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Analysis of vapor phase organics in air of Beijing, Langfang and Tianjin by capillary GC and GC/MS

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Abstract—The vapor phase organics (VPOs) in the air of Beijing, Langfang and Tianjin were detected by a capillary gas chromatography and GC/MS during the winter and the summer separately. The tentatively identified compounds include alkanes, cyclic hydrocarbons, alkenes, aromatics, acids, alcohols, aldehydes, ketones, esters, halocarbons and so on. The numbers of VPOs found are 118 in Beijing, 83 in Langfang and 65 in Tianjin in the winter, and 56, 39 and 72 in the summer respectively. Based on the data of some representative compounds determined quantitatively by GC and GC/MS, a profile of organic pollution in the air of the three cities is presented.
Keywords: vapor organics; air pollution; GC;GC/MS; analysis

INTRODUCTION

The air pollution of photochemical smog is produced by photochemical reactions among atmospheric NO_x, SO_2 and vapor phase organics. Because the photooxidation of organics in the atmosphere is associated with the formation of photochemical oxidants such as ozone, peroxyacyl nitrate (PAN) and peroxypropiony nitrate (PPN), which have long been recognized to be dangerous to plants and human health (Tuesday, 1971; Gordon, 1968), and greatly increase atmospheric NO_x concentration, which aggravate the damage of acid rain (Wark, 1981), the vapor phase organics (VPOs) are ignorant in the research of air pollution. Recently, more and more attentions have been paid to the atmospheric VPOs (Singh, 1981; Makide, 1979; Singh, 1979; Kimitake, 1985).

In order to understand the composition and the distribution of the atmospheric VPOs in the area of Beijing, Langfang and Tianjin, to test the sampling and analytical methods established in our laboratory and, to identify the source and fate of VPOs and the potentiality of smog in the three cities, we conducted simultaneous air samplings in the three cities in December, 1983 and June, 1984 separately. The duration of continuous sampling was seven to ten days. Based

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on the data of capillary GC and GC/MS analysis, we obtained a profile of organic air pollution in the three cities for the first time.

In this paper, we intend to report the results of GC and GC/MS analysis, and to compare the similarities and differences of the VPOs around the three cities at different seasons by means of qualitative and quantitative analysis.

EXPERIMENTAL

Reagents and Equipment

Coconut Charcoal (40–60 mesh, Beijing Guanghua Timber Mill). Prior to the use, the charcoal was heated in oven at 600 °C under the protection of nitrogen stream for four hours to remove possible adsorbed organics, then it was stored in a sealed glass vessel for further use.

49-Superfine glass fibre filter (Shanghai Hongguang Paper Works). The filter was heated in oven at 400 °C for four hours, then stored in a glass dryer for further use.

KB-120 air sampling pump equipped with air sampler (Qingdao Laoshan Institute of Electronic Instrument, Qingdao, China).

Glass Soxhlet extractor (Beijing Glass Instrument works).

Glass K-D concentrator (Beijing Glass Instrument Works).

Dichloromethane (A. G., Beijing Chemical Works), Redistilled.

Methylbenzene, Ethylbenzene, Dimethylbenzene, Octane, Nonane, Decane, Dodecane, Tridecane, Tetradecane, Pentadecane (GC Standard, GC Grade, Shanghai Chemical Reagent Works).

HP-5880 Gas Chromatography with Level 4 Chromatographic Data Processor (Hewlett-Packard Co., USA).

Finnigan 4021 Gas Chromatography-Mass Spectra with Mass Data Library (Finnigan-Mat Co., USA).

Sampling and Sample Analysis

Sampling and Sample pre-treatment

The procedure used in this study is as follows: A glass sampling tube packed with two grams charcoal was connected to the pump. A glass fibre filter was covered on the inlet of the pump to remove air paticulates (Fig. 1). After sampling for six hours, the charcoal was transfered into a sealed test-tube and stored in darkness. The sample-contained charcoal was extracted with 60 ml redistilled dichloromethane in Soxhlet extractor for 24 hours as soon as it was brought back to laboratory. The solution obtained then was concentrated in K-D concentrator under a nitrogen stream. When the volume of the sample solution was reduced to 0.1 ml, it was ready for analysis.

