Review

Application of chromatographic studies of air pollution in China

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Abstract

A review of chromatographic studies on air pollution in China is presented. Gas chromatography and high-performance liquid chromatography are two of the techniques most commonly used. Various aspects of investigations of environmental potential carcinogens, such as polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons, are discussed. In addition, studies on greenhouse effect trace gases and other hazardous or toxic pollutants on air particulates from or in the vapour phase (gaseous phase) in many cities in China have also been carried out.

Contents

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1. Introduction

Coal accounts for more than 70% of the fuels used in China. Serious pollution by polycyclic aromatic hydrocarbons (PAHs) from coal combustion, especially during winter in northern cities, has been found by chromatographic analysis in many studies. Other pollutants, such as aldehydes, phthalates and alkanes, and also greenhouse effect trace gases are present in ambient air or in workplaces. Analytical investigations will serve as the basis for the assessment of air quality source identification and the evaluation of secondary reaction. Based on the data obtained, pollution abatement measures can be suggested.

2. Chromatographic methods used for studies on air pollution in China

Various chromatographic methods have been developed in China for the determination of many pollutants in the ambient atmosphere or in emission sources. Among them, gas chromatography (GC) with both capillary and packed columns, and various detection methods, including thermal conductivity (TCD), electron-capture (ECD), flame ionization (FID), flame photometric (FPD) and mass spectrometric (MS) detection, accounts for more than 70% of the analytical studies, while the growing use of high-performance liquid chromatography (HPLC) with UV and fluorescence detection, etc., is evident, especially because of its sensitivity and the possible avoidance of decomposition during the analysis. In addition, photodiode-array detection (DAD) has been proved useful, especially for some advanced studies [1–4].

Ion chromatography (IC) has been widely used in recent years, especially in studies of anions and organic acids relating to acid precipitation investigations. Supercritical fluid chromatography (SFC) possesses the advantages of both GC and HPLC. Studies on SFC methods of analysis are in progress.

3. Target compound analyses

3.1. Polycyclic aromatic hydrocarbons (PAHs)

Suspended particulate matter, consisting of both adsorbed organic and inorganic substances, is one of the most important atmospheric pollutants of nationwide concern in China. The concentrations of total suspended particles (TSP) are comparatively high all year round, with higher values in northern than in southern cities. Owing to the increased amount of coal burning for heating in winter, the level is generally higher than in summer. Many large cities located in northern China are heavily contaminated by PAHs, e.g., the well known carcinogen benzo[a]pyrene [B(a)P], adsorbed on dense air particulates.

GC, GC–MS and especially HPLC methods have been applied to the systematic study of the distribution of 10–17 PAHs in atmospheric suspended particulates from many cities [5–19]. In the early 1980s, the concentration of B(a)P in residential areas in the urban districts of Beijing ranged from 4 (summer) to 74 ng/m^3 (winter), and in some industrial sites where coal was used as the main fuel, the concentration of B(a)P may be as high as 500 ng/m^3. Near some petrochemical complexes, however, the value of 1–14 ng/m^3 was close to those in clean areas (0.6–6.7 ng/m^3) [5]. In general, the B(a)P concentration accounts for less than 10% of the total PAHs studied. Over 120 PAH compounds were identified by GC–MS in a sample collected from an area near a steel works, including thirteen sulfur-containing, fifteen nitrogen-containing and ten oxygenated heterocyclic compounds [6].

Regular seasonal and diurnal variations of PAH have been observed [5]. Excessive concentrations in the winter are related to the increased use of coal for heating purposes. Two maxima in PAH concentration have been detected during the day, as summarized briefly in Ref. [2]. The maximum concentration that occurred at 5–9 a.m. is coincident with rush-hour traffic and morning cooking. Some degradation by sunlight and higher wind velocities might be

the cause of the minimum concentration observed after 9 a.m. The second maximum occurred in the evening, probably corresponding to the traffic at the end of the day and also to cooking. Fig. 1 shows the monthly variation of B(a)P in air particulates collected from three typical locations in Beijing [8]: (1) is a heavily polluted area where each institution has its own boilers or heating devices, (2) is a location where a central heating facility was established and (3) is a rural clean site [8].

Some correlations between different PAHs have been observed, and in most places samples collected at noon are higher in PAHs with three and fewer rings than those collected in the morning, while the reverse holds for compounds with four and more rings [5,14].

Systematic data indicating the concentration of B(a)P and PAHs on very fine particles [5,14] and the mutagenicity results confirmed the regularity that mutagenic compounds are mainly adsorbed

Fig. 2. Percentages (w/w) of air particulates of different sizes (from coke plant, Dec. 1983) [5].

on fine inhalable particles (see Figs. 2, 3 and 4) [5].

It is very interesting that several PAHs, such as perylene, B(a)P, benzo[*ghi*]perylene and coronene, are very similar even quantitatively in their size-based percentage concentrations.

Cocaine (whether from tobacco leaves processing or from cigarette smoking) was detected for the first time [9] in Chengdu city.

