Asian Journal of Chemistry; Vol. 25, No. 16 (2013), 8994-8996

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14959

Determination of Phenanthrene and Naphthalene in the Loess Area by Synchronous Fluorimetry

HUIYING ZHAN[1,*] and YUFENG JIANG[2]

[1]Chemical Engineering College, Gansu Lianhe University, Lanzhou 730000, P.R. China
[2]Department of Environmental Engineering, Lanzhou Railway University, Lanzhou 730070, P.R. China

*Corresponding author: E-mail: hyzhan2012@163.com

(*Received*: 12 December 2012; *Accepted*: 13 September 2013) AJC-14099

The synchronous flourimetry has been established for simultaneous determination of phenanthrene and naphthalene in the mixed liquor of these two components. The linear ranges of phenanthrene and naphthalene are 0.001-0.101 and 0.0025-0.25 mg/L, their detection limits are 0.47 and 0.14 ng/mL and their relative standard deviations are 0.48 and 0.89 %, (n = 12), respectively. The method could be used to study the simultaneous determination of phenanthrene and naphthalene in the upper clear liquor after the sorption equilibrium of the loess soils on the mixed liquor. The results show that the sorption isotherm of natural loess soils on phenanthrene and naphthalene satisfies Freundlich-Equation and provided a fast and simple way to forecast and govern pollution of soils.

Key Words: Synchronous flourimetry, Phenanthrene, Naphthalene, Loess soils, Simultaneous determination.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) resulting from the producing process of petroleum and other industries, continuously discharged into atmosphere, water and soil and caused great damage to natural environment and human being. Due to the similarity of serval polycyclic aromatic hydrocarbons, the determination of each compound in a mixture by routine analysis methods can be a difficult problem.

Fluorescence spectroscopy is a useful technique for the analysis of aromatic hydrocarbons in the environment. Synchronous fluorimetry depicted the spectra by simultaneously scanning two monochromator wavelengths[1], which could simplify spectra, decrease superpositions, attenuate effects of scattered light and thus was easy to perform. Therefore, synchronous fluorimetry offers the advantages of greater sensitivity and selectivity for aromatic molecules in simultaneous determination of similar coumpounds than conventional ultra-violet absorption measurements[2]. In the present paper, study on simultaneous determination of phenanthrene (CR) and naphthalene (CA) in the loess area by synchronous fluorimetry was undertaken to investigate its possibility of rapid analysis. Some determination protocols were set up to observe the absorbing manner of phenanthrene and naphthalene mixtured solutions in loess. Samples were easy to perform without any filtration.

EXPERIMENTAL

RF-540 fluorescence spectrometer(Shimazu, Japan); THZ-C desktop constant temperature oscillator (Jiangshu Taichang experimental equipment factory, China); 800 electric centrifugal precipitator (Jiangxu Longgang medical treatment factory, China).

Phenanthrene was purchased from medicinal materials supply station, Academy of Military Medical Sciences; naphthalene was bought from No. 1 factory of Tianjin chemical reagent.

Phenanthrene stock solution (100 mg/L): Accurate 50 mg phenanthrene was dissolved by methanol until a constant volume of 500 mL.

Naphthalene stock solution (200 mg/mL): Accurate 100 mg was dissolved by methanol until a constant volume of 500 mL.

Natural loess: Natural loess was sampled from deep underground soil of Lanzhou Northwest Normal University, Ganshu without any pollution. Samples were air-dried and grinded, filtrated through 100 mesh sieves and stored for further application. Characteristics of the soils were as follows: cation exchange capacity was 3.21 cmol/kg; organic carbon content was 0.10 %; pH value (water/soil = 1) was 7.73; specific gravity was 1.38 g/cm^3; components of granules were 18.8 % of sand, 53.9 % of silt and 27.4 % of clay.

Determination methods: Certain stock solution was added to 50 mL volumetric flask and then deionized water was added until a constant volume of 50 mL. Samples were agitated and then transferred into a 1 cm quartz liquid pool. Synchronous fluorescence spectra was scanned at $\Delta\lambda$ of 30 nm and the resultant peak height of 333.5 and 366.5 nm were

used to assay the fluorescence intensity F of phenanthrene and naphthalene's synchronous fluorescence peak along with a blank test. Standard curve was plotted with ΔF against the concentration of phenanthrene and naphthalene.

