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Determination of polycyclic aromatic hydrocarbons by liquid chromatography–electrospray ionization mass spectrometry using silver nitrate as a post-column reagent

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Abstract

Liquid chromatography–electrospray ionization mass spectrometry (LC–ESI-MS) using silver nitrate as a post-column reagent has been used for the determination of 10 polycyclic aromatic hydrocarbons (PAHs) in river water. In this method, after all the PAHs were separated by reversed-phase liquid chromatography, analytes formed complexes with silver cation by mixing with silver nitrate solution. The complexes then transfer the molecular ion, $[M]^+$, of the PAHs by charge transfer using in source collision-induced dissociation. The positive ion ESI mass spectra of all PAHs tested in this study showed $[M]^+$ as the base peak and abundant $[M+Ag]^+$, $[2M+Ag]^+$ with very weak or no $[2M+Ag]^+$. For the sample extraction, several solid-phase extraction parameters using the blue-chitin column were optimized. The limits of detection ($S/N=3$) of all PAHs for the spiked river water sample ranged from 0.001 to 0.03 ng/ml, and the detector responses were linear up to 1 ng/ml (correlation coefficients $\geq$0.0998). Repeatability and reproducibility were in the range from 4.3 to 6.8% and from 6.2 to 9.5%, respectively.

Keywords: Post column reagent; Blue-chitin column; Polynuclear aromatic hydrocarbons; Silver nitrate

1. Introduction

Currently, atmospheric pressure ionization (API) techniques for liquid chromatography–mass spectrometry (LC–MS) are of increasing importance [1–4]. In API techniques, due to the relatively low temperature at which nebulization and ionization take place, decomposition of thermally labile compounds is not as important as in other ionization techniques. Nowadays, API instruments are available commercially and a large number of applications using API techniques have been published [5–9]. In atmospheric pressure chemical ionization (APCI), ionization takes place in the gas phase after evaporation of the LC eluent. A corona discharge from a needle is used as primary ionization of the mobile phase and these reagent ions produce the analyte ions via processes such as ion–molecule reactions.

Another API technique, electrospray ionization (ESI), is adequate for compounds that exist as ions in the LC eluent. Further, ESI is also adequate for non-ionic compounds that can produce complexes

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with small ions such as Na^+, NH_4^+ or Cl^-. In classical ESI, ion evaporation from the liquid phase by evaporation of charged liquid phase droplets is the main mechanism. However, current ESI is pneumatically assisted electrospray and may also involve electrochemical reactions [5]. Therefore, ESI seem to be a useful technique also for non-ionic compounds. Regarding the application of LC–ESI-MS in the environmental field, most examples deal with the separation, identification and quantification of pesticides, their metabolites, surfactant and toxins [10–14]. However few data for neutral and low polarity compounds such as polycyclic aromatic hydrocarbons (PAHs) using ESI are available.

The conventional analytical method for PAHs is gas chromatography–mass spectrometry (GC–MS) because of its high separation efficiency [15,16]. However, analysis of nitro-PAHs or high molecular PAHs by GC–MS encounters problems such as the thermal decomposition and the adsorption to the inlet and column. These problems can be overcome by using LC. Therefore, methods based on LC coupled with a fluorescence detector have been extensively used for the analysis of PAHs in environmental samples [17]. Nevertheless, LC–MS would be a more useful method because of the high sensitivity, selectivity and identification capability of the MS system. For the LC–MS method, the particle beam (PB) interface and APCI have been used for the determination of nitro- and non-substituted PAHs in environmental samples [18–20]. The APCI mass spectra of non-substituted PAHs were dominated by $[M+H]^+$ or $[M]^+$, indicating that proton transfer or charge exchange was the dominant mechanism of ionization [20]. However, the estimated limit of detection (LOD) for PAHs by the APCI method is several hundred ppb and insufficient for the analysis of the PAHs in environmental waster samples such as river water or sea water [20].

Recently, LC–ESI-MS has been used to determine nitro- and non-substituted PAHs [21,22]. In this method, PAHs were detected by monitoring the PAH–tropylium complexes, which formed after the LC separation upon mixing with tropylium tetrafluoroborate. The tropyliumn cation (TR^+) is a strong electron acceptor which almost quantitatively forms the $[PAH–TR]^+$ complex. However, it was difficult to detect the tropylium complexes of some species of PAHs. Further, the detection limits of PAHs were fivefold higher than for GC–MS and LC–fluorescence [22].

