Monitoring of potential carcinogenic polycyclic aromatic compounds in the emission from coal combustion*

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Abstract — A comprehensive summary for the study on the monitoring of potential carcinogenic polycyclic aromatic compounds (PACs) in the emission of coal combustion is presented in this paper. Some PACs in the stack gases of coal-fired boilers have been determined with a procedure which consists of isokinetic stack sampling, extraction, preseparation and some instrumental analysis steps such as gas chromatography/mass spectrometry (GC/MS), high performance liquid chromatography (HPLC), room temperature phosphorimetry (RTP) and synchronous fluorescence spectroscopy (SFS) and so on. The results indicate that the air pollution of PACs in China are related closely to the coal combustion.

Keywords: polycyclic aromatic compounds; coal combustion; carcinogenic analysis.

1 Introduction

CO_2, NO_x, SO_2, coal flyash and carcinogenic PACs are emitted from coal combustion sources. CO_2 and NO_x are considered to be the most important greenhouse gases, SO_2 is believed to be the main cause of acid rain, so they have been deeply concerned as global or regional environmental issues. However, to the coal flyash and carcinogenic PACs, close attention should also be paid because the air pollution by the latter is detrimental to human health. In fact, it has been widely accepted that these carcinogenic PACs are responsible for some respiratory organs diseases and cancers. Coal is the important energy resource now and for the long time base in China. The coal combustion impacts the air quality especially in the northern cities of China in winter. So it is important and necessary to study the monitoring and evaluation of air pollution by coal flash and PACs related with coal combustion.

2 Monitoring procedure for PACs in the emission from coal fired boilers

Monitoring of PACs in the stack emission is a challenging work. The procedure for monitoring of PACs in the emission of coal fired boilers consists of sampling and determining steps as shown in Fig. 1.
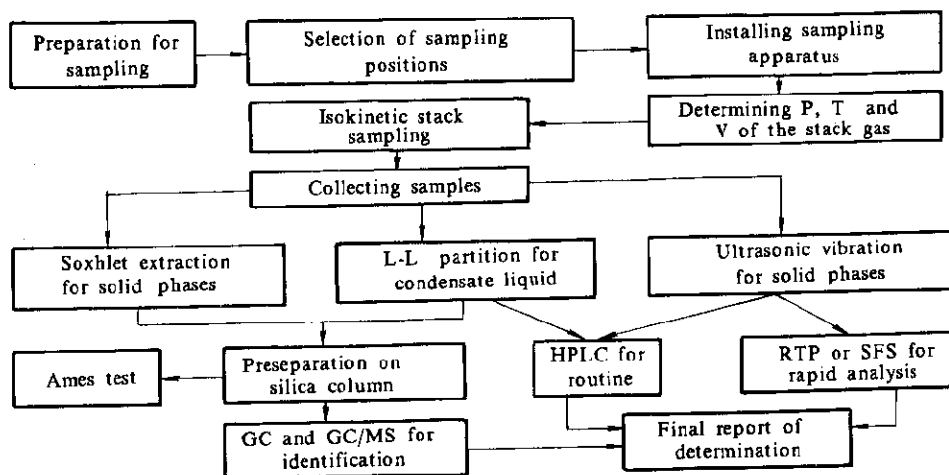
Fig. 1 Scheme of monitoring procedure for PACs from coal fired boilers

Two sampling systems, modified USEPA method 5 and method 17, have been developed for isokinetic stack sampling of coal fired boilers (Cui, 1989). The USEPA sampling method 5 (Fed. Regist, 1971) and method 17 (Fed. Regist, 1977) were originally established for the collection of particles from stacks. However, for the collection of organic pollutants in the stack emission filters alone are rendered ineffective with the marked temperature dependence of the relation between the vapor and particulate phases. The USEPA method 5 procedure was modified firstly by the Battle, Columbus, Laboratory with incorporating an adsorbent sampler between the filter and impingers and Tenax GC or Amberlite XAD resin was used for the adsorbent materials (Jones, 1976). Yao and Cui (Yao, 1987) used self-made apparatus which was similar with Battelle sampling system but with a condenser arrangement for stack water vapour between filter holder and adsorbent, and domestic GDX 101 resin was used as adsorbent materials. In addition, another similar system so called modified USEPA method 17, in which the filter holder was in the interior of stack

instead of in the outside of stack as in the method 5, was used for sampling in the cases of lower emission temperature, generally bellow 100 ℃ (Yao, 1987) .

