Ultra Low Level Determination of Bisphenol A and Poly Aromatic Hydrocarbons in River Water Using Column-Switching HPLC with Fluorescence Detection

Yoshiyuki WATABE [*1], Takashi HINE [1], Tetsuya TANIGAWA [2], Takuya KUBO [2], Ken HOSOYA [3],
1.Analytical Applications Department, Shimadzu corporation,, Kyoto 604-851, Japan
2.Graduate School of Environmental Studies, Tohoku University, Sendai, 980-8579, Japan
3. Graduate School of Life and Environmental Sciences, Kyoto Prefectural University, Kyoto 606-8522, Japan

Introduction

We have introduced multi-valve column switching HPLC system with a specially designed pretreatment column. This column-switching system solved a recurrent issue of column clogging and the MASK-ENV pretreatment column provided remarkable performance for removal of humic compounds from environmental water samples. 1 ng/L of bisphenol A (BPA), one of endocrine disruptors could be detected by using typical and universal fluorescence detector RF-20Axs along with the 2-valve column switching pretreatment system. Expensive MS or MSMS detection was not always necessary even at ng/L level of trace analysis.

Poly aromatic hydrocarbons (PAHs), which are generally recognized as strong carcinogens can be often adsorbed on the surface of HPLC flow line especially resin-made parts of solvent delivery pump such as suction tubing. To avoid this phenomenon during auto-concentration, we employed “sample dilution” device, which provided reliable recovery and repeatability. Real water samples were collected and certain amount of acetonitrile (around 30%) were added to suppress adsorption of PAHs. To increase the recovery at pretreatment column, the sample solution containing organic solvent was diluted with pure water before concentration. Hence, such switching techniques can be used for trace level analysis of environmental contaminants, carcinogens and additives in varied samples with complex matrices. These techniques may therefore assist in sample clean-up, target compound concentration, separation etc. Similar exercises combined with an appropriate choice of a sensitive detection system enable one to carry out ng/L and sub-ng/L level analysis with ease and required sensitivity.

Experimental

HPLC-fluorescence system with automated on-line sample pretreatment

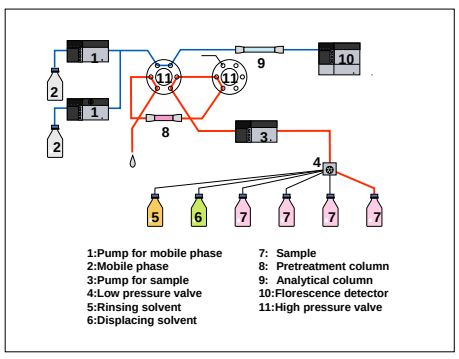


Fig.1 Shimadzu Prominence 2-Valve column switching HPLC system for BPA

Difficulties for auto-pretreatment analysis of PAHs

1. Crude sample concentration results poor recovery or peak missing for strongly retained PAHs due to adsorption onto resin parts in wet surface.
2. Adding organic solvent to water sample improves above-mentioned problem but provides deteriorated peak shape and poor recovery as well for weakly retained PAHs due to eluting power of added organic solvent.

Actual samples were filtered with 0.22 ㎛m membrane filter prior to use and added 30% of acetonitrile only the case of PAHs analysis .

PAHs contained in diluted sample is concentrated properly

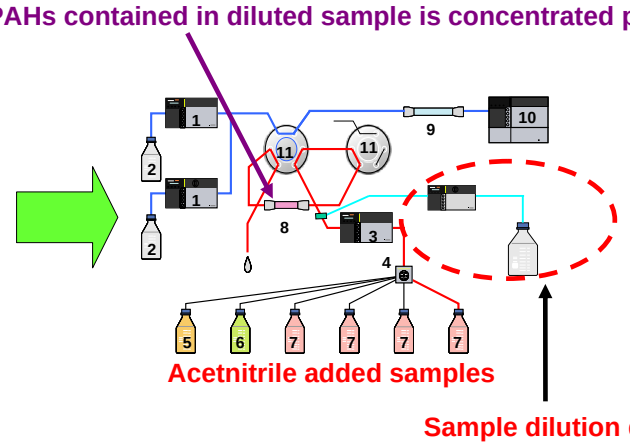


Fig.2 Shimadzu Prominence 2-Valve column switching HPLC system for PAHs

Results and discussion

Effect of interference removal and fluorescence trace analysis of BPA

Comparison of chromatograms obtained by using pretreatment column with and without surface modification is shown in Fig.3. Humic interference was effectively removed by MASK-ENV containing surface modified column packing. Fig.4 is real trace analysis of BPA in river water.

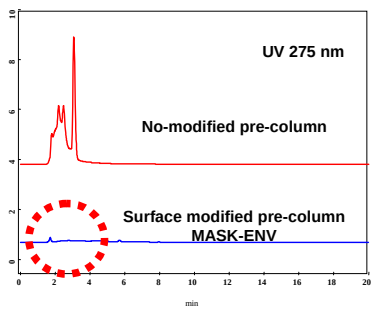


Fig.3 Removal of interference in river water

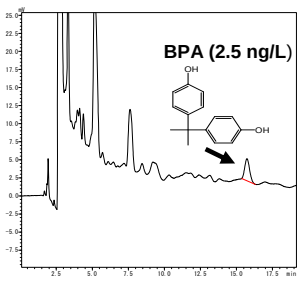
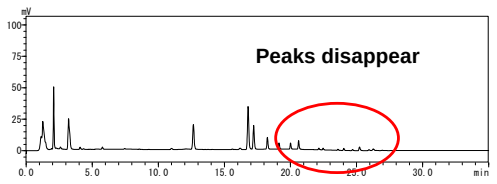