Metal cations such as zinc or silver have also been known as electron acceptors. In this study, after the separation of PAHs by reversed-phase LC, a silver nitrate solution as a post-column reagent was used to form silver complexes of the PAHs. The generated silver complex cations were detected by ESI. Although the identification of PAHs in air particulate materials (due to incomplete combustion of gasoline, diesel, wood) or in coal tar contaminated sediments [23,24] is useful, concentration measurement of specific PAHs in water samples such as sea water is also of considerable importance because certain PAHs are mutagens and carcinogens (e.g., benzo-[*a*]pyrene, dibenzo[*ah*]anthracene). Typically, the trace-level determination of these PAHs in aqueous samples requires selective enrichment of these analytes prior to chromatographic analysis. In 1983, Hayatsu et al. discovered that rayon bearing covalently bound copper phthalocyanine trisulfonate (blue rayon) is a specific adsorbent for compounds with polycyclic structures [25]. However, as the concentration of PAHs in environmental water is several ppt, blue rayon must be hung in the water for 24 h [26]. Further, the amount of PAHs sampled by blue rayon depends on the intensity of the water flow together with the level of PAHs in water. Therefore, a time-weighted average (TWA) concentration of PAHs must be correlated with the water stream intensity, which was measured by the plaster ball method [27]. Recently, Hayatsu and co-workers found that chitin (a poly-*N*-acetylglucosamine) powder bearing covalently linked copper phthalocyamine trisulfonate is suitable for preparing a short packed column and they reported that the blue-chitin column is useful for monitoring heterocyclic amines in two Japanese rivers [28,29]. In this study, a rapid screening method for PAHs in river water was developed by using LC–ESI-MS with silver nitrate as the post-column reagent combined with solid-phase extraction (SPE) with the blue-chitin column for the first time.

2. Experimental

2.1. Materials

The 16 PAH mixture solution (1000 μg/ml)

containing naphthalene, acenaphthylene, acenaphthene, fluorene, phenaththrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo-[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*ah*]anthracene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene was purchased from Supelco Japan (Tokyo, Japan). HPLC-grade acetonitrile, reagent-grade methanol and concentrated ammonia were purchased from Wako (Osaka, Japan). Silver nitrate solution was purchased from Kanto (Tokyo, Japan). Water was purified with a Milli-Q system (Millipore, Tokyo, Japan). The blue-chitin cartridge column (120 mg) was purchased from Funakoshi (Tokyo, Japan).

2.2. Instrumentation

2.2.1. Liquid chromatography–mass spectrometry

An Agilent 1100 Series liquid chromatograph (Agilent, Waldbronn, Germany), consisting of a vacuum solvent degassing unit, a binary high-pressure gradient pump, an autosampler and a column thermostat was used for LC–MS analysis. Further a Model Agilent 1100 Series diode array detector was connected on-line with a mass-selective detector. The LC flow was introduced into the ESI interface without any splitting after detection by the photodiode-array detector. LC separation was performed on a 75×4.6 mm I.D. column packed with 3 μm Supelcosil LC-PAH, ODS (Supelco Japan). Gradient elution was carried out with a linear program from solvent A (acetonitrile)–solvent B (water) (60:40) to 100% solvent A in 10 min. The column was conditioned with solvent A–solvent B (60:40) for 10 min before injection of the next sample. The flow-rate was 0.8 ml/min. 0.2 m*M* silver nitrate solution was introduced into the LC eluent flow after the column at a flow-rate of 0.2 ml/min by using a T-connector and an isocratic pump. The injection volume was 20 μl.