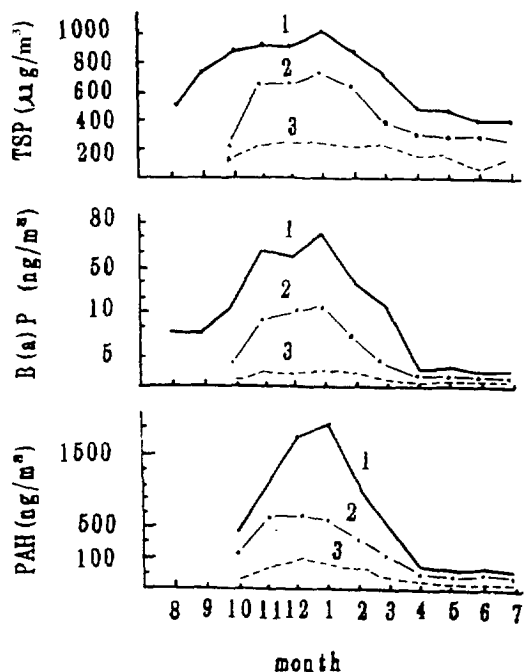In a Chinese–Japanese cooperative study (1981–84) on elements, organic constituents,

Fig. 1. Monthly changes in the concentrations of TSP, B(a)P and PAH pollutants at different sites [8]: 1 = Zhong-guan-cun; 2 = Qing-hua University; 3 = Shi-san-ling Reservoir.
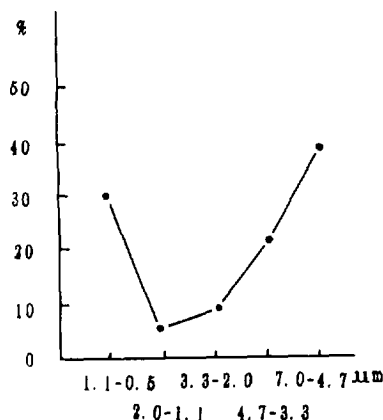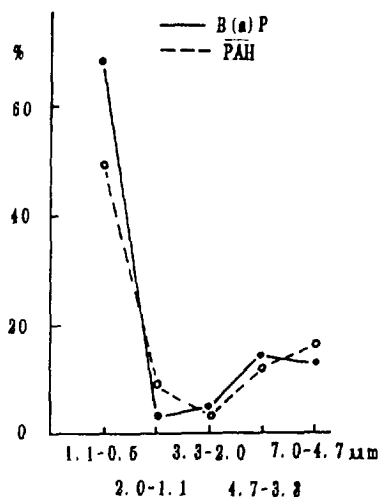

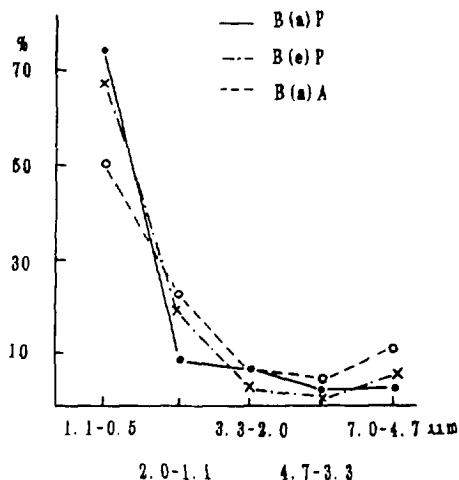Fig. 3. Percentages of B(a)P and PAHs in air particulates of different sizes (from coke plant) [5].

Fig. 4. Percentages of PAHs in air particulates of different sizes (from Yan-shan area) [5]. B(e)p = Benzo[e]pyrene; B(a)A = benz[a]anthracene.

TSP, SO$_2$, NO$_2$ of atmospheric pollutants in Beijing, PAHs in airborne particles were determined by HPLC and GC–MS in both summer and winter [10]. The major components found were fluoranthene, B(a)P, benzofluoranthenes (sum of [b,j,k] isomers), indeno[1,2,3-cd]pyrene, benzo[ghi]perylene and dibenzo [a,c]pyrene. Chlorine and sulfur compounds were also found at the sampling sites. The concentrations in the industrial, urban and rural areas generally decreased in that order, and those in winter were 2–5 times higher than those in summer.

The concentrations of B(a)P and benzo [ghi]perylene in ambient air in Tokyo (urban site) were slightly lower [10] than those at the rural area in Beijing and as low as 10–20% of those at the urban area in Beijing.

The data obtained were used for the study of source identification. For example, samples of suspended particulate matter were collected during the period of 26 October–4 November 1982 and 27 January–2 February 1983 in five sampling locations of Beijing. Non-polar, moderately polar, polar and strongly polar fractions of particulate organic matter (POM) were sequentially extracted with cyclohexane, dichloromethane, acetone and methanol for chemical analy-

sis. Atmospheric concentrations of total POM were used in factor analysis to identify emission sources. The results of multiple regression analysis indicated that the contribution of coal combustion was almost three times those of oil-burning and motor vehicles [11].

Many studies have also been carried out on the evaluation of alternative fuels and emissions from different stoves and furnaces as PAH pollution sources [20–26].

