (0.6g). The sample was dissolved in a benzene-methanol solution (1:1 by volume) using an ultrasonic vibration machine for 10 minutes, covered and cured for 1 day. The solution was absorbed and filtered with filter paper (mesh: No3). We reweighed the filter paper and glass beaker. The solution in the filter paper was evaporated by evaporator. After evaporation, it was dissolved with normal hexane (20 ml), covered and cured for 1 day. We repeated the process from filtering to evaporation. Then, the filtrate was dissolved in a small amount of normal hexane and stored in a small glass beaker.

TEST METHOD

The samples of SPM, bitumen, summer radial and DEP stored in small glass beakers were subjected to HPLC. They are classified according to four components: saturated hydrocarbon (paraffin component, FRP), aromatic hydrocarbon with 1 ring (FRM), aromatic hydrocarbon with 2 rings (FRD), and aromatic hydrocarbon with 3 or more rings (PP). They were stored in small glass beakers, each of whose weight was measured. Then, the solution was evaporated using nitrogen gas. Thereafter, FRP samples were performed using Field Desorption Mass Spectroscopy

(FD-MASS, JEOL JMS-SX102A, Inlet: direct, Normal Ion: MF-Linear, RT: 2.27 min., BP: m/z 57.0000) and the molecular weight distribution (200-1500) was measured.

TEST RESULTS

Figures 1, 2, 3 and 4 show FD-MASS spectra for SPM, DEP, bitumen and summer radial. The peaks of molecular weight for those samples were 532, 504, 616 and 434, respectively.

The spectrum of SPM was similar to that of DEP and different from that of summer radial.

