

Simple Fluorimetric Determination of Benzo[a]pyrene in Cigarette Smoke without Preseparation Procedure

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Abstract: Constant-energy synchronous fluorimetry was used for the identification of benzo[a]pyrene in mixtures with a detection limit of 1.34 nmol/L. The recovery experiments in cigarette smoke samples have also obtained satisfactory results of 99.1-103.5% for benzo[a]pyrene.

Keywords: Banzo[a]pyrene, synchronous fluorescence scan, polycyclic aromatic hydrocarbon mixtures, cigarette smoke.

Polycyclic aromatic hydrocarbons (PAHs) are important environmental pollutions originating from a wide variety of natural and anthropogenic sources. Benzo[a]pyrene is frequently sought as an indicator of the presence of other PAHs. Fluorescence spectrometry serves as a good technique to analyze PAHs with high sensitivity. However, this technique is unfavorable for the analysis of benzo[a]pyrene in multi-component PAHs because of spectral overlap. This complication can be simplified by using special techniques, such as synchronous fluorescence spectrometry (SFS)¹. Constant-energy synchronous fluorescence spectrometry (CESFS)^{2,3}, one important embranchment, has been successfully applied to benzo[a]pyrene identification in PAH mixture^{4,5}. But, The typical clean-up procedures are based on multi-step separations⁶⁻¹¹ due to severe spectral overlap from other PAHs.

The object of this investigate was to develop a simple, fast and selective method suitable for the identification of benzo[a]pyrene in PAH mixtures and cigarette smoke by constant-energy synchronous fluorescence spectrometry without preseparation procedure.

Experimental

All spectra were obtained on a laboratory-constructed, microcomputer-controlled spectrofluorimeter equipped with a 350W xenon lamp. Both excitation and emission slits were set at 5 nm and scan speed 240 nm/min. Benz[2,3]fluorene, fluoranthbene, perylene, pyrene, benzo[a]pyrene and phenanthrene were obtained from Sigma-Aldrich.

Collect the ash after burning the cigarette (Fujian Brand) and extract PAHs with

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cyclohexane. The extraction was repeated thrice. The solvent was then evaporated by gently heating and the residue dissolved in methanol for further analysis.

Results and Discussion

As seen from **Figure 1**, the fluorescence emission spectrum of benzo[a]pyrene shows three different vibrational bands. The maximum excitation/emission wavelength is at 380/404 nm. Other PAHs such as perylene also contribute in this spectral region, which shows a spectral band at 434 nm.

Synchronous fluorescence scanning (SFS) gives a narrower and simpler spectrum compared to the conventional excitation/emission spectrum. Therefore it is more effective for distinguishing overlapping spectra. The parameters needed to optimize in SFS are ‘wavenumber interval ($\Delta\bar{\nu}$)’ and ‘synchronous fluorescence maximum (λ_{SFS}^{max})’. The synchronous fluorescence spectra were recorded in the range 250~500 nm at different wavenumber intervals (**Table 1**).

Figure 1 Fluorescence emission spectra of benzo[a]pyrene (---), 6-component PAH mixture (---) and cigarette smoke (—) $\lambda_{ex} = 380$ nm

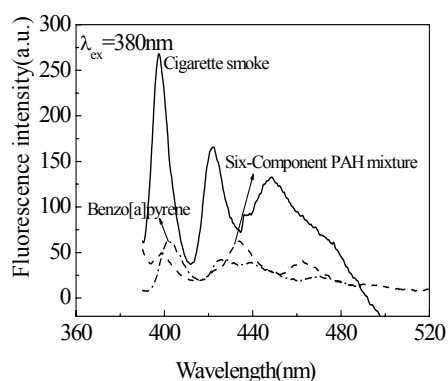
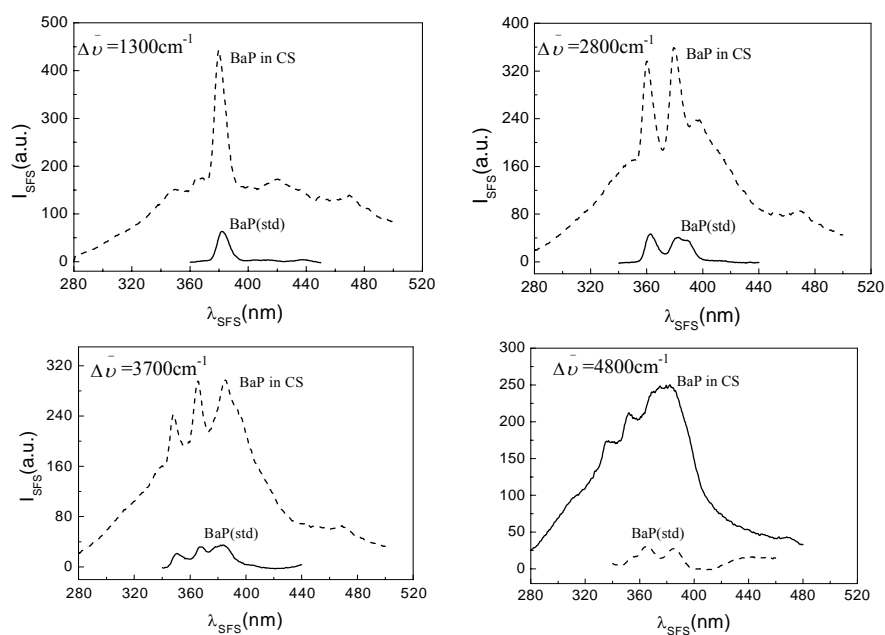