An Agilent 1100 series mass-selective detector single quadrupole instrument equipped with orthogonal spray-ESI (Agilent, Palo Alto, CA, USA) was used for this investigation. Nitrogen as the nebulizing gas and the drying gas was generated from compressed air using a Whatman Model 75-72 nitrogen generator (Haverhill, USA). The nebulizing gas pressure was set at 50 p.s.i. and the drying gas was held at 10 l/min (1 p.s.i.=6894.76 Pa). The drying gas temperature was kept at 350°C. Fragmentor voltage for in-source collision-induced dissociation (CID) was set at 160 V. Further, skimer1,2 and entrance lens voltages in the ion source of the mass-selective detector were automatically optimized using a calibration standard at m/z 118, 322, 622, 922, 1522 and 2122 (Agilent) and set at 23, 47 and 57 V, respectively. LC–MS determinations were performed by operating the mass-selective detector in the positive ion mode. Mass spectra were acquired over a mass range range m/z 100–600. The scan speed was 2 s. Quantitative analysis was carried out using selected ion monitoring (SIM) of base peaks at m/z 202 (fluoranthene, pyrene), 228 (benzo[*a*]anthracene, chrysene), 252 (benzo[*b*]fluoranthene, benzo-[*k*]fluoranthene and benzo[*a*]pyrene), 276 (benzo-[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene) and 278 (dibenzo[*ah*]anthracene) with a dwell time of 500 ms per ion.

2.3. Preparation of standard solutions

The mixture of 16 PAHs of 1 and 10 μg/ml were prepared in methanol for a method development. Working solutions with concentrations of 5 to 500 ng/ml of each PAH were prepared in methanol.

2.4. Sample preparation

A 1000-ml volume of Syuku river water sample (Hyogo, Japan) was collected in a polyethylene terephthalate (PET) bottle and was filtrated by a glass-fiber filter. The blue-chin column was set to a vacuum manifold (J&W Scientific, Folsom, CA, USA) and conditioned with methanol containing 2% ammonia water (20 ml), then with pure water (30 ml), at a flow-rate of about 20 ml/min using a aspirator. The filtrate was passed through the blue-chitin column and washed with pure water (30 ml) at a flow-rate of about 20 ml/min. The blue-chitin column was eluted with methanol containing 2% ammonia water (40 ml) at a flow-rate of about 5 ml/min. The eluent was evaporated to dryness under reduced vacuum, and the residue was dissolved in methanol (1 ml).

3. Results and discussion

3.1. Optimization of the [PAH–silver] complex formation

In a preliminary mass spectral experiment by ESI using flow injection of the PAH–methanol solution (10 μg/ml of all PAHs), there were no peaks assignable to the PAHs. On the other hand, injection of the solution of PAHs containing 0.1 m*M* silver nitrate gave $[M+Ag]^+$, $[2M+Ag]^+$ and $[M]^+$ for PAHs having four or more fused rings when the fragmentor voltage was set at 60 V. However, there were no peaks for naphthalene, acenaphthylene, acenaphthene, fluorene, phenaththrene and anthracene, which have two or three fused rings, but these PAHs can be measured by GC–MS. Therefore, these PAHs were not included in this study. On the other hand, PAHs having three or more fused rings have been reported as mutagens and caricinogens and are also present in the water environment at a very low level. Therefore, for monitoring mutagenicity, it is important to measure only the PAHs with four or five fused rings. Since the maximum flow-rate which can be introduced into the ESI source without any splitting is 1 ml/min, the flow-rate of silver nitrate was fixed at 0.2 ml/min for the optimization of the $[PAH–Ag]^+$ complex formation and only the concentration of silver nitrate solution as a post-column reagent was investigated. Total ion currents of the 10 PAHs were monitored using the full scan mode and the intensities of relative total ion currents obtained at 0.05 m*M* silver nitrate are shown in Fig. 1. Except for indeno[1,2,3-*cd*]pyrene, the relative intensities increased with increasing silver nitrate concentration until 0.2 m*M* and they decreased at 0.25 m*M*. For indeno[1,2,3-*cd*]pyrene, the relative intensities slightly decreased at levels above 0.1 m*M*. Therefore, in order to obtain the maximum sensitivity, the concentration of silver nitrate was set to 0.2 m*M*. In addition, the increase of the relative intensities of larger PAHs was 1.5-fold less than those of smaller PAHs. These results indicated that the affinity of larger PAHs for the silver ion are much higher and the Ag complexes of these PAHs are formed even at low concentrations of silver nitrate