Fig.4 Fluorescence detection ofBPA

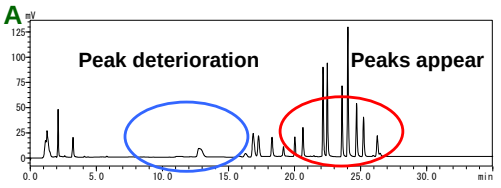
Analytical conditions for Fig.4
Analytical Column : Shim-pack VP-ODS(150 mm L. X 4.6 mm I.D.), Pretreatment column: Chemco MASK ENV(10 mmL. x 4 mmI.D.), Mobile phase : (Sodium) Phosphate Buffer (pH 2.6) / Acetonitrile = 65 / 35 (v/v), Flow rate: 0.8 mL/min. for analysis and 2 mL for sample pretreatment, Sample volume : 50mL, Column temperature : 40 deg.C, Detection : RF-20AXS Ex. at 230 nm, Em. at 310 nm, Cell Temp. : 30 deg.C, water samples were taken from Takano-river.

Fluorescence analysis of trace level of 16 PAHs in river water

Sample condition A: Crude water sample



Sample condition B: 30% Acetonitlie added to A



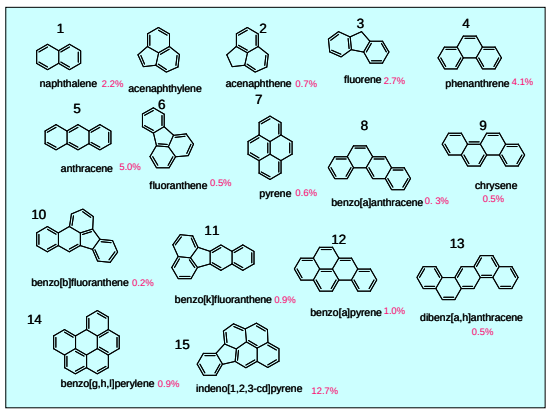


Fig. 5 EPA-assigned 16 PAHs and area-repeatabilities(%)

Sample condition C: five times auto-dilution of sample B before concentration
30-3000 ng/L for each PAH spiked in river water

Area-repeatabilities were ranged from 0.2 to 5% (n=5)

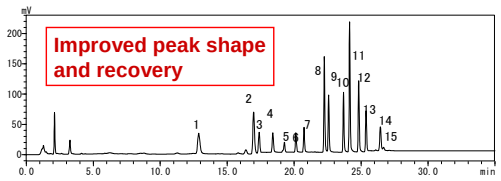


Fig. 6 Effect of dilution device in 16 PAHs determination

Analytical conditions for Fig.6
Analytical Column : Restek Pinacle Ⅱ PAH (250 mmL. x 4.6 mmI.D.), Pretreatment column: Chemco MASK ENV(30 mmL. x 4mmI.D.), Mobile phase : Water / Acetonitrile =40 / 60 (v/v), →0 / 100 multi-liner gradient, Flow rate: 1.5 mL/min for analysis 2.0 mL/min for sample pretreatment, Sample volume : 10mL, Column temperature : 40 deg.C, Detection : RF-20AXS time programmed Ex / Em wave length, Cell Temp. : 30 deg.C, Concentration: 2,3,4,7,8,12,13,14,15; 10 ng/L; 5,6,9,10,11; 20 ng/L ;1,13 ; 100 ng/L, Real-life water samples were taken from Takano-river.

Fundamental performance of the system

Table1 . Fundamental performances of 2-Valve column switching HPLC system

Recovery [1)]	97%
Repeatability [2)]	1.4%RSD
LOD [3)]	0.09 ng/L
Linearity [4)]	R^2=0.9999

1) Recovery was calculated by using peak areas of 50 mL of 200 ng/L BAP added river water and 1 mL of 10 mg/L BPA standard solution.

2) Repeatability was shown as relative standard deviation calculated by using peak areas of six analyses of river water added 10 ng/L BPA.

3) LOD (the limit of detection) was estimated by following ASTM method (S/N=3 is employed as LOD)

4) Linearity was estimated within the range of 1-1000 ng/L

Robustness evaluation

The variations of analytical and pretreatment column pressures are shown in Fig.7. Pressure increases for both analytical and pretreatment columns used with this column switching HPLC were considerably small and no particular pressure increase was not be observed up to150 analyses.

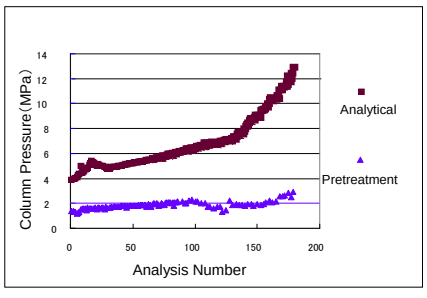


Fig. 7 column pressure increase in 180 times repeated analyses

Conclusion

1. Fluorescence detection and column switching HPLC afforded cost-effective, reliable and highly sensitive HPLC methods
2. Dilution device provided good recovery and reliable repeatability for simultaneous analyses of PAHs
3. Column clogging problem has been solved by washing remained water sample in pretreatment column with clean solvent

References

[1] Y. Watabe, T. Kondo, H. Imai, M. Morita, N. Tanaka, K. Hosoya Anal. Chem. 76, 105-109 (2004)
[2] Y. Watabe, T. Kubo, T. Nishikawa, T. Fujita, K. Kaya, K. Hosoya J.Chromatogr. A, 1120, 252-259 (2006)