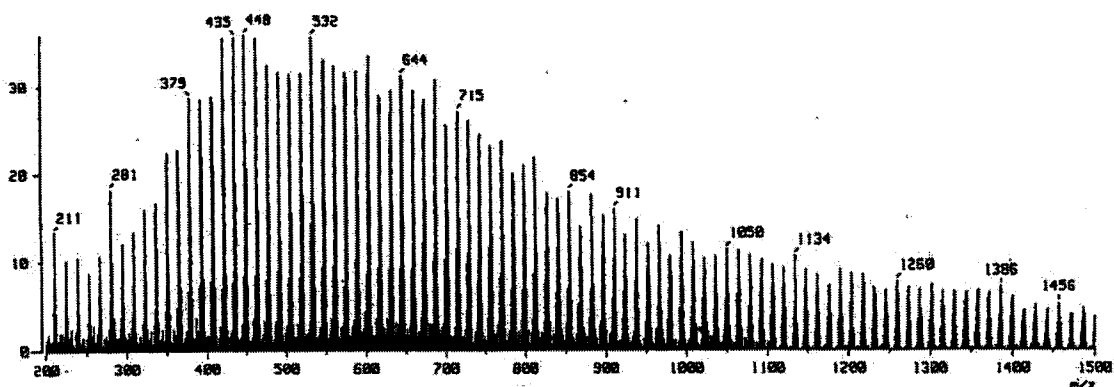


Fig.1 SPM

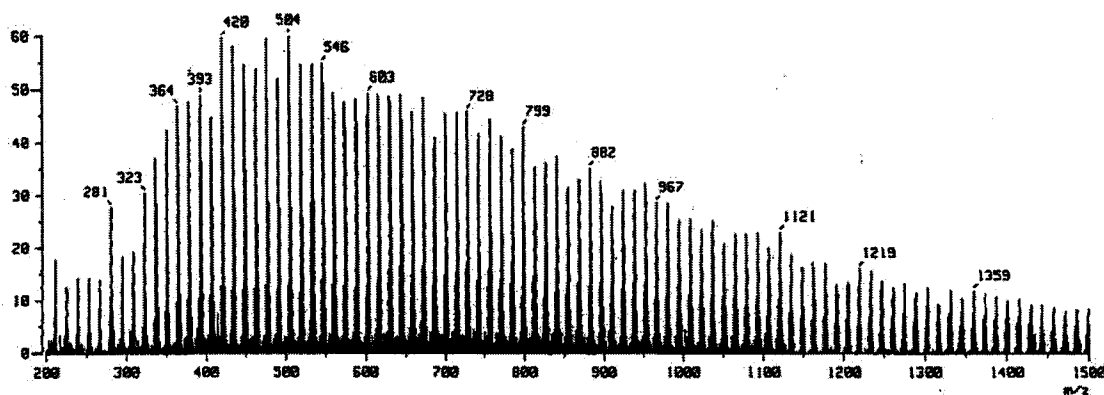


Fig.2 DEP

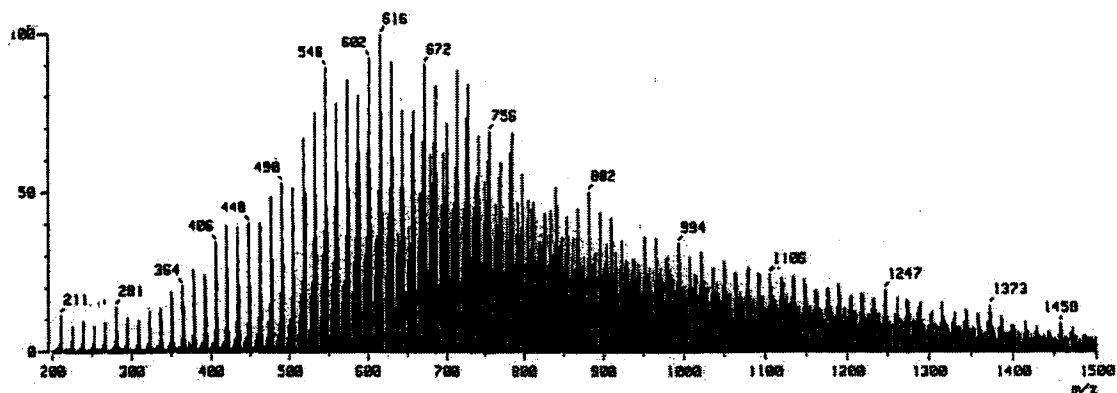


Fig.3 Bitumen

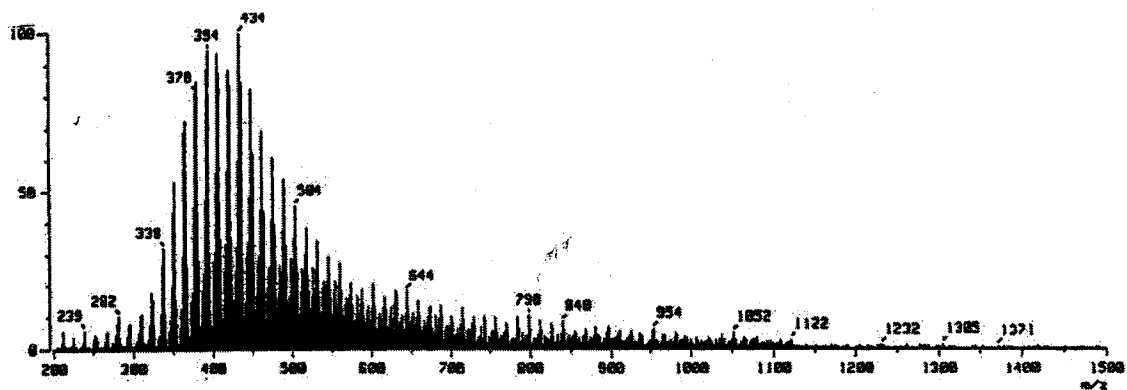


Fig.4 Radial Summer Tire

ANALYSIS RESULTS

We used linear theory to obtain correlation factors of SPM for those spectra, for every molecular weight from 200 to 900. Table 1 shows that the correlation factors of DEP (D) are almost as large as those of bitumen (B) for every molecular range and that they equal or exceed 0.9 for every molecular weight range. However, correlation factors

averaged for both DEP and bitumen exceed those only for DEP in the distribution range of 200-600, considering with peak molecular values of each sample. In general, their correlation factors are lower for the molecular weights exceeding 600. It is thought that the contribution ratio to SPM for DEP (D) and bitumen (B) is not always 1:1. We concluded that the contribution ratio to SPM was affected not only by DEP but also by bitumen.