3.2. Evaluation of ESI parameters

The main operating parameters that have an

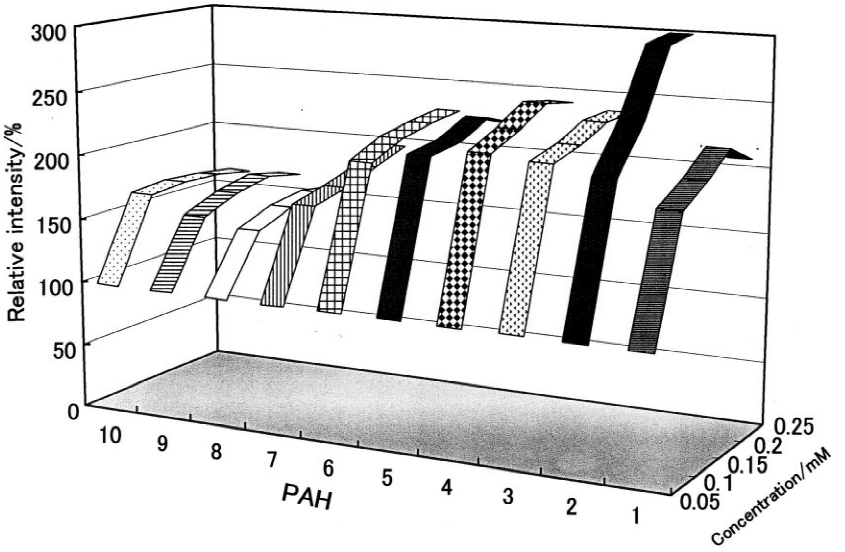

Fig. 1. Influence of silver nitrate concentration as a post-column reagent on total ion currents of $[PAH–Ag]^+$ complex as measured by LC–MS in full scan mode. Concentration: 10 ng/ml. For other conditions, see Experimental. 1: fluoranthene, 2: pyrene, 3: benzo[*a*]anthracene, 4: chrysene, 5: benzo[*b*]fluoranthene, 6: benzo[*k*]fluoranthene, 7: benzo[*a*]pyrene, 8: dibenzo[*ah*]anthracene, 9: benzo[*ghi*]perylene, 10: indeno[1,2,3-*cd*]pyrene.

impact on the performance of ESI are the drying gas temperature, flow-rate, nebulizer pressure and fragmentor voltage. However, optimum drying gas temperature, flow-rate and nebulizer pressure are not compound dependent and typical values of these parameters are 350°C, 10 l/min and 50 p.s.i., respectively [12]. Only the fragmentor voltage was, therefore investigated.

3.2.1. Effect of fragmentor voltage on the mass spectra

The fragmentor voltage is applied to the exit of the glass capillary and affects the transmission and fragmentation of sample ions by the in-source CID in this region [22]. In general, the higher the fragmentor voltage, the more fragmentation will occur and the optimum fragmentor voltage is compound dependent. Therefore, an effect of the fragmentor voltage on the mass spectra of each of the $[PAH–Ag]^+$ complexes was investigated under the chromatographic conditions using linear gradient elution with a mobile phase of acetonitrile–water at a flow-rate of 0.8 ml/min and 0.2 m*M* silver nitrate at a flow-rate of 0.2 ml/min via a T-connector. The results for four typical PAHs are shown in Fig. 2. For fluoranthene (A), and chrysene (B), which have four and five rings, respectively, $[2M+Ag]^+$ was observed as the base peak in the mass spectra at less than 80 V and the relative intensity of this ion decreased at higher fragmentor voltages. On the other hand, the relative intensities of $[M]^+$ and $[M+Ag]^+$ increased by increasing the fragmentor voltage and only $[M+Ag]^+$ decreased at above 120 V. For benzo[*a*]pyrene and indeno[1,2,3-*cd*]pyrene which have five and six rings, respectively, $[M]^+$ was observed as the base peak at all fragmentor voltages and the relative intensities of $[M+Ag]^+$ and $[2M+Ag]^+$ were much lower than those of fluoranthene and chrysene. These results indicate that reactions potentially competing with complex formation take place in the ESI chamber and charge transfer may takes place by in-source CID between the exit of capillary and the skimmer. Finally, since $[M]^+$ of all PAHs showed maximum intensity, these ions were selected as monitor ions for the SIM mode. Under these conditions (fragmentor voltage, 160 V; post-column reagent, 0.2 m*M* silver nitrate), the mass spectra of all 10 PAHs showed $[M]^+$ as the base peak and abundant $[M+Ag]^+$, $[2M+Ag]^+$ with very weak or no $[2M+Ag]^+$ (Table 1).