Analysis

The optimal GC conditions are:

Column: 30m × 0.25 mm i.d. fused silica capillary column Stationary phase: SE-54 (Crosslinked)

Detector: FID

Carrier gas: nitrogen

Split ratio: 81

Injector temperature: 270°C

Detector temperature: 280°C

Column temperature program: 50°C (3min) $\overset{4°C/min}{- - - - -}$ 280°C (30min)

Sample volume injected: 2μl

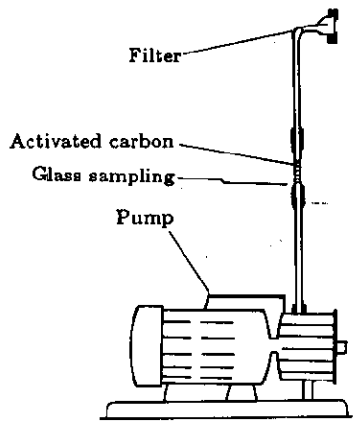

Fig. 1 The sampling device

In order to avoid the interferes from the secondary pollution formed by sunlight irradiation, the samples for GC/MS analysis were taken from later night to early morning (22:00 to 4:00). The samples were taken on December 7, 1983 and June 17, 1984 separately. The working conditions for GC/MS were similar to that for GC analysis.

The qualitative analysis of GC/MS was conducted by the GC/MS data library search, which compared the four most possible mass fragmentograms with that of samples. To ensure the reliability, the GC relative retention time of some standard compounds were compared. However, most of the VPOs were determined chiefly by GC/MS data library system owing to the lack of standard GC samples. Similarly, the GC quantitiative analysis were carried out by the level 4 Chromatographic data processor using its standard external standard method.

RESULT AND DISCUSSION

Fig. 2, Fig. 3 and Fig. 4 show the chromatograms of the air samples taken from Beijing, Langfang and Tianjin in the winter and summer respectively. They illustrate the VPOs