Before the instrumental determination, the samples were pretreated by soxhlet extraction with dichloromethane or ultrasonic vibration with benzene for particulates (Yao, 1983), benzene/water liquid-liquid partition for steam condensate as well as preseparation by silica column chromatography or thin layer chromatography. All solvents were of analytical grade, distilled in glass before use, or of chromatographic grade.

A GC/MS system (JMSD model 300C), SE-30 glass capillary column (30m, 0.2 mmid) and temperature program from 70 ℃ to 220 ℃ at 4 ℃ /min. 70eV for MS, was used for identification of PACs in the coal fired boiler emissions.

A HPLC apparatus (Shimadzu model LC-3A) with Dupont Zorbax- ODS column (25cm, 4.6mm id), UV-2 ultraviolet and FL-510 fluorescence detectors, was used for determination of 15 PACs (naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, fluoranthane, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo (e) pyrene, benzo (a) pyrene, dibenzo (a, h) anthracene, benzo (ghi) perylene and coronene).

For rapid determination of pyrene and BaP, the RTP and SFS signals were obtained with a Perkin-Elmer luminescence spectrometer (model LS-5). For total RTP measurements of pyrene, a delay time, Td, of 0.05ms and a gate time, *Tg*, of 9 ms were used. Xinhua 201 quantitaive analysis filter paper was selected out of ten different species for solid substrate and impregnated with ethanol/water solution of TIAc/Pb(Ac), (1:1 mol) prior to spotting the analyze solution (Tuan Vo-Dihn, 1984). For the rapid analysis of BaP by SFS technique, a constant wavelength difference of excitation (Ex) and emission (Em) 10 nm was used, and Em scanning was from 360 to 450 nm (Tuan, 1982; Lloyd, 1977).

3   Results and discussions

3.1   Determining methodology

The monitoring procedure was designed for studying systematically PACs from the emission of coal combustion. Each item of the scheme is just suitable for certain research purpose and each instrumental method has good points and disadvantages. So, some items could be adopted according to research requirements. For example, capillary GC/MS is satisfied in separation for complex mixtures and can supply MS information for each compound for qualitative identification. Comparatively, HPLC neither has good enough resolving power for some uneasily separated pairs such as benz (a) anthracene/chrysene and benzo (k) fluoranthene/benzo (a) pyrene and so on,

nor can give characteristics ultraviolet or fluorescence stop-scanning spectra of each HPLC peak for qualitative confirmation. However, on the other hand, the selective detectors-ultraviolet, especially fluorescence, can give much higher sensitivity than MS (so far as to other detectors such as FID) for capillary GC. In fact the detection limits of ultraviolet or fluorescence for PACs, frequently extending to $10^{-11}-10^{-12}$ gram (Yao, 1983), are at least one or even two order of magnitude lower than those in MS detection. Furthermore, remarkable shorter time is need for HPLC separation compared with capillary GC and in many cases, only some PACs of important environmental significance, for example BaP having significant carcinogenic character and being often regarded as an indicator of PAC pollution, are required to be determined. So HPLC is, in general, more likely to be selected for routine analysis of special PACs and the precision is satisfied for reliable quantitation of BaP in fairly complex sample matrix such as coal flash, air particles (Fig. 2).

