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Determination of polycyclic aromatic hydrocarbons with supercritical fluid extraction and chromatography (SFE/SFC) *

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Abstract—This paper showed the on-line supercritical fluid extraction and supercritical fluid chromatography (SFE/SFC), which have been used for the extraction and analysis of PAHs in the air particulates nearby the coke oven and the traffic island. This method combined the extraction, separation and analysis into one operating procedure. It saves a lot of operation time, and removes the concentrating step of extracts before doing the analysis. This method is simple, rapid and accurate. The average recovery of 16 kinds of PAHs is nearly 90% and relative standard deviation is 1.9%—6.0%.

Keywords: supercritical fluid extraction (SFE); supercritical fluid chromatography (SFC); polycyclic aromatic hydrocarbons (PAHs); determination; separation.

1 Introduction

Supercritical fluid chromatography (SFC) has the advantages of both GC and HPLC. It has been widely used as an analytical tool for the separation of relatively high volatile, thermally unstable and high molecular weight solutes. Supercritical fluid extraction (SFE) can save a lot of time than a conventional Soxhlet extracted method (SFE: 0.5h and Soxhlet: 8—24h), in the last ten years the SFE/SFC has being developed very quickly (Lee, 1990).

Polycyclic aromatic hydrocarbons (PAHs) are a kind of environmental pollutants widely existed in natural world. The USEPA put forward the 16 priority monitoring PAHs including some carcinogenic compounds (Lee, 1990; Paschke, 1992). This paper reported the determination by on-line SFE/SFC. The advantages are trace analytic capability, sample preparation with minimal contamination, high reproducibility and so on (Jinno, 1992; Chester, 1992). When carbon dioxide is used as supercritical fluid, the operation is low cost and low toxicity without second pollution. During the SFE/SFC is run, it only consumes about 80 ml CO_2 each time. 16 kinds of PAHs can be separated better after the extraction. Their recovery is higher.

2 Experimental

2.1 Chemicals and reagents

All solvents are commercially available from chemical suppliers, they are GC or spectral grade. Stock solutions of PAHs standards are prepared by dissolving weighed amounts of the hydrocarbons in haxen/benzene (90/10, v/v). Standard PAHs solutions used to determine calibration graphs are prepared by dilution with methylene chloride.

2.2 Apparatus

The experimental on - line SFE/SFC system is shown in Fig. 1. It is constructed from SUPREX mode MPS/225 (Suprex corporation, PA, USA). Packed column: Nocleosil ODS: 5μm, 10cm × 1mm I. D. (Keystone Scientific Inc.). Column oven: 100℃, CO_2: 99.995%, flow rate 50 ml/min, at 100℃, 100 atm; air: 1000 ml/min; H_2: 600 ml/min; flame ionization detection (FID): 350℃; Captive trap: - 40℃ (SFE)/180℃ (SFC).

2.3 Procedure

The SFE/SFC behavior of analytical sample is first determined by using standard PAHs mixture solutions. These samples collected nearby the coke oven and the traffic island are put into the extracting vessel. The pressure program and the results of separation are shown in Table 1 and Fig. 1, respectively.

Table 1 Pressure program of SFE/SFC system

Pump mode	System pressure, atm	CO_2 density, g/cm³	Stage time, min	4 - port elector	10 port switching valve
Init	100	0.191	–	Position 2#	Inject
Step	100	0.191	1.0	Position 3#	Load
Ramp	100—360	0.191—0.728	1.5	Position 3#	Load
Step	360	0.728	15.0	Position 3#	Load
Ramp	360—100	0.728—0.191	1.5	Position 3#	Load
Step	100	0.191	5.0	Position 4#	Inject
Ramp	100—450	0.191—0.793	17.5	Position 4#	Inject
Step	450	0.793	5.0	Position 4#	Inject
Ramp	450—100	0.793—0.191	2.0	Position 4#	Inject
Step	100	0.191	1.0	Position 4#	Inject

3 Results and discussion

The SFC graphs of the air particulate samples from the coke oven and the standard samples are more similar, but there are more peaks in air particulate samples (Fig. 2).