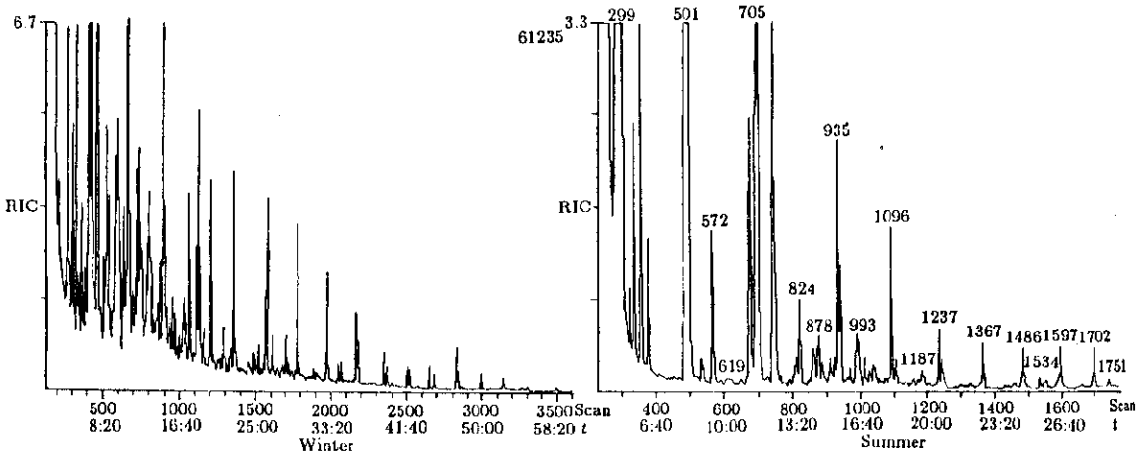

Fig. 2 Ion chromatogram of VPOs in the air of Beijing

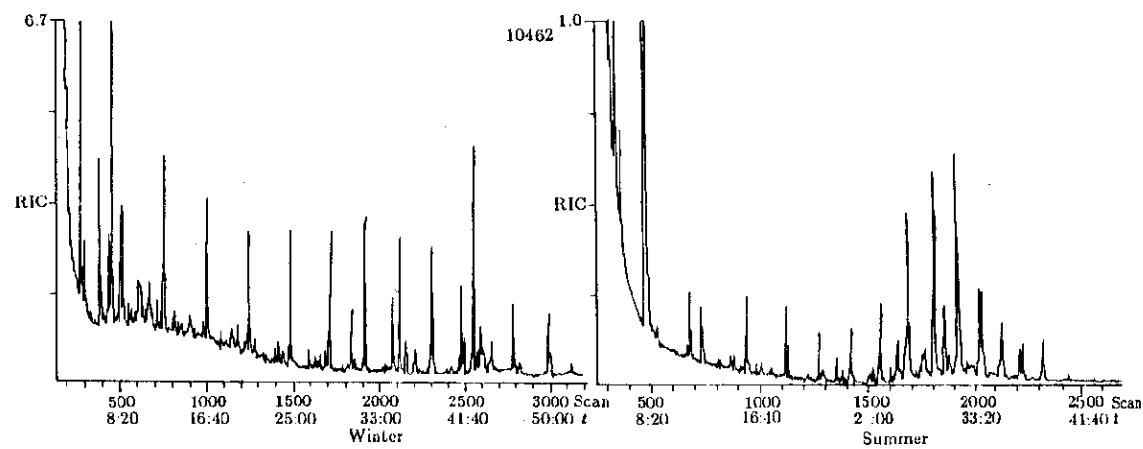

Fig. 3 Ion chromatogram of VPOs in the air of Langfang

pollution situations of the three cities.

It was windless when the samples were collected. Therefore, the wind-effect on the transportation and diffusion of the VPOs could be omitted. The data listed in Table 1 indicate that the identified VPOs have numerous numbers as well as various types. Some of them were analyzed quantitatively and were listed in Table 2 and Table 3. From these data, it is found that the concentration level of the VPOs at night is generally higher than that in daytime, and greater in the winter than in the summer.