Solid surface RTP has recently been developed as an analytical technique for quantitative determination of a variety of organic compounds. Vo-Dinh had given an extensive survey of RTP (Vo-Dinh, 1984). Since the main advantage of RTP is its simplicity and fast speed, we have used this technique to determine pyrene in coal-fired flash as a rapid measuring technique. The domestic filter paper used is unexpensive and commercially available, while the corresponding sample preparation is also simple and rapid. The sensitivity of RTP can be drastically increased by the external heavy-atom effect. TIAc and Pb(Ac)$_2$ (1:1 mol) were used as the heavy atom agents because high enhancement factors have been found with Tl$^+$ and Pb^{2+} for PAHs (Abbott, 1985). In our test, the limits of detection in about 0.2ng for pyrene and 2 ng for
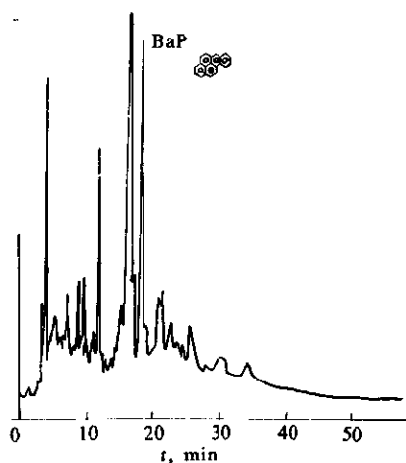

Fig. 2 HPLC chromatogram of routine measuring for BaP in the coal flyash from a tea boiler stack in Beijing
Column: Dupont Zorbax ODS, 25 cm-4.6mm id; detector: fluorescence Ex/Em: 296/410; content of BaP is 1.5 ng and the C.V% is 2.6% for eight runs

BaP have been achieved. What should be mentioned here is higher power source, for example 150 W Xe lamp is required for improving the sensitivity and the red sensitive photomultipliers should be used for BaP because its RTP signal is at 698 nm. SFS signal has been examined and about 0.4 ng detection limit has been obtained.

So SFS may be considered as an acceptable rapid measuring technique. The selection of Ex and Em is crucial to eliminate the error caused by BKF interference to ignorable.

3.2 Pollution evaluation

The results of bioassay Ames tests showed that the benzene extracting matter of coal-fired boiler effluent samples are mutagenic activity (Yao, 1991). About 110 organic compounds, including polyaromatic hydrocarbons (PAHs), alkyl-PAHs, sulfur or oxygen containing heterocyclic compounds in the medium polar fraction and alkanes, alkenes in non-polar fraction of preseparation with silica column chromatography, have been identified with GC/MS (Table 1).

Table 1 PACs identified by GC/MS in the emission sample from coal fired tea boiler in Beijing

Peak No.	Name	Molecular formula (weight)
1	Benzene	C_6H_6 (78)
2	Phenol	C_6H_6O (94)
3	Methylphenol	C_7H_8O (108)
4	Ethyldimethylbenzene	$C_{10}H_{14}$ (134)
5	Naphthalene	$C_{10}H_8$ (128)
6	2-Methylnaphthalene	$C_{11}H_{10}$ (142)
7	1-Methylnaphthalene	$C_{11}H_{10}$ (142)
8	Unknown	
9	Biphenyl	$C_{12}H_{10}$ (154)
10	2-Ethylnaphthalene	$C_{12}H_{12}$ (156)
11	Dimethylnaphthalene	$C_{12}H_{12}$ (156)
12	Dimethylnaphthalene	$C_{12}H_{12}$ (156)
13	Acenaphthylene	$C_{12}H_8$ (152)
14	Ethylnaphthalene	$C_{12}H_{12}$ (156)
15	Acenaphthene	$C_{12}H_{10}$ (154)
16	Unknown	
17	Methylbiphenyl	$C_{13}H_{12}$ (168)
18	Methylbiphenyl	$C_{13}H_{12}$ (168)
19	Unknown	$C_{11}H_7N$ (153)
20	Dibenzofuran	$C_{12}H_8O$ (168)
21	Trimethylnaphthalene	$C_{13}H_{14}$ (170)
22	Trimethylnaphthalene	$C_{13}H_{14}$ (170)
23	Trimethylnaphthalene	$C_{13}H_{14}$ (170)
24	Fluorene	$C_{13}H_{10}$ (166)
25	Trimethylnaphthalene	$C_{13}H_{14}$ (170)
26	9-Methylfluorene	$C_{13}H_{10}$ (180)
27	Trimethylnaphthalene	$C_{13}H_{14}$ (170)