The on - line SFE/SFC method is simple, rapid and accurate: when pressure program is automatically run on pre - set program, 16 kinds of PAHs can be separated better after doing the extraction.

The recovery is determinated by using a stock solution of PAHs standards and the fibreglass paper as a carrier. This operation needs to be done seven times. The average recovery of 16 kinds of PAHs is nearly 90% and relative standard deviation was 1.9%—6.0%.

The PAHs from air particulates samples nearby the coke oven is about 10 times than it nearby the traffic island of the city (Fig. 3 and Table 2).

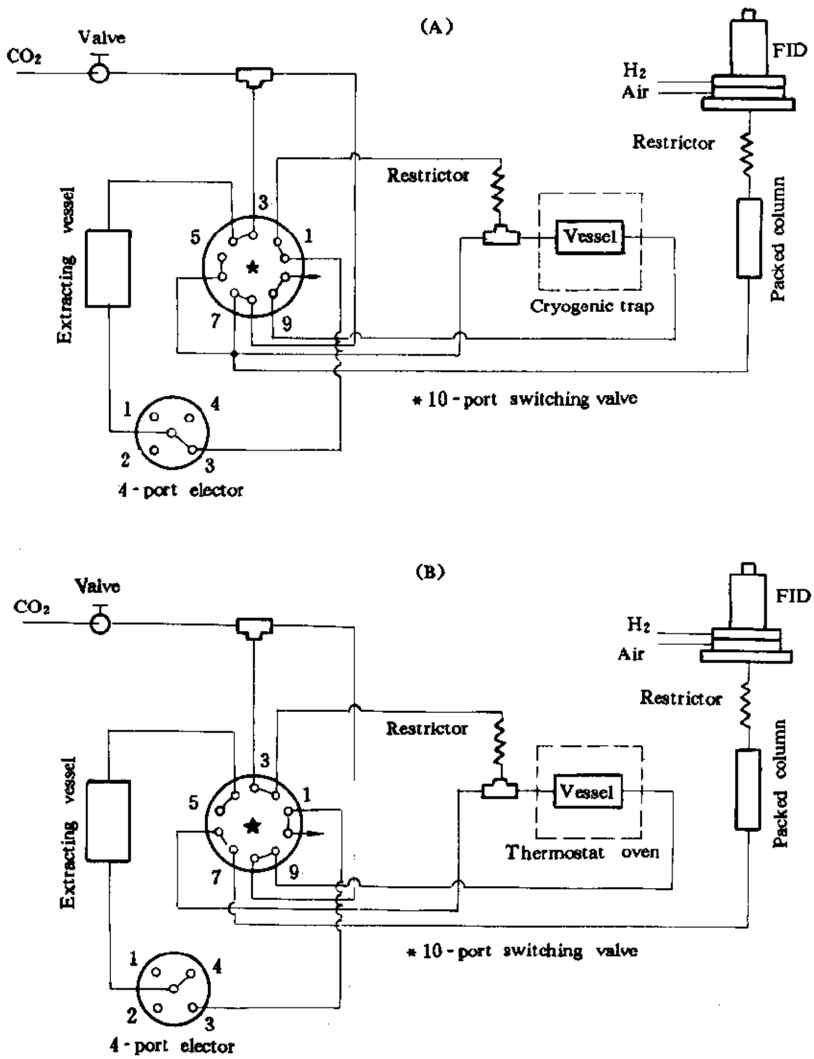

Fig. 1 Schematic diagram of the on - line SFE/SFC system

A: SFE position B: SFC position

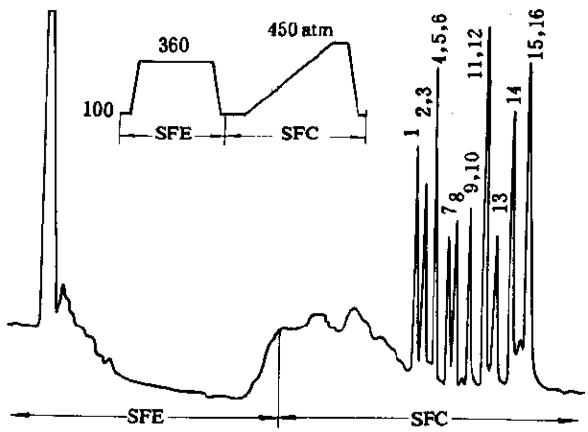

Fig. 2 The separation of PAHs with on line SFE/SFC system

1. Naphthalene(NA) 2. Acenaphthylene(AY) 3. Acenaphthene(AE) 4. Fluorene(FL)
5. Phenanthrene(PH) 6. Anthracene(AN) 7. Fluoranthene(FA) 8. Phyene(PY)
9. Benz(a)anthracene(BaA) 10. Chrysene(CH) 11. Benzo(b)fluoranthene(BbF)
12. Benzo(k)fluoranthene (BkF) 13. Benzo(a)pyrene(BaP) 14. Dibenz(a,h)anthracene(DBA)
15. Benzo(ghi)perylene(BghiPe) 16. Indeno(1,2,3-cd)pyrene(IcdP)

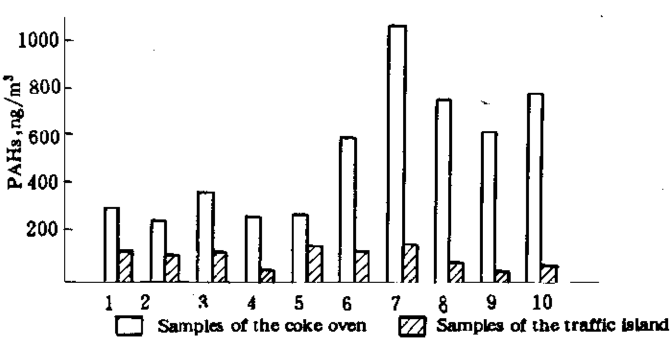

Fig. 3 Comparison of PAHs from air particulate samples

In general, the conventional Soxhlet extraction needs 8—24 hours for extracting one sample, but the SFE only consumes 0.5 hour. It saves many operating time.

The on-line SFE/SFC method combines the extraction, the severation and the analysis into one operating procedure. It removes the concentrating step of the extracts before doing the analysis. It may not consume any organic solvents and the accuracy is increased. These results by the on-line SFE/SFC in Table 2 are similar to the results by other methods (Zhong, 1980; Hong, 1983).