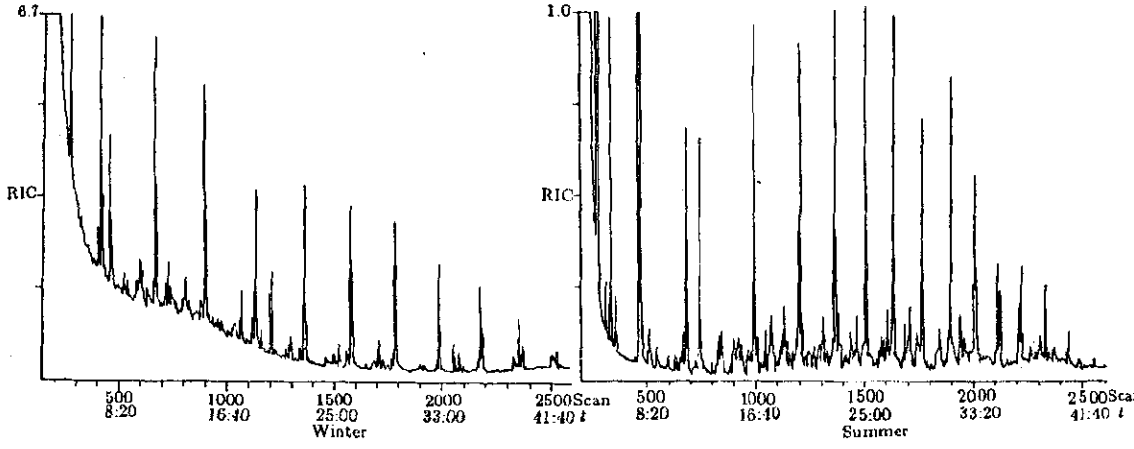

Fig. 4 Ion chromatogram of VPOs in the air of Tianjin

Table 1 Classification of VPOs in Beijing, Tianjin, and Langfang air samples

	Beijing				Langfang				Tianjin			
	Winter, %		Summer, %		Winter, %		Summer, %		Winter, %		Summer, %	
Alkanes	42	35.6	17	29.3	27	32.5	20	51.3	21	32.3	32	44.4
Cyclic hydrocarbons	20	16.9	7	12.1	5	6.0	2	5.1	10	15.4	10	13.9
Aromatics	24	20.3	12	20.7	13	15.8	3	7.7	13	20.0	12	16.7
Alkenes	9	7.7	4	6.9	2	2.4			1	1.6	1	1.4
Alkines	1	0.8										
Alcohols	9	7.6	4	6.9	6	7.3	1	2.6	9	13.9	6	8.3
Esters	3	2.5	1	1.7	4	4.8	3	7.7	3	4.7	4	5.6
Acids					1	1.2						
Aldehydes	1	0.8	3	5.2			1	2.6			1	1.4
Ketones	1	0.8	5	8.6	1	1.2	3	7.7	1	1.6	1	1.4
Halocarbons	4	3.4	5	8.6	20	24.0	4	10.2	2	3.1	5	6.9
Others	4	3.4			3	3.6			5	7.7		
Total	118	100	58	100	83	100	39	100	65	100	72	100

Table 2 Some typical VPOs concentrations of the three cities in winter ($\mu g/m^3$)

Organics	Beijing				Langfang				Tianjin			
	Day		Night		Day		Night		Day		Night	
	Ave.	Max.	Ave.	Max.	Ave.	Max.	Ave.	Max.	Ave.	Max.	Ave.	Max.
Methylbenzene	7.53	33.3	7.63	14.01	4.17	9.2	3.68	11.44	12.90	31.4	26.18	128.3
Octane	1.87	7.81	0.95	2.59	0.74	2.39	0.52	2.59	2.40	7.54	2.66	12.52
Ethylbenzene	2.03	8.13	2.53	6.91	0.97	2.07	0.92	2.54	5.67	12.29	1.81	5.36
Dimethylbenzene	10.28	40.46	7.43	18.97	2.15	5.34	2.52	6.35	11.99	45.87	21.29	109.36
Nonane	2.86	10.83	13.94	81.8	0.86	1.55	0.68	2.81	4.99	16.45	8.43	43.73
Decane	2.28	9.94	3.68	14.76	0.89	1.57	1.04	2.54	5.22	14.12	8.49	43.73
Dodecane	0.56	1.91	0.81	1.2	0.34	0.48	0.73	0.99	0.62	1.21	2.52	11.82
Tridecane	0.76	1.73	1.11	1.23	0.43	0.56	1.09	1.10	0.86	0.99	0.64	0.87
Tetradecane	0.59	1.16	0.87	0.98	0.38	0.48	0.92	0.92	0.6	0.78	0.59	1.05
Pentadecane	0.59	0.97	0.68	0.73	0.42	0.52	0.93	0.98	0.8	0.91	1.89	3.92

Table 3 Some typical VPOs concentrations of the three cities in summer ($\mu g/m^3$)

Organics	Beijing				Langfang				Tianjin			
	Day		Night		Day		Night		Day		Night	
	Ave.	Max.	Ave.	Max.	Ave.	Max.	Ave.	Max.	Ave.	Max.	Ave.	Max.
Methylbenzene	4.14	10.5	29.46	47.5	15.60	51.8	44.63	106.24	8.23	20.92	15.66	36.39
Octane	0.31	0.70	0.30	0.54	0.02	0.02	0.41	1.10	1.28	3.73	5.99	9.34
Ethylbenzene	0.60	1.65	2.17	5.01	0.15	0.15	0.58	1.32	0.99	2.75	3.74	8.40
Dimethylbenzene	2.08	3.91	1.50	2.18			2.45	6.87	5.69	13.82	9.30	14.44
Nonane			0.92	0.92			2.54	2.54	1.36	3.55	6.72	16.17
Decane	1.21	1.81	0.86	0.86					0.32	0.32	0.49	1.19
Dodecane							0.79	0.79	1.70	1.21	1.71	7.18
Tridecane							0.81	0.82	1.31	1.83	1.53	2.40
Tetradecane	0.27	0.35	0.10	0.15	0.28	0.28	0.27	1.03	0.33	1.26	0.54	2.19
Pentadecane	0.09	0.13	0.07	0.1	0.07	0.11	0.39	0.70	0.35	0.86	0.63	1.75