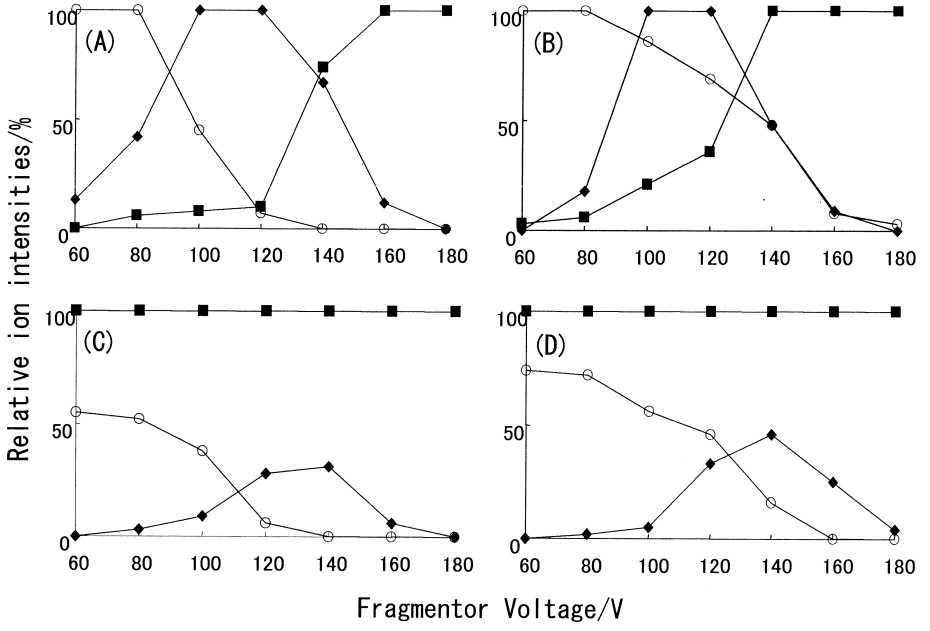

Fig. 2. Effect of fragmentor voltage on ion intensity of four PAHs. Concentration: 10 ng/ml. For analytical conditions of LC–MS, see Experimental. ■=$[M]^+$, ◆=$[M+Ag]^+$, ○=$[2M+Ag]^+$. A: Fluoranthene, B: chrysene, C: benzo[*a*]pyrene, D: indeno[1,2,3-*cd*]pyrene.

Table 1
m/z and relative intensities (RIs) of the main ions formed in ESI-MS of PAHs using 0.2 m*M* $AgNO_3$

Compound	*m/z* (RI, %)		
	$[M]^+$	$[M+Ag]^+$	$[2M+Ag]^+$
Fluoranthene	202 (100)	309 (12)	511 (4)
Pyrene	202 (100)	309 (2)	511 (6)
Benzo[*a*]anthracene	228 (100)	335 (3)	563 (2)
Chrysene	228 (100)	335 (9)	563 (8)
Benzo[*b*]fluoranthene	252 (100)	359 (45)	611 (3)
Benzo[*k*]fluoranthene	252 (100)	359 (9)	611 (7)
Benzo[*a*]pyrene	252 (100)	359 (6)	–
Dibenzo[*ah*]anthracene	278 (100)	385 (33)	663 (3)
Benzo[*ghi*]perylene	276 (100)	383 (36)	–
Indeno[1,2,3-*cd*]pyrene	276 (100)	383 (31)	–

Concentration: 10 ng/ml, fragmentor voltage: 160 V.

Table 2
Recovery from 0.2, 0.5 and 1 l river water with the blue-chitin column

Compound	Recovery means (%)[a]
Fluoranthene[b]	91–93
Pyrene[b]	93–97
Benzo[*a*]anthracene[c]	92–97
Chrysene[c]	91–97
Benzo[*b*]fluoranthene[c]	93–95
Benzo[*k*]fluoranthene[c]	91–97
Benzo[*a*]pyrene[c]	90–95
Dibenzo[*ah*]anthracene[c]	91–94
Benzo[*ghi*]perylene[c]	88–93
Indeno[1,2,3-*cd*]pyrene[c]	91–93

[a] $n=3$, all RSDs were 3–7%.
[b] Concentration: 5 ng/ml.
[c] Concentration: 1 ng/ml.