Modified US EPA Methods 5 and 17 were used for stack sampling. More than 110 organic compounds (including PAHs and alkanes) have been identified by capillary GC–MS from stack samples [25]. An HPLC method with dual detection (UV at 254 nm and fluorescence at 296/427 nm) was developed [20] in order to obtain higher sensitivities for all different PAHs (see Fig. 5).
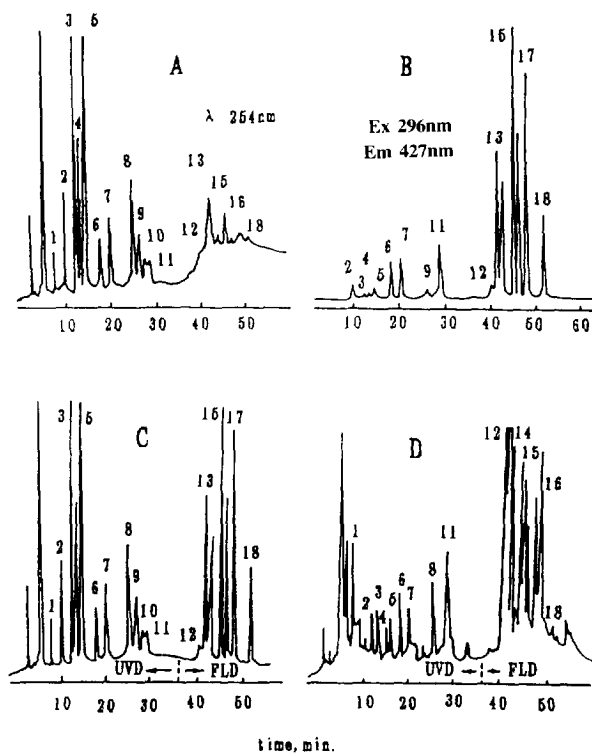

Fig. 5. HPLC of PAHs. (A) Mixture of 18 standard PAHs with UV detection (UVD); (B) mixture of 18 standard PAHs with fluorescence detection (FLD); (C) mixture of 18 standard PAHs with dual UVD–FLD; (D) extract of emission sample from coal-burning boiler with dual UVD–FLD [20].

Eighteen PAHs in different stack samples were quantified by this HPLC method. Fluorescence spectra of PAHs in real samples could be recorded by the stopped-flow method and compared with those in standard mixtures for identification. However, during routine analysis the retention values of peaks were checked under control of the same chromatographic conditions.

Differences of several orders of magnitude in the emission concentration factor of B(a)P in different cases were observed (see Table 1) [25]. It is evident that small domestic stoves give rise to much more B(a)P pollution than other combustion sources. In order to protect the environment, city coal gasification systems are being developed and some interim measures, such as using coal briquettes instead of raw coal, have been suggested.

3.2. Nitro-PAHs

HRGC–electron impact (EI) MS and HRGC–negative ion chemical ionization (NICI) MS have been used for the detection of nitro-PAHs such as 9-nitroanthracene, 1-nitropyrene and nitrofluoranthene in air particulate samples collected from the Beijing area [3,27]. The results were checked by HPLC with fluorescence detection after reduction of nitroarenes to the corresponding amino-PAHs, and 6-nitrochrysene was also found [28–30].

Different reducing agents for the reduction–HPLC–fluorescence detection method have been carefully compared and NaBH$_4$ was found to be better than Zn–HCl with regard to extent of reduction of compounds with higher numbers of

rings and their stability during storage. In addition, this method has been applied for the quantification of nitro-PAHs in various air samples. Table 2 shows some of our results in comparison with data from other workers [29,31–35].

With proper selection of wavelengths of excitation and emission, minimum detectable amounts of most amino-PAHs are 0.02–0.2 ng. However, with derivatization of amino compounds with heptafluorobutyric anhydride, the detection limits may be as low as 0.25–11 pg [35]. Nitro-PAHs were also detected in the vapour phase (Table 3). However, further work is required to identify many undefined peaks on the chromatograms after reduction when more standard chemicals are available.

3.3. n-Alkanes and vapour-phase organics

Analyses of vapour-phase organics in air were carried out by capillary GC–FID and GC–MS [36–56]. The compounds tentatively identified included alkanes, cyclic hydrocarbons, alkenes, aromatics, acids, alcohols, aldehydes, ketones, esters and halocarbons.

In a study [7] with GC–ion trap detection (ITD) and GC–FID, C$_{19}$–C$_{34}$ n-alkanes were found at concentrations in the range of 2.0–92 ng/m^3 (higher in winter than in summer). For n-alkanes it has been reported that the CPI value [carbon preference index = sum (content of odd carbon number n-alkanes)/sum (content of even carbon number n-alkanes)] of n-alkanes from anthropogenic activities such as combustion of fossil fuels is close to 1, whereas those origina-

Table 1
Emission coefficients of B(a)P from various coal-fired boilers and stoves [25]

Boiler type or stove	Emission coefficient (mg/ton coal)	B(a)P concentration (μg/m^3)
Power plant, 35 t/h	0.2–0.4	0.14–0.16
Industry, 10 t/h	0.2–0.35	
Industry, 4 t/h	2.1–9.7	0.3–0.8
Industry, 2 t/h	1.4–5.9	0.2–0.4
Tea boiler, 0.2 t/h	20–677	1.7–96
Household stoves	350–20000	

Table 2
Concentrations of nitro-PAHs in air particulates (pg/m³) [29,32–35]

Sample source	4-NBP	2-NF	3-NFL	1-NP	6-NCH	6-NB(a)P	Ref.
Beijing							[33]
S-2	–	57.7	420	117	55.7		
S-3	–	10.4	342	29.8	8.5		
S-4	14.9	1.9	259	77.1	12.1		
S-5	21.5	16.5	318	99	7.1		
W-2	162	23.3	38.7	299	393		
W-3	305	–	31.7	293	334		
W-4	101	8.8	8.7	132	269		
W-5	234	12.3	83	265	93		
Shandong (A)				110			[34]
Shandong (B)				55			
Tunnel				1400			[29]
PC, China				162			[35]
Warren				20		35–65	[32,34]
Detroit				19–30		100–280	
Washington			1.1 ppm				
Japan				21			
Copenhagen			<100			<100	
Columbus			5–200				

4-NBP = 4-Nitrobiphenyl; 2-NF = 2-nitrofluorene; 3-NFL = 3-nitrofluoranthene; 1-NP = 1-nitropyrene; 6-NCH = 6-nitrochrysene; 6-NB(a)P = 6-nitrobenzo[*a*]pyrene.

ting from natural sources are >5. Alkanes in atmospheric aerosols were studied by different workers [36,47,55]. It has been found that different values and different seasonal changes of *n*-alkane CPI are characteristics of aerosols from different cities in China, e.g., Guangzhou and Beijing. Also, the *n*-alkane CPI decreases with increasing particulate size. This means that the smaller the particulate, the larger is the contribution of *n*-alkanes from anthropogenic sources. The *n*-alkane CPI is useful for identifying their sources in aerosol particulates.