Mol. wt.	DEP	Bitumen	(D+B)/2	Mol. wt.	DEP	Bitumen	(D+B)/2
200-300	0.9720	0.9702	0.9783	400-600	0.8868	0.8086	0.9138
200-400	0.9777	0.9783	0.9827	400-700	0.9152	0.7134	0.8791
200-500	0.9040	0.9482	0.9567	400-800	0.9269	0.6645	0.8576
200-600	0.9133	0.8071	0.9241	400-900	0.9276	0.6483	0.8507
200-700	0.9297	0.7172	0.8853	500-600	0.9268	0.8478	0.9360
200-800	0.9373	0.6669	0.8581	500-700	0.9549	0.7735	0.9080
200-900	0.9368	0.6421	0.8444	500-800	0.9609	0.7277	0.8900
300-400	0.9832	0.9797	0.9864	500-900	0.9571	0.7144	0.8845
300-500	0.8949	0.9466	0.9546	600-700	0.9904	0.7543	0.8972
300-600	0.9067	0.7971	0.9215	600-800	0.9838	0.7110	0.8865
300-700	0.9252	0.7019	0.8821	600-900	0.9734	0.6961	0.8808
300-800	0.9338	0.6503	0.8559	700-800	0.9827	0.6656	0.8781
300-900	0.9340	0.6281	0.8448	700-900	0.9717	0.6380	0.8653
400-500	0.8508	0.9539	0.9392	800-900	0.9629	0.5556	0.8357

Table 1 Correlation factors for DEP (D) and bitumen (B) , and the average of both samples

Table 2 shows correlation factors of SPM for different contribution ratios of DEP (D) and bitumen (B). This analysis revealed that large correlation factors (> 0.9) were obtained for the ratio of (5 DEP + 5 Bitumen) / 10 or (6 DEP + 4 Bitumen) / 10. These correlation factors were: 1:1 or 3:2

(DEP:bitumen) for the molecular weight range of 200 to 600. Table 2 shows that a contribution ratio to SPM of more than 0.93 was obtained for DEP and bitumen at 1:1 or 3:2 for molecular weight range of 200-600.

Mol. wt.	(1D+9B) /10	(2D+8B) /10	(3D+7B) /10	(4D+6B) /10	(5D+5B) /10	(6D+4B) /10
200-300	0.9747	0.9772	0.9784	0.9787	0.9783	0.9775
200-400	0.9817	0.9833	0.9836	0.9834	0.9827	0.9819
200-500	0.9602	0.9659	0.9665	0.9631	0.9567	0.9481
200-600	0.8375	0.8653	0.8895	0.9094	0.9241	0.9331
300-400	0.9836	0.9856	0.9864	0.9866	0.9864	0.9859
300-500	0.9596	0.9657	0.9661	0.9620	0.9546	0.9448
300-600	0.8295	0.8592	0.8851	0.9062	0.9215	0.9307
400-500	0.9621	0.9639	0.9601	0.9515	0.9392	0.9241
400-600	0.8362	0.8616	0.8836	0.9013	0.9138	0.9204
500-600	0.8809	0.8990	0.9154	0.9296	0.9360	0.9480
Mol.wt	(7D+3B) /10	(8D+2B) /10	(9D+1B) /10	DEP	Bitumen	
200-300	0.9764	0.9751	0.9736	0.9721	0.9702	
200-400	0.9809	0.9798	0.9787	0.9777	0.9783	
200-500	0.9381	0.9272	0.9157	0.9041	0.9482	
200-600	0.9362	0.9337	0.9258	0.9133	0.8071	
300-400	0.9853	0.9846	0.9839	0.9832	0.9797	
300-500	0.9334	0.9210	0.9080	0.8949	0.9466	
300-600	0.9334	0.9299	0.9208	0.9067	0.7971	
400-500	0.9071	0.8888	0.8699	0.8507	0.9539	
400-600	0.9209	0.9151	0.9036	0.8869	0.8086	
500-600	0.9508	0.9484	0.9405	0.9268	0.8478	