When carbon dioxide is used as a supercritical fluid. It is easy to get higher purity, the whole operation is low cost and low toxicity without second pollution. During the SFE/SFC is run, it only consumes about 80 ml CO_2 each time. By the way, it will get the best separations of 16 kinds of PAHs if the capillary column is instead of the packed column in the SFC system (Pago, 1993; Langenfeld, 1993).

Table 2 PAHs of the air particulate samples by SFE/SFC

No.	PAHs	The nearby coke oven, ng/m^3	The nearby traffic island, ng/m^3	No.	PAHs	The nearby coke oven, ng/m^3	The nearby traffic island, ng/m^3
1	NA	143	52	2	AY+AE	116	43
3	FL+PH+AN	179	49	4	FA	126	14
5	PY	135	64	6	BaA+CH	246	55
7	BbF+BkF	538	70	8	Bap	373	34
9	DBA	312	14	10	BghiPe+IcdP	386	25

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References

Chester TL, Pinkston JD, Raynie DE. Analytical Chemistry, 1992; 64(12):153R

Hong Weixiong, Yang Xiaobei. Huanjing Kexue, 1983; 4(5):43

Jinno K. Hyphenated techniques in supercritical fluid chromatography and extraction. Netherlands: Elsevier Science Publishers, 1992

Langenfeld JJ, Hawthorne SB, Miller DJ, Pawliszyn J. Analytical Chemistry, 1993; 65:338

Lee ML, Markides KE. Analytical supercritical fluid chromatography and extraction. Chromatography Conferences, Inc. Provo, Utah, 1990

Pago SH, Yun Hao, Lee ML, Goates SR. Analytical Chemistry, 1993; 65:1493

Paschke T, Mawthorne SB, Miller DJ. Journal of Chromatography, 1992; 609:333

Zhong Jinxian, Li Honghai, Zhang Fengzhu. Huanjing Kexue, 1980; 1(1):1

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