For other hydrocarbons in air, a method was developed for the simultaneous determination of low- and high-molecular-mass hydrocarbons in the atmosphere by means of preconcentration with cyrogenic trapping (liquid nitrogen), split-less injection and capillary column GC–MS [36]. Using this method, 45 out of about 100 chromatographic peaks were identified for atmospheric samples collected from a petrochemical production area in Beijing. Table 4 shows the analytical results for this sample obtained with GC–FID and GC–MS. In a separate study the

Table 3
Concentration of nitro-PAHs in gaseous phase of ambient atmosphere (Beijing) (ng/m³) [28]

Season	1-NO$_2$-naphthalene/ 2-NO$_2$-naphthalene[a]	2-NO$_2$-fluorene[b]	1-NO$_2$ pyrene[b]
Winter	2.25	2.84	0.39
Summer	0.44	0.35	8.4×10^{-3}

[a] Calculated as 1-NO$_2$-naphthalene.
[b] According to retention time.

Table 4
Analytical results for an air sample from a petrochemical complex district in Beijing [36]

Peak No.	Retention time (min)	Compound	Identification method	Concentration (mg/m^3)
11	21.50	1-Butene	MS	0.353
14	22.58	2-Methylbutane	MS	0.500
21	26.94	Ethylcyclobutane	MS	0.151
22	27.33	2-Methyltetrahydrofuran	MS	0.341
23	28.55	3-Methylpentane	MS	1.054
26	30.19	Hexane	MS	0.596
27	37.72	2-Methyl-1-pentene	MS	0.934
29	35.26	Benzene[a]	GC–MS	0.805
31	36.33	Cyclohexane	MS	0.853
32	37.52	3-Methylhexane	MS	0.078
33	38.46	1,3-Dimethylcyclopentane	MS	0.083
35	41.34	n-Heptane[a]	GC–MS	5.725
36	43.33	Methylcyclohexane	MS	1.313
37	44.64	Ethylcyclopentane	MS	0.082
39	45.14	2,4-Dimethylhexane	MS	1.451
43	47.15	Toluene[a]	GC–MS	2.065
44	48.00	2-Methyl-3-ethylpentane	MS	0.182
46	48.84	4-Methylheptane	MS	1.364
47	49.45	2,5-Dimethylhexane	MS	0.105
49	50.58	2,5-Dimethyl-1-hexene	MS	0.075
53	52.20	n-Octane[a]	GC, MS	0.175
54	53.86	2,3,5-Trimethylhexane	MS	1.223
56	54.64	2,3,4-Trimethylhexane	MS	3.571
58	55.10	3-Ethylheptane	MS	0.026
59	55.55	2-Methyl-2-hepten-4-one	MS	0.063
61	56.20	2,6-Dimethyl-3-heptene	MS	2.964
62	56.77	Xylene	MS	0.039
63	57.06	Styrene[a]	GC–MS	0.078
64	57.38	Xylene	MS	0.104
67	58.39	Trimethylhexane	MS	0.521
69	59.66	3-Methyloctane	MS	0.084
70	59.57	1-Nonene	MS	0.043
72	60.93	Dimethyloctene	MS	0.102
73	61.45	n-Nonane[a]	GC–MS	0.070
76	63.09	5-Methylnonane	MS	0.185
78	64.12	Camphene	MS	0.455
79	64.39	3-Methylnonane	MS	0.371
80	64.83	2,6-Dimethyloctane	MS	0.067
84	66.07	Methylnonane	MS	0.069
85	66.59	4-Methylnonane	MS	0.045
86	66.82	Isodecane	MS	0.061
87	67.36		MS	0.123
88	67.90	5-Methyldecane	MS	0.109
89	68.08	Isoundecane	MS	0.553
96	72.39	Methyldecane	MS	0.111

[a] Checked with standard compounds.

analytical results for the main components of exhaust from a rubber tire refining factory were reported [57].

It is important to point out that many compounds having comparatively high vapour pressures under ambient conditions are present both in the gaseous phase (or vapour phase) and on particulates, such as PAHs and phthalates, when both filters and adsorbents such as XAD resin or polyurethane foam (PUF) were used for air sampling. Higher concentrations of four-ring and smaller PAHs were found in the vapour phase of the atmosphere (see Table 5) [39].

The quantitative relationship suggested by Yamasaki [40] is recommended for comparison with real measurements [38]:

$$\log \left(\frac{\text{PAH}_v}{\text{PAH}_p/\text{TSP}} \right) = -A/T + B$$

where PAH_v = concentration of PAH in vapour phase (ng/m^3), PAH_p = concentration of PAH on particulate (ng/m^3), TSP = concentration of total suspended particles (mg/m^3), T = absolute temperature (K) and A and B are constants.