Table 2 Correlation factors for various ratios of DEP (D) to bitumen (B)

Then, we calculated correlation factors of SPM for DEP, bitumen and summer radial (T) using both ratios (D:B=1:1 and 3:2). Table 3 shows that summer radial does not affect the correlation factor for ratios lower than 4:4:1 (D:B:T),

when the ratio of DEP to bitumen is kept at 1:1. Larger correlation factors of SPM were obtained for 4:4:1 (D:B:T), when a ratio of 1.1 (D:B) was kept.

Mol. wt	Tire		(D+B+T) /3	(2D+2B+T)/ 5	(3D+3B+T)/ 7	(4D+4B+T) /9
200-300	0.7723		0.9568	0.9784	0.9791	0.9792
200-400	0.7496		0.8707	0.9534	0.9659	0.9717
200-500	0.7568		0.8335	0.9397	0.9484	0.9521
200-600	0.6579		0.8559	0.9323	0.9345	0.9342
300-400	0.7848		0.8789	0.9653	0.9756	0.9802
300-500	0.7667		0.8318	0.9441	0.9511	0.9538
300-600	0.6468		0.8599	0.9372	0.9375	0.9360
400-500	0.7697		0.8119	0.9379	0.9417	0.9428
400-600	0.6065		0.8629	0.9357	0.9335	0.9307
500-600	0.5681		0.9289	0.9401	0.9410	0.9413
Mol.wt	(5D+5B+T)/ 11	(6D+6B+T)/ 13	(7D+7B+T)/ 15	(8D+8B+T)/ 17	(9D+9B+T)/ 19	(10D+10B+T) /21
200-300	0.9792	0.9791	0.9791	0.9790	0.9790	0.9789
200-400	0.9749	0.9768	0.9781	0.9789	0.9796	0.9801
200-500	0.9539	0.9550	0.9556	0.9560	0.9563	0.9565
200-600	0.9333	0.9325	0.9317	0.9311	0.9305	0.9300
300-400	0.9825	0.9839	0.9847	0.9853	0.9856	0.9859
300-500	0.9550	0.9555	0.9558	0.9559	0.9560	0.9560
300-600	0.9344	0.9330	0.9318	0.9309	0.9300	0.9294
400-500	0.9430	0.9430	0.9427	0.9425	0.9424	0.9422
400-600	0.9284	0.9266	0.9252	0.9240	0.9231	0.9223
500-600	0.9413	0.9413	0.9413	0.9412	0.9412	0.9412

Table 3 Correlation factors of SPM when the ratio of DEP (D) to bitumen (B) is 1:1

In contrast, Table 4 shows that larger correlation ratio was obtained for (6:4:1)/11 or (9:6:1)/16 (D:B:T), when the ratio was kept at 3:2 (D:B). Therefore, summer radial (T) also is

shown to contribute to SPM, by the increase in correlation factors of SPM for both cases with addition of summer radial.

Mol. Wt	(3D+2B+T)/6	(6D+4B+T)/11	(9D+6B+T)/16	(12D+8B+T)/21	(15D+10B+T)/26	(18D+12B+T)/31
200-300	0.9783	0.9784	0.9782	0.9781	0.9780	0.9779
200-400	0.9629	0.9753	0.9785	0.9798	0.9804	0.9808
200-500	0.9410	0.9478	0.9490	0.9492	0.9492	0.9492
200-600	0.9384	0.9397	0.9386	0.9376	0.9369	0.9364
300-400	0.9741	0.9834	0.9854	0.9860	0.9863	0.9864
300-500	0.9433	0.9476	0.9477	0.9474	0.9471	0.9469
300-600	0.9416	0.9404	0.9383	0.9369	0.9359	0.9351
400-500	0.9306	0.9307	0.9295	0.9285	0.9278	0.9273
400-600	0.9367	0.9325	0.9295	0.9276	0.9263	0.9255
500-600	0.9476	0.9484	0.9484	0.9484	0.9483	0.9483