Static absorption balance experiment: 5.0 g loess was added to 50 mL iodine volumetric flask and then series of phenanthrene and naphthalene solutions ranged from 0.25-2.5 mL were transferred into 50 mL volumetric flasks. The mixture solutions were diluted by 0.01 mol/L $CaCl_2$, transferred into iodine volumetric flasks and agitated at the THZ-C desktop constant temperature oscillator for 24 h until completely achieving absorption equilibrium (preliminary experiment suggested that 24 h was more than enough) with plug tightened. Supernatant was centrifuged at 4000 r/min for 15 min and then was undertaken to assay the phenanthrene and naphthalene concentration by synchronous fluorimetry. Results showed that the volatilization, photolysis and microbial degradation during the process of absorption could be neglected[3].

RESULTS AND DISCUSSION

Parameters selection: Corrected excitation and emission (5-20 nm) scans were made on the samples of interest to determine the general fluorescence characteristics of the hydrocarbons present. Synchronous scanning of the excitation and emission wavelengths indicated that when slit was lower than 10 nm, sensitivity was low and data was unstable with a poor reproducibility while slit over 10 nm was out of the scope of the measurement. Therefore, throughout this investigation, slits for the excitation and emission monochromators were 10 nm at a scanning and recording rate of 300 nm/min and 30 nm/cm, respectively with high plus.

Δλ selection: Δλ was defined as the wavelength interval between excitation wavelength (λ_{ex}) and emission wavelength (λ_{em}) and a paramount parameter of synchronous fluorescence spectra which played a critical role in the sensitivity and selectivity of the determination. The synchronous spectras of each solution were recorded at increments (Δλ) of 10, 20, 30, 40 and 50 nm in order to observe effects of Δλ on the peaks. According to the resolution situation and smooth level of peaks, Δλ = 30 nm was undertaken to assay phenanthrene and naphthalene mixture solutions[4,5].

Synchronous fluorescence spectra of phenanthrene and naphthalene: Excitation and emission spectra of phenanthrene and naphthalene are depicted in Figs. 1 and 2, respectively.

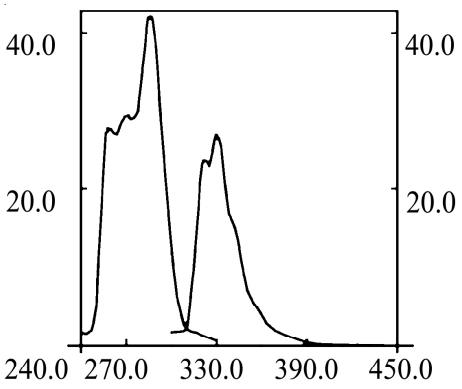

Fig. 1 Emission spectrum of phenanthrene

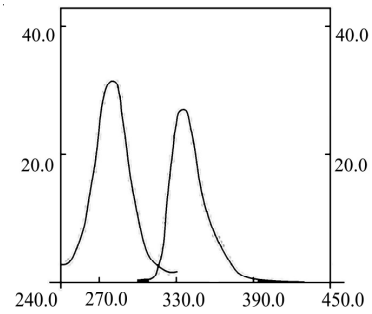

Fig. 2. Emission spectrum of naphthalene

As seen from figures, phenanthrene and naphthalene overlaped both in excitation and emission direction. It was tough to analysis the mixture of these two compounds by typical fluorescence spectroscopy. However, phenanthrene and naphthalene were well investigated by synchronous fluorescence spectroscopy, as seen from Fig. 3, synchronous fluorescence peaks of the two compounds were well distinguished without any mutual interference.

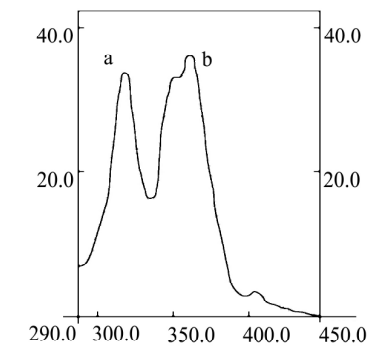

Fig. 3. Emission spectrum of (a) naphthalene (b) phenanthrene

Standard curve: Serial standard solutions of phenanthrene (CR) and naphthalene (CA) were prepared to plot the standard curve. A linear relationship between fluorescence intensity and phenanthrene and naphthalene concentration ranged at the scope of 0.001-0.101 and 0.0025-0.25 mg/L, respectively was obtained and its linear fitting equation and related parameters were as follows:

$$I_{fCR} = 3.387 + 30.22C, R_{CR} = 0.9991$$
$$I_{fCA} = 0.9681 + 192.1C, R_{CA} = 0.9996$$

where I_f represented fluorescence intensity, cm; C was concentration of components to be determined, μg/mL.