HPLC determinations of separated PAHs were carried out both in the vapour phase and on particulates from residential areas and clean meadow areas in winter and summer. The results also showed that over half of the PAHs with four and fewer rings were found in the vapour phase, and most of the PAHs with five rings were found in particulates. Moreover, the distribution of

PAHs in clean meadow samples was different from those in the residential area [42].

Both vapour phase and particulate phthalate esters in atmospheric samples collected from a city in Inner Mongolia were studied and compared with those from a clean meadow [44]. After extraction and preseparation, dibutyl o-phthalate and di(2-ethylhexyl) o-phthalate (DEHP) were detected and analysed by GC–FID. In the samples from this city, where small domestic stoves were used for heating purposes, very high concentrations of both phthalates (up to 1.3–1.9 μg/m^3) were found in particulates in winter and in the vapour phase in summer, and a high TSP (up to 1.65 mg/m^3) was found in winter. However, in the clean meadow samples, total phthalates in both the vapour phase and particulates were as low as 0.2–0.4 μg/m^3. The results suggest that the phthalates are derived mostly from anthropogenic or industrial sources.

An automatic and continuous analysis device for aromatic compounds in ambient air has been developed [45]. This device is composed of a GC–FID system, a six-way valve and a vacuum pump, which is controlled by a microprocessor. Air samples from Huhehot have been analysed qualitatively and quantitatively with this device and sixteen kinds of compounds, such as C_6–C_9 n-alkanes, benzene and eleven C_1–C_4 alkylbenzenes were detected and the trend of the changes in their concentrations was observed. Many other papers have dealt with analyses for benzene and alkylbenzenes [48–50,53–56].

Table 5
Atmospheric polycyclic aromatic hydrocarbons in vapour phase

PAH	VPO/POM	Reference VPO/POM	
Naphthalene	40:1		
Biphenyl	40:1		
Phenanthrene	100:1	Phenanthrene + anthracene	
Anthracene	40:1	245:1	
Methylphenanthrene	20:1	Methyphenanthrene + methyanthracene	
Methylanthracene	20:1	64:1	
Fluoranthene	4:1	20:1	
Pyrene	4:1	12:1	

Comparison of PAH samples adsorbed on polyurethane (VPO) with PAHs on particulates (POM) [39].

3.4. PCBs, PCDDs, chlorinated PAHs and pesticides

Systematic determinations of PCBs began in the late 1970s and early 1980s [57,58–60]. Two commercial products, PCBs No. 1 (41% Cl) and 2 (53% Cl) were analysed and confirmed with different methods: elemental analysis, GC–microconductivity detection, GC–ECD and GC–MS. They were recommended to be used as reference standards [58]. With computerized multi-ion monitoring techniques, quantification of PCBs and organochlorine pesticides became possible without preseparation [59].

Dimethylformamide solution was used to absorb PCBs and, after extraction with petroleum, GC–FID was used to determine PCBs in air with recoveries of 89–106% and a detection limit of 20–30 ng/m^3 (sampling volume 60 l) [60,61]. In most cases, preseparation is not necessary.

A two-dimensional separation system of GC (SE-54 column)–GC (FFAP column) with dual parallel FID–ECD [62] was developed for fractionating and analysing complex mixtures as in the case of trace analyses for PCDD and PCB toxins in environmental samples. Fractions cut from the SE-54 column were separated instantly by the FFAP column without the necessity for using cold trapping. Other papers [63,64] were concerned with the ubiquitous pollutants PCDDs and PCDFs.

Polychloronaphthalene (PCN) congeners were found to induce enzymes such as AHH (aryl hydrocarbon hydroxylase) in a similar way as dioxins and therefore have received considerable attention. An improved packed column GC method [65] for determining PCNs in fly ash from municipal incinerators was proposed. Using a short packed column, 1-chloronaphthalene can be well separated from 2-chloronaphthalene at column temperatures as low as 110°C.

Hexachlorocyclohexane (HCH) and DDT in rain and snow were determined with packed column GC–ECD [66]. Organophosphorus pesticides in exhaust samples or in the workplace air of a pesticide factory were determined by packed column GC–FPD after enrichment with a solid adsorbent. The adsorption tube was first de-

sorbed with acetone and the eluate was concentrated with a Kuderna–Danish concentrator. The detection limit was as low as 0.04 μg/m^3 when a 250-l air sample was analysed [67,68].

3.5. Malodorous sulfur compounds

Combined techniques for sampling and determination of the main malodorous compounds in air have been developed [69–72]. With CH$_3$SH and (CH$_3$)$_2$S$_2$ as typical pollutants, the complete set of apparatus, including adsorbent sampling tube, constant-flow sampling pump, thermodesorption device and gas mixer for the preparation of calibration gas mixtures has been established. Commercial GDX-105 was found to be suitable for the collection of these compounds at the room temperature. The methods afford recoveries between 60 and 100%, a detection limit of 0.2 ng and an accuracy of ±3%.

In a case study of an emergency (which lasted for several days and affected 400 000 individuals) that occurred in November 1988 in a city in Jiangxi Province, GC–FID and GC–MS were used to determine the organic pollutants in the effluent waste water from a refinery factory. Concentrations of 29 ppm of C$_2$H$_5$SH in waste water and 800 ppm of (CH$_3$)$_2$S$_2$ in original oil and 0.001 ppm in air (sampling volume 0.6 m^3) were detected and identified. The threshold values of odor were 0.00019 ppm (water) and 0.0037 ppm (air), respectively [71,72].