Table 4 Correlation factors of SPM when ratio of DEP (D) to bitumen (B) is 3:2

It was concluded that ratios of three materials having larger correlation factors (D:B:T) were best in (4:4:1)/9 or (6:4:1)/11 or (9:6:1)/16 in shown in Table 3 and Table 4. Therefore, the largest correlation factor (D:B:T) for the

molecular weight range of 200-600 in Table 5 (0.9397) was for (6D:4B:1T)/11. Contribution ratios (D:B:T) to SPM for these three materials were 54.5 %: 36.4 %: 9.1 % for summer in Sapporo.

Mol. wt	DEP	Bitumen	Tire	(4D+4B+T)/9	(6D+4B+T)/11	(9D+6B+T)/16
200-300	0.9721	0.9702	0.7723	0.9792	0.9784	0.9782
200-400	0.9777	0.9783	0.7496	0.9717	0.9753	0.9785
200-500	0.9041	0.9482	0.7568	0.9521	0.9478	0.9490
200-600	0.9133	0.8071	0.6579	0.9342	0.9397	0.9386
300-400	0.9832	0.9797	0.7848	0.9802	0.9834	0.9854
300-500	0.8949	0.9466	0.7667	0.9538	0.9476	0.9477
300-600	0.9067	0.7971	0.6468	0.9360	0.9404	0.9383
400-500	0.8507	0.9539	0.7697	0.9428	0.9307	0.9295
400-600	0.8869	0.8086	0.6065	0.9307	0.9325	0.9295
500-600	0.926790	0.8478	0.5681	0.9413	0.9484	0.9484

Table 5 Correlation factors of SPM when ratio of DEP (D) to bitumen (B) is varied

CONCLUSIONS

These conclusions were obtained.

1. Organic matters in SPM include DEP, bitumen, and summer radial tire.
2. Correlation factors for those materials in SPM differ slightly at various molecular ranges, but they increase with addition of bitumen and summer radial tire.
3. Correlation factors of SPM for DEP (D) are almost as large as those of bitumen (B) for every molecular range: They are almost 0.9 or greater.
4. The FD MASS analysis method is very effective in determining the contribution ratio to SPM for DEP, bitumen and summer radial tire.

5. Contribution ratios (D:B:T) of organic matters to SPM in Sapporo in summer for the molecular weight range of 200-600 are 56 %, 38 % and 6 % for DEP, bitumen and summer radial, respectively.

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REFERENCES

1. U.S. Dhew, National Air Poll. Contr. Adminst. No.AP-49, 119(1969)
2. Gross, G.P., SAE Paper, 720210 (1972)
3. S.Ohta, N. Kaneyasu, Atmos. Environ. 24A (1990)
4. William R. Pierson and Wanda W. Brachaczek, Aerosol Science and Technology 2:1-40 (1983)

5. Kaneyasu, N. Ohta, S., Murao, N. and Mizoguchi, I., J. Climate, 4 (1991)
6. John H. Seinfeld, John Willey & Sons, Atmospheric Chemistry and Physics of Air Pollution, pp68(1986)
7. Sheldon K. Friedlander, Smoke, Dust, and Haze, Oxford University Press, pp380-385(2000)
8. Philip K. Hopke, Receptor modeling for air quality management, Elsevier, pp3-8(1991)
9. R.C.Lao, R.S.Thomas, H. Oja and L. Dubois, Analytical Chemistry, Vol. 45, No. 6, 908-915(1973)
10. M. Ogasawara, Chemistry, Vol. 54, No. 9, 28-30 (1999) (in Japanese)

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