Precision and detection limit: 12 0.120 mg/L solutions were prepared and fluorescence intensity at each wavelength peak were assayed with a blank test. Relative standard deviation of phenanthrene and naphthalene was 0.48 and 0.89 %, respectively. Detection limit was calculated as 3 times standard deviation of reagent blank. Through calculation, least detection limit of phenanthrene and naphthalene was 0.47 and 0.14 ng/mL, respectively[6].

Adsorption isotherm: Aqueous phenanthrene and naphthalene in loess were assayed by synchronous fluorimetry and adsorption isotherm was depicted in Fig. 4. Such isotherm was in agreement with Freundich equation, which could be denoted as follows:

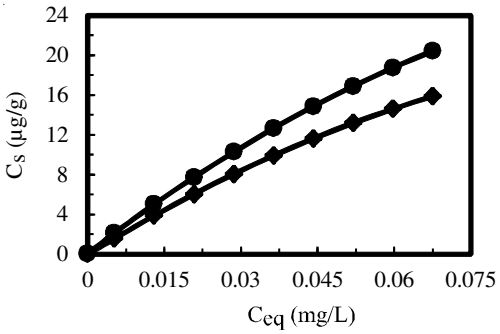

Fig. 4. Sorption isotherms of phenanthrene and naphthalene on loess soils
—•— naphthalene —■— phenanthrene

$$C_s = K_d C_{eq}^{n} \text{ or } \log C_s = n \log C_{eq} + \log K_d$$

where C_s was adsorption capacity in equilibrium, μg/g; C_{eq} was aqueous phenanthrene and naphthalene concentration in equilibrium, mg/mL; K_d was adsorption constant; n was constant of exponential term. Regression equation was as follows:

$$\text{Phenanthrene, } C_s = 262.66\ C_{eq}^{0.92347},\ R = 0.9968$$

$$\text{Naphthalene, } C_s = 220.60\ C_{eq}^{0.94671},\ R = 0.9947$$

Organic carbon content in natural loess was quite low and the adsorption of phenanthrene and naphthalene mainly ascribed to distribution role in combination with surface adsorption. According to the adsorption isotherm and regression data, it is inferred that isotherm of phenanthrene and naphthalene in loess was nonlinear and their adsorption manner was in line with dual-mode adsorption theory, namely the adsorption process of phenanthrene and naphthalene in loess contained two processes of distribution and pore filling[7].

Conclusion

It was easy and rapid to determine phenanthrene and naphthalene level simultaneously in the loess area by synchronous fluorimetry. linear range of phenanthrene and naphthalene was 0.001-0.101 and 0.0025-0.25 mg/L, respectively; detection limit was 0.47 and 0.14 ng/mL, respectively; relative standard deviation was 0.48 and 0.89 %, respectively, which indicated that synchronous fluorimetry offers the advantages of greater sensitivity and selectivity for loess in simultaneous determination of phenanthrene and naphthalene.

Adsorption isotherm of phenanthrene and naphthalene in loess was in agreement with Freundich equation and their adsorption manner was in line with dual-mode adsorption theory.

ACKNOWLEDGEMENTS

The authors expressed their gratitude to the Natural Science Foundation of China for supporting the research with Project No 21067005. A partial fund was offered by the teaching reform project No 2012101.

REFERENCES

1. E.R. Weiner, *Anal. Chem*., **50**, 1583 (1978).
2. S. Rubio, A. Gomer-Hens and M. Valcarcel, *Talanta*, **33**, 633 (1986).
3. X.C. Jin, The Chemistry of Organic Compounds Pollution, The Press of Tsinghua University, pp. 287-306 (1990).
4. G.Z. Chen, X.Z. Huang and J. Xu, Fluorescent Analytical Chemistry, Sciences Press, pp. 201-223 (1990).
5. Y. Zhang, S.X. Li and Y.X. Zhu, *J. Anal. Sci*., **11**, 29 (1995).
6. Y. Zhang, X.Z. Huang and J. Xu, *Anal. Chem*., **22**, 445 (1994).
7. Z. Dang, H. Yu and W.L. Huang, *Chem. J*., **63**, 81 (2001).