GC–photoionization detection (PID) [10] was used to analyse low-pressure gas and exhaust samples. Concentrations of 14 ppm of C$_2$H$_5$SH and 19 ppm of (CH$_3$)$_2$S were found in the latter. With the application of PID, the pretreatments of samples can be simplified. Other malodorous compounds, such as indole and butyric acid, have also been determined [73].

3.6. Aldehydes, etc.

A simplified method was used to evaluate the amounts of aldehydes emitted from an oil-fuelled boiler and a gasoline engine under different operating conditions [74]. Low-molecular-mass aldehydes in the sample were directly collected

and derivatized with a catalyst in a bubbler containing a methanol or acetonitrile solution of 2,4-nitrophenylhydrazine (2,4-DNPH), HPLC being used for further separation and determination. The recoveries achieved for formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde all exceeded 85%, with detection limits of 0.6, 1.3, 0.4 and 0.5 ng, respectively. Table 6 shows the emission concentrations of aldehydes in automobile exhaust gas. A similar method has been applied to determine formaldehyde in air [75].

With a commercial preconcentration and derivatization tube (with 2,4-DNPH), concentrations of C_1–C_3 aldehydes as low as 2–13 ppb in ambient air of Guiyang have been detected [76]. Ambient C_2–C_5 aldehydes can also be determined by GC [77].

Methyl nitrite (MeONO) and methyl nitrate (MeONO$_2$) concentrations in exhaust gas from an engine fuelled with methanol were measured by GC, with detection limits of 20 and 50 ppb, respectively (sample volume 1 ml). The exhaust from a Santana M100 engine contained 5–250 ppm of MeONO and less than 50 ppb of MeONO$_2$ [78].

Analysis using GC–FID also provided data on CH_3OH concentration in the assessment of the effects of exhaust from methanol–gasoline combustion and catalytic purification of exhaust from a methanol-fuelled vehicle [79–81].

3.7. Greenhouse effect and trace gases

Carbon dioxide, CH_4, chlorofluorocarbons (CFCs), N_2O, etc., are now considered to be responsible for global climatic changes and ozone layer depletion. These are two of the main environmental problems currently of concern all over the world. Many international research projects have examined reliable monitoring methods, mechanisms and extents of emissions and reduction measures. In this respect, China has also played an important role in the monitoring and study of greenhouse gases.

After examination of the data for year-round temperature and precipitation in China at 160 observation stations during 1951–1989, a rise of about 0.23°C in the annual temperature was deduced [82].

CO_2 is present in much higher concentrations in the atmosphere than other trace gases. Among the prevailing methods for CO_2 measurement, the non-dispersive IR absorption (NDIR) method tends to be the most precise continuous method, with precision up to 0.1 ml/m^3, and GC is still the most popular and readily available methodology. Both FID and

Table 6
Concentrations of aldehydes in automobile exhaust [74]

Aldehyde	Operating conditions			
	Low speed (25–30 km/h)		High speed (70–80 km/h)	
	Emitted concentration (ppm, v/v)	Emitted amount (μg/h)	Emitted concentration (ppm, v/v)	Emitted amount (μg/h)
Formaldehyde	6.7	52.1	14.1	164.5
Acetaldehyde	6.3	72.4	1.2	20.5
Acrolein	7.2	103.9	1.3	27.8
Propionaldehyde	1.1	16.4	n.d.[a]	n.d.
Butyraldehyde	0.8	15.5	n.d.	n.d.
Benzaldehyde	–	–	n.d.	n.d.

[a] Not detected.

TCD can be used, but prior conversion of CO_2 into CH_4 is required in the former case. Using this approach, other hydrocarbons in air may also be measured simultaneously [83]. Thus it has been applied for the multi-component determination of a few samples collected from the troposphere.

Both IR and GC are now used in China to determine N_2O. Mass spectrometry and volumetric analysis (pressure method) for the determination of N_2O have recently been reported, but few data are available [84–86].

Many detection methods, such as TCD and FID, were used for N_2O monitoring in the early years. However, GC–ECD is now the simplest and most accurate and precise method. In March–July 1992 a study [84] of ground level N_2O concentrations (in ppb, v/v) in some typical environments found that the mean concentration was 349 in a campus, 352 in a rice field and 345 in a forest, and higher (362) in an organic source (manure). Various combustion processes are also sources of air N_2O. Improvements in the continuous injection of two consecutive samples led to a 30% decrease in analysis time [84].

Nitrous oxide flux has been studied in a typical winter wheat field in Northern China [85]. Gaseous samples were collected from a sampling chamber of $1 \times 1 \times 1$ m^3 located in the field and analysed by GC–ECD. With similar (soil) conditions, the fluxes on winter wheat field and alfalfa farm land did not show obvious differences. The effects of fertilization, irrigation, soil temperature, etc., are conducive to the emission.

The emission factors of nitrous oxide have also been determined during the combustion of rice straws, wheat stalks and maize stalks in an enclosed combustion system [86]. They were 84.4 g/t for rice straws, 132 g/t for maize stalks and 27.3 g/t for wheat. The N_2O-N (nitrogen in nitrous oxide emission) accounts for 0.59% and 0.87% of the total nitrogen in rice straws and maize stalks, respectively.

GC–ECD with ambient temperature injection and a freezing technique was successfully used to determine the concentrations of halocarbons in ambient atmospheric samples collected in the suburbs of the Beijing area [87]. The stainless-steel columns used were (1) 25% DC-200 Chromosorb W AW DCMS (60–80 mesh) (3 m × 3 mm I.D.) and (2) gas–solid Carbopack CHT (80–100 mesh) (2 m × 3 mm I.D.). The detection limit can be as low as 0.04–0.3 pg.