Table 1 (Continued)

Peak No.	Name	Molecular formula (weight)
28	Dimethylbiphenyl	$C_{14}H_{14}$ (182)
29	Methylfluorene	$C_{14}H_{12}$ (180)
30	Methyldibenzofuran	$C_{13}H_{10}O$ (182)
31	Methyldibenzofuran	$C_{13}H_{10}O$ (182)
32	9H-Xanthene	$C_{13}H_{10}O$ (182)
33	Phenylbenzoate	$C_{13}H_{10}O_2$ (198)
34	Methoxybiphenyl	$C_{13}H_{12}O$ (184)
35	Methylfluorene	$C_{14}H_{12}$ (180)
36	Methylfluorene	$C_{14}H_{12}$ (180)
37	9-Fluorenone	$C_{13}H_8O$ (180)
38	Dibenzothiophene	$C_{12}H_8S$ (184)
39	Dimethylfluorene	$C_{15}H_{14}$ (194)
40	Phenanthrene	$C_{14}H_{10}$ (178)
41	Anthracene	$C_{14}H_{10}$ (178)
42	Anthranone	$C_{14}H_{10}O$ (194)
43	Anthraquinol	$C_{14}H_{10}O_2$ (210)
44	Phenylanphthalene	$C_{16}H_{12}$ (204)
45	Methyldibenzothiophene	$C_{13}H_{10}S$ (198)
46	Unknown	$C_{14}H_{10}O_2$ (210)
47	Methylphenanthrene	$C_{15}H_{12}$ (192)
48	4H-cyclopenta(def) phenanthrene	$C_{16}H_{10}$ (190)
49	Methylphenanthrene	$C_{15}H_{12}$ (192)
50	9,10-Anthraquinone	$C_{14}H_8O_2$ (208)
51	Phenylnaphthalene	$C_{16}H_{12}$ (204)
52	Methyl-methylpenta- decanoate	$C_{17}H_{34}O_2$ (270)
53	Dimethylphenanthrene	$C_{16}H_{14}$ (206)
54	Dimethylphenanthrene	$C_{16}H_{14}$ (206)
55	4H.5H-pyrene	$C_{16}H_{12}$ (204)
56	Fluoranthene	$C_{16}H_{10}$ (202)
57	Acephenanthrylene	$C_{16}H_{10}$ (202)
58	Pyrene	$C_{16}H_{10}$ (202)
59	Ethyl-$C_{15}H_9$*	$C_{17}H_{14}$ (218)
60	Ethyl-$C_{15}H_9$*	$C_{17}H_{14}$ (218)
61	Ethyl-$C_{15}H_9$* *4H-cyclopenta(def)phen anthrene	$C_{17}H_{14}$ (218)
62	Terphenyl	$C_{18}H_{14}$ (230)
63	Benzo(a)fluorene	$C_{17}H_{12}$ (216)
64	Benzo(b)fluorene	$C_{17}H_{12}$ (216)

Table 1 (Continued)

Peak No.	Name	Molecular formula (weight)
65	Benzo(c)fluorene	$C_{17}H_{12}$ (216)
66	Methylpyrene	$C_{17}H_{12}$ (216)
67	Dimethylpyrene/or Dimethylfluoranthene	$C_{17}H_{12}$ (216)
68	Benzo(b)naphtho(2.1-d) thiophene	$C_{16}H_{10}S$ (234)
69	Benzo(ghi)fluoranthene	$C_{18}H_{10}$ (226)
70	Benzo(b)nathpho(1.2-d) thiophene	$C_{16}H_{10}S$ (234)
71	Chrysene	$C_{18}H_{12}$ (228)
72	Benzo(a)anthracene	$C_{18}H_{12}$ (228)
73	Triphenylene	$C_{18}H_{12}$ (228)
74	Methylchrysene	$C_{19}H_{14}$ (242)
75	Methylbenz(a)anthrancene	$C_{19}H_{14}$ (242)
76	Methyltriphenylene	$C_{19}H_{14}$ (242)
77	Benzo(j)fluoranthene	$C_{20}H_{12}$ (252)
78	Benzo(k)fluoranthene	$C_{20}H_{12}$ (252)
89	Benzo(e)pyrene	$C_{20}H_{12}$ (252)
80	Benzo(a)pyrene	$C_{20}H_{12}$ (252)