Alkanes and cyclic hydrocarbons

The alkanes and cyclic hydrocarbons detected in the three cities are quite a lot. In order to identify the source of alkanes, we have compared the C (odd)/C (even) domination of the linear alkanes (Kimitake, 1983; Eglinton, 1967) in our air samples and have found that there was no such a domination. In other words, these hydrocarbons are not from the nature but from some other sources such as evaporation of volatile components of coal and oil products during their storage or combustion. From the data presented in Table 1, it can be found that a similar percentage of alkanes of the three cities in the winter, which can be considered as an evidence of the common source of the alkanes. However, the different percentage of the alkane in the summer might be resulted from the difference of the component of fuel used in summer in the three cities. For the cyclic hydrocarbons, these ratios of Beijing and Tianjin are higher than that of Langfang without seasonal differences. It infers that they may come from some other sources.

Aromatics

Methylbenzene, dimethylbenzene and ethylbenzene are typical components of automobile exhaust (Seizinger, 1972). They were all detected in the three cities. We have noticed from Table 2 and Table 3 that the concentration of the three compounds of Langfang, which is located between Beijing and Tianjin, is lower than those of the other two cities. It is also correspond with the fact that the numbers of automobile is fewer in Langfang than in the other two cities. In addition, we observed the percentage of aromatics of Langfang is the least in the three cities. That implys that most of the aromatics detected are related with automobile.

Alkenes

Of all the three cities, Beijing has a largest alkene number despite the fact that there are exploiting oil and nature gas around Langfang and Tianjin. This means the sort and the concentration of alkenes have no relation with the exploition. It must be pointed out that an increasing alkenes in atmosphere, either their concentrations or their categories, tends to speed up the photochemical reaction and smog formation. For this reason, we must pay more attention to this phenomena.

Oxygenated hydrocarbons

Several oxygenated hydrocarbons were identified in the air of the three cities. These compounds include aldehydes, ketones, acids, esters and some higher alcohols and esters which have not been reported priviously. Although there are reports indicate that the compounds are usually associated with the automobile (Seizinger, 1972) and are formed as secondary products from photochemical reactions (Tuesday, 1971), however, because of the great regional and categorical differences, it is very difficult for us to identify their sources. But we must point out that this type of compound has a large percentage in summer. Considering with the report that the ozone concentration goes as high as 100 ppb in recent summer at Beijing, we have reason to believe that the organics have been involved in photochemical reactions.

Halogenated compounds

The result for halogenated compounds is interesting. According to reports (Urone, 1976), most of the halocarbons detected in air are lower halocarbons, Freon vapors and pesticides. However, besides those reported pollutants like chloroform, trichloroethylene, tetrachloroethane and BHCs, we detected a lot of compounds which had not appeared in the reports concerning air pollution (Urone, 1976), such as chloroaceticacid ethylester, dichloropropanol, chloropentadecyne, chlorotetradecane and chlorinated benzenes etc. in the air of Langfang in the winter. To determine their sources, there are lots of work to be done. One thing we want to stress is that some halocarbons we detected, such as chloroform, trichloroethene, pentachlorocyclopropane etc., have been recognized being carcinogenics. Because they are dangerous to human being, their appearence in atmosphere should not be overlooked.

CONCLUTION

The GC and GC/MS measurements of VPOs in the atmosphere of Beijing, Langfang and Tianjin show us the present situations of the air qualities of the three cities. Of all the detected organics, most of them, though we can not indicate their sources, are obviously not belong to global biosphere cycle but come from human activities. Because these compounds tend to stay in the atmosphere for a long time and produce serious secondary pollutants through photochemical reactions and greatly degenarate the environmental quality, we must pay more attention to this kind of pollution.

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