The measured concentrations of CFC-11, CFC-12, $CHCl_3$, CH_3CCl_3, CCl_4, $CHCl = CCl_2$ and CCl_2CCl_2 were 127 ± 24, 275 ± 12, 49 ± 32, 80 ± 27, 60 ± 18, 8 ± 2, and 30 ± 17 ppt, v/v, respectively. These values are lower than those of global concentrations, but the relative concentrations of CCl_4 are close.

No. 407 macroreticular resin adsorbent (made in China) has also been used as a stationary phase to separate CFC-12 (CCl_2F_2) from $CHCl_3$, CCl_4, C_2H_6, CH_4 and CFC-11 by GC–FID with direction injection of a 1-ml sample from a workplace. The detection limit was 5 ppm [88].

Direct measurement of trace isoprene monoterpenes in the atmosphere has been made possible by using GC–PID. The experiments showed that the rate of release of α- and β-pinene from some oriental pine trees is faster during the day than at night [89].

The contribution of volatile organic acids has also been taken into consideration in studies on acid rain. A rapid GC procedure consisting of (1) collection by adsorption on Amberlite XAD-2 resin, (2) esterification with benzyl bromide in the presence of silver oxide as catalyst and (3) derivatizing followed by determination of volatile organic acid by GC–FID was suggested [90]. The experimental results indicated that C_1–C_4 (even up to C_6) organic acids can be effectively separated and determined. Concentrations of formic acid, acetic acid and propionic acid were found in the ranges 0.005–0.234, 0.023–0.542 and 0.030–1.60 mg/m^3, respectively, in air samples collected from six different locations. However, C_4 and higher organic acids were not detected in these samples. Other references are given in Section 4.

3.8. Miscellaneous compounds

Packed column GC with a liquid crystal stationary phase was used to determine phenol,

cresol, dimethylphenol, etc., after adsorption on GDX-502 macrorecticular resin. The detection limit was 0.01 mg/m^3 with R.S.D. 10% [91]. p-Chlorophenol in workplace air was desorbed from a resin adsorption tube with CS$_2$ solvent and determined by GC-FID. A detection limit of ca. 6 mg/l [92] can be achieved.

Derivatization followed by GC was used for the determination of hydrazine and unsymmetrical dimethylhydrazine after collection in a tube containing the special solid adsorbent SG-2 coated with sulfuric acid and then extraction with water [93]. An FFAP conventional column was used to separate isopropyl alcohol after extraction from air with active carbon [94].

Benzoyl methyl ester (BME) and substituted PTME in air as the by-products of terephthalic acid methyl ester (PTME) production were determined by GC [95]. After CS$_2$ elution from the active carbon adsorption tube, 10% silicone elastomer on a silanized carrier 101 packed column was used satisfactorily with detection limits down to 1 ng. Other pollutants such as acrolein, vinylchlorobutadiene and cyclooxypropane were determined using similar procedures [96-98].

GC coupled with an element-specific detector now has wide application in the speciation analysis of organometallic compounds. Among them, GC–atomic absorption spectrometry is the most popular [99].

3.9. Urinary 1-hydroxypyrene as a possible biomarker for human exposure to ambient PAHs

Jongeneelen et al. [100] suggested that urinary 1-hydroxypyrene, a major metabolite of pyrene, was a sensitive and specific marker for detection of occupational exposure to genotoxic PAHs from tar products. Since 1987, Zhao and co-workers have carried out a series of investigations on this metabolite [41,101-103]. 1-Hydroxypyrene in urine was determined using HPLC with synchronous fluorescence detection after hydrolysis of urine in the presence of β-glucuronidase/aryl sulphatase and preseparation on a Sep-Pak column. Samples of urinary 1-

hydroxypyene from residents in several cities, workers at two coke plants, a steel plant and an aluminium factory, groups of people with different occupations, including traffic policemen and bankers, and persons in several control groups were determined in parallel at the same time when PAHs of airborne particulate to which they were exposed were determined using GC–MS. The ratio of pyrene to B(a)P in PAHs samples was fairly constant in certain environments or from similar emission sources. Statistical analysis showed a significant correlation of urinary 1-hydroxypyrene with the concentration of pyrene and B(a)P with correlation coefficients of 0.978 and 0.959, respectively. It is therefore suggested that urinary 1-hydroxypyrene can be used as a biological monitoring index for human exposure to PAHs.

4. Ion chromatography and supercritical fluid chromatography

Ion chromatography (IC) is an increasingly popular analytical technique. The good separations of many chemically similar species, the provision of reliable information on the presence or absence of a wide variety of ions, its speed and simplicity of operation, the readily availability of reagents together with its versatility and high sensitivity make this technique attractive for the monitoring of atmospheric pollution and acid precipitation and analyses of soil, food and biota samples [104,105].

In China, large-area monitoring of acid precipitation has already been carried out. Although precipitation samples have been collected and analysed for acidity and chemical composition since the late 1970s, extensive research and sample monitoring only began after IC had become more popular [106-112]. Major water-soluble chemical constituents of airborne particulates collected in different cities were analysed by IC and are found to be related to the particle size.

It was reported that acid precipitation with pH values lower than 5.6 occurred in some southern parts of China, especially in Sichuan, Guizhou

and Jiangxi Provinces. In two major cities, Chongqing and Guiyang, the annual mean pH value of precipitation is only 4.1.