Table 1 The variation of synchronous fluorescence maximum (λ_{SFS}^{max}) with wavenumber interval ($\Delta\bar{\nu}$) for benzo[a]pyrene (BaP), fluoranthrene (Flt), perylene (per), pyrene (pyr), phenanthrene (phen), benz[2,3]fluorene (2,3-BF)

$\Delta\bar{\nu}$ (cm^{-1})	λ_{SFS}^{max} (nm)					
	BaP	Flt	Per	Pyr	Phen	2,3-BF
1300	380		438			321
2800	362		413	335		308
3700	367		402	337		315
4800	354	360	384	335	298	303
7400		344				
7800					291	
Blue shift (nm)	28	16	54			18

Figure 2 Synchronous fluorescence spectra of benzo[a]pyrene in standard (std) methanol solution and in cigarette smoke (CS) in $\Delta\bar{\nu}=1300, 2800, 3700, 4800\text{ cm}^{-1}$



Except for pyrene and phenanthrene, the other PAHs gave a blue shift in λ_{SFS}^{\max} with an increase in $\Delta\bar{\nu}$. The blue shift of the maximum absorption peaks of perylene, benzo[a]pyrene, benz[2,3]fluorene and fluoranthrene were 54, 28, 18, 16 nm, respectively.

In order to identify effectively benzo[a]pyrene in PAH mixtures, the synchronous fluorescence spectra of the standard methanol solution of benzo[a]pyrene and cigarette smoke were investigated at $\Delta\bar{\nu}$ of 1300, 2800, 3700 and 4800 cm^{-1} , respectively (**Figure 2**). It was shown that the $\Delta\bar{\nu}$ of 1300 cm^{-1} was the most ideal condition, because of its narrow single spectrum and highest selectivity.

In order to confirm the validity of the proposed method, we performed the determination of real samples. As seen from **Figure 3a**, the characteristic peak of benzo[a]pyrene at 380 nm can be observed clearly in cigarette smoke (CS) and PAH mixture.

For the estimation of benzo[a]pyrene, a calibration graph (**Figure 3b**) was constructed by measuring the synchronous fluorescence intensity at λ_{SFS}^{\max} and $\Delta\bar{\nu}=1300\text{ cm}^{-1}$ at various benzo[a]pyrene concentrations. The linear equation was $y = -3.43x + 0.96$ (r of 0.9992) and the detection limit of 1.34 nmol/L was obtained. The concentration of benzo[a]pyrene in cigarette smoke after three individual measurements was 36.4 nmol/L.

The reported value was 35.5 nmol/L⁵.

The method has also been applied to the recovery determination of benzo[a]pyrene in cigarette smoke samples and the results were satisfactory (**Table 2**).

Figure 3 (a) Comparison of synchronous fluorescence spectra of 80 nmol/L standard methanol solution of benzo[a]pyrene (std), in six-component PAH mixture (480 nmol/L totally) and cigarette smoke (CS); (b) Calibration graph the standard methanol solution of benzo[a]pyrene (std). $\Delta\nu = 1300\text{ cm}^{-1}$

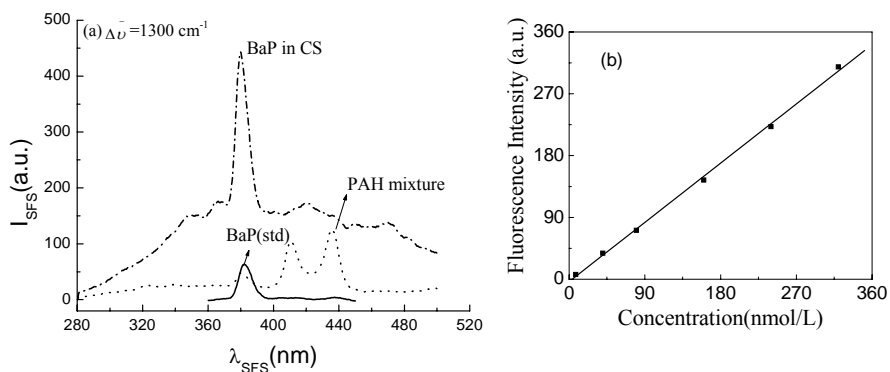


Table 2 Recoveries of benzo[a]pyrene in cigarette smoke

No.	Amount present (nmol/L)	Amount added (nmol/L)	Total amount found (nmol/L)	Recoveries (%)
1	36.4	39.7	77.0	101.2
2	36.4	47.6	86.9	103.5
3	36.4	59.5	97.6	101.8
4	36.4	71.4	109.1	101.2
5	36.4	79.4	119.4	103.1
6	36.4	87.3	122.6	99.1

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