BaP has been believed to be carcinogenic and certainly present in any PAC emissions from various combustion sources. So it is generally regarded as an indicator of PAC pollution. The emission coefficients of BaP are quite different for varieties of coal fired boilers. In general, smaller size boilers for example tea boilers and coal fired household stoves emit much more BaP per unit weight of coal burned than larger boilers do (Table 2). Other PACs are also in the same case and more details

Table 2   Emission coefficients of BaP from varities of coal fired boilers and stoves

(Unit: mg/N ton coal)

Power plant, 35t/h	Industry, 10t/h	Industry, 4t/h	Industry, 2t/h	Tea boiler, 0.2 t/h	Household stoves
0.2 — 0.4	0 .2—0.35	2.1—9.7	1.4—5.9	20—677	350—20000
0.14—0.16 ($\mu g/nm^3$)		0.3—0.8	0.2—0.4	1.7—96	

of evaluation will be given in future publications. From Table 3 (about the air pollution of BaP in some cities in China), we can see that the BaP concentrations in air particulates in winter are much higher than those in other seasons. These data may indicate that the air pollution by BaP is related closely to coal burning. In fact, BaP as well as other PACs accompanied with flyash particulates, besides SO_2 and NO_2, are also main pollutants by the coal combustion.

Table 3 BaP contents of air in some cities in China

(Unit: ng/m^3)

Cities	Summer to winter		Cities	Summer to winter	
Beijing	5.7 − 77	(urban area)	Shanghai	2.9 − 58	(urban area)
	1.0 − 14	(clean area)		12 − 42	(industry area)
Tianjin	6.8 − 260	(urban area)		0.7	(clean area)
Shenyang	4.6 − 180	(urban area)	Hangzhou	4.2 − 14	(urban area)
Lanzhou	8.5 − 42	(industry area)	Nanjing	7.3	(urban area)
Taiyuan	11 − 240	(urban area)		1.5	(clean area)
	17 − 367	(industry area)	Fuzhou	4.0	(urban area)
	7.6 − 13	(clean area)			
Harbin	26 − 130	(urban area)			

Data source: Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences

The main composition of the primary energy in China is and will, for the foreseeable future, be based coal. Only very small part of the coal converted in the secondary energy source including electricity and coke while the remaining portion is used in the form of direct combustion by various boilers and stoves. Most of these boilers and stoves work in low efficiency and high pollutant emission. So it can be estimated the air pollution of PACs will be fairly serious for a quite long time. To control and rebate the air pollution resulted from coal combustion, some measures may be benefitial and should be taken, for example to pursuing the policy of energy conservation, reduce the per unit energy consumption, develop new coal-fired technique such as briquettes in replace of raw coal, develop city coal gasification system and large scale energy plants in order to improve energy efficiency and reduce the number of smaller boilers and household stoves.

References

Abbott DW, Vo-Dinh T. Anal Chem, 1985; 57:41

Cui Wenxuan. Environmental Chemistry, 1989; 8(2):55

Federal Register. 1971; 36(247):24876

Federal Register. 1976; 41(11):23076

Gregor AJ, Brian AJ. International Lab, 1984, Jan/Feb:10

Jones RW, Giammar RD. Environ Sci Technol, 1976; 10:806

Lloyd JBF. Anal Chem, 1977; 49(12):1710

Tuan Vo-Dinh. Applied Spectra, 1982, 36(5):576

Tuan Vo-Dinh. Room temperature phosphorimetry for chemical analysis. New York: John Willey & Sons, 1984

Yao Weixi. Environmental Sciences, 1982;3(1):18

Yao Weixi. Environmental Sciences, 1983; 2(2):22

Yao Weixi, Cui Wenxuan, Xu Xiaobai. Environmental Science, 1987;8(3):86

Yao Weixi, Cui Wenxuan, Xu Xiaobai. Environmental Science, 1991; 12(2):9