IC is now accepted as the optimum procedure for the study of acid rain. Both cations (such as K^-, Na^+, NH_4^+, Ca^{2+} and Mg^{2+}) and anions (F^-, Cl^-, NO_2^-, PO_4^{3-}, Br, NO_3^- and SO_4^{2-}) can be determined by IC using a single IC column with dimethyl phthalate as eluent and conductivity detection [113].

In addition to inorganic ions, some organic acids, including formic, acetic, maleic, chloroacetic, benzoic and ascorbic acid, can also be determined by IC [112].

IC was used in the early 1980s to determine SO_2 and NO_2 in ambient air [106]. A simple portable sampler with a solid absorption tube containing molecular sieve 13X soaked with triethylanolamine was used and dilute $NaHCO_3$ solution was used for extraction (NO_2 as NO_2^-, NO_3^- and SO_2 as SO_4^{2-} after oxidation with H_2O_2). Later it was used for the simultaneous determination of F^-, Cl^-, NO_2 and SO_2, and has now been applied for low-level routine analysis [114]. With Dionex 2120 IC, ammonia in air can be determined with a detection limit of 0.01 ppm, and hydrazine in air from a pesticide factory was determined with a detection limit of 0.001 mg/m^3 when the sampling volume was 60 l [110].

Regarding supercritical fluid chromatography (SFC), work is continuing with promising results. The various advantages of SFC should provide considerable success in the future [115].

5. Some regulation information

Air pollution, like water pollution, is very much of concern to both the public and the government in China. Great efforts have been made to minimize the pollution level accompanying the extraordinarily rapid recent economic growth. A national air quality monitoring network, consisting of 103 monitoring stations selected from 2131 stations, has been organized, engaging in regular monitoring of nation-wide air quality, but since China is a developing country,

most of the current regulations on air pollution are focused mainly on the inhalable total suspended particle (TSP), SO_2, NO_2, CO and a few others, including some cations and anions of wet precipitations.

Methods so far available for air quality determination are limited. However, in accordance with our obligation to global environmental protection, concerns for public health and integrity of the ecosystem, more regulatory controls and stricter standards will be promulgated. Table 7 shows a revised draft of concentration limits in an ambient air quality standard [116].

6. Discussion and conclusion

Ambient air samples and stack samples as pollution sources, like other environmental samples, are very complex in nature and composition. They usually consist of hundreds of trace potential carcinogens, such as PAHs, heavy metals and various organic components of different polarities. Various types of chromatography, including coupled techniques (e.g., HRGC–MS, HPLC–FT-IR), have been shown to be efficient for detection and quantification as discussed, and have wide applications in the characterization and determination of these pollutants in China, as briefly reviewed in this paper.

The analytical data obtained are usually the requisite basis for many environmental studies. They indicate not only the environmental quality, but also the transformation, transport and fate of pollutants. Further, they suggest directions for solving problems and the possible impact on the ecosystem and human health. The quality of analytical data affects to a significant extent the success of various types of pollution studies undertaken.

Air pollution is closely related to energy consumption. Traditional coal combustion results in serious pollution problems in China. Modernization also increases vehicle emissions. Great efforts have been made to keep contamination levels of the ambient atmosphere stable or lower, in spite of extremely rapid progress in

Table 7
Concentration limts in "Ambient Air Quality Standard", revision draft [116]

Pollutant	Sampling time[a]	Concentration limit (mg/STP m³)			
		Class 1	Class 2	Class 3	Remarks
Sulfur dioxide	Yearly av.	0.02	0.06	0.10	
	Daily av.	0.05	0.15	0.25	[b]
	Hourly av.	0.15	0.50	0.70	
TSP	Yearly av.	0.10	0.20	0.30	
	Daily av.	0.15	0.30	0.50	[b]
Inhalable particulates	Yearly av.	0.04	0.10	0.15	mg/m³
	Daily av.	0.05	0.15	0.25	[b]
Nitrogen oxide	Yearly av.	0.05	0.05	0.10	
	Daily av.	0.10	0.10[b]	0.15[b]	
	Hourly av.	0.15	0.15	0.30	
Nitrogen dioxide	Yearly av.	0.04	0.04	0.08	
	Daily av.	0.08	0.08	0.12	
	Hourly av.	0.12	0.12	0.24	
Carbon monoxide	Daily av.	4.00	4.00	6.00	[b]
	Hourly av.	10.00	10.00	20.00	
Ozone	Hourly av.	0.12	0.16	0.20	[b]
Lead	Season av.		1.50		
	Yearly av.		1.00		
Benzo[a]pyrene	Daily av.		0.01		μg/m³
Fluoride	Daily av.		7		
	Hourly av.		20		

[a] av. = Average.
[b] Same value as those in GB 3095-82 "Ambient Air Quality Standards" (analytical standard method in China) now used.

the national economy and the continuous increase in energy consumption. A network of over 1000 air monitoring stations has been established. New methods of analyses and standards will be developed. Based on the results of scientific investigations, including chromatographic studies, measures are being taken to reduce pollution, such as coal gasification, use of natural gas, centralization of power plants and some interim measures, e.g., using coal briquettes. China is also participating in many projects of global interest such as studies of acid rain, ozone depletion and climatic changes.

China is now developing its own environmental protection industry. Various materials, equipment and instruments are produced in either local or internationally collaborating factories to support environmental studies. These will greatly speed up the progress of environmental science in China.

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