3.3. SPE using the blue-chitin cartridge column

Critical parameters in this SPE procedure are the volume of eluent (methanol containing 2% ammonia water) required to elute the trapped analytes from the cartridge and breakthrough volumes of the analytes. At first, the eluent volume was investigated using Syuku river water samples in which no traces of naturally occurring PAHs were found, spiked at 5 ng/ml of fluoranthene and pyrene, respectively, and 1 ng/ml of the other PAHs. Methanol containing 2% ammonia water as the eluent solvent was used and the eluent volume was changed from 10 to 50 ml. The recovery of representative PAHs is shown in Fig. 3. Elution with 10 ml methanol–ammonia resulted in only 30–45% recovery of all PAHs and larger PAHs showed insufficient recovery with 20 ml eluent: apparently larger PAHs have a much higher affinity to the blue-chitin. The recovery of all PAHs with more than 30 ml eluent was over 90% and essentially the same yields. Therefore, the eluent volume was set to 30 ml. In order to obtain an estimate of the breakthrough volumes on the blue-chitin column, 0.2, 0.5 and 1 l river water samples spiked at 5 ng/ml of fluoranthene and pyrene, respectively, and 1 ng/ml of the other PAHs were analyzed. The data in Table 2 indicate that the average recoveries of all PAHs exceeded 88% for all sample volume. Furthermore, the present relative

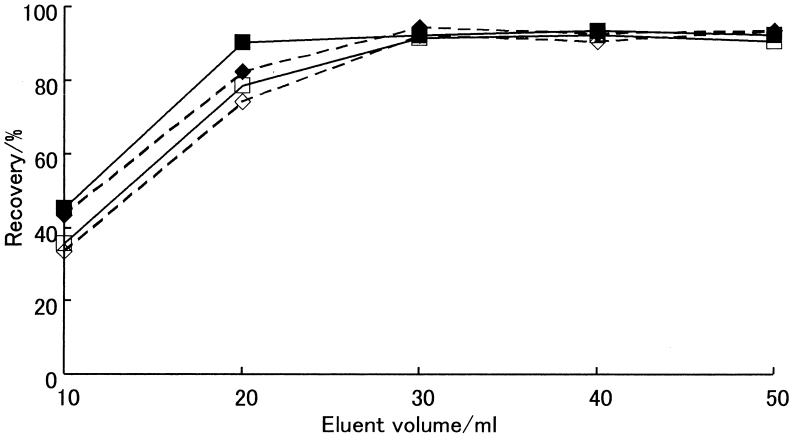

Fig. 3. The effect of eluent volume on recovery of PAHs. Eluent: methanol containing 2% ammonia water spiked amount; fluoranthene: 5 ng/ml, the other PAHs: 1 ng/ml ■=fluoranthene, ◆=chrysene, □=benzo[*a*]pyrene, ◇=indeno[1,2,3-*cd*]pyrene.

standard deviation (RSD) value of 3–7% for the recovery of all PAHs is fully satisfactory. Therefore, the sample volume was set to 1 l.

3.4. Linearity, detection limits and precision

In order to achieve optimum sensitivity, all experiments were carried out under SIM conditions and the molecular ions were selected as SIM ions for all PAHs. The linearity and sensitivity of this method was performed with the river water spiked with all PAHs in the concentration range from 2 to 1000 pg/ml (nine data points) in the injection solutions, corresponding to 0.04–2 pg on-column. However fluoranthene, pyrene and benzo[*b*]fluoranthene could not be detected at 0.002 ng/ml. Therefore, the linearity of these compounds was tested in the concentration range from 5, 10 and 50 to 1000 pg/ml, respectively. This river water sample was collected in the upstream in the Syuku river showing no traces of these PAHs. As shown in Table 3, the linearity was very good for all PAHs with correlation coefficients (r^2) higher than 0.998. The sensitivity of this analytical procedure for real samples such as river water was evaluated in terms of the limit of detection (LOD) calculated using an S/N of 3. The LOD of each PAH by this method was in the range of 1 to 30 pg/ml. The LODs of pyrene and benzo-[*a*]pyrene by this method were 4- and 60-fold lower than for LC–ESI-MS with tropylium cation, respectively. The intra-day precision (repeatability) was estimated by injecting a river water sample spiked at 100 pg/ml five times during a working day. The inter-day precision (reproducibility) was evaluated by analyzing the same sample three times over 3 working days. The repeatability and reproducibility for all PAHs ranged from 4.3 to 9.5%. The quantitative results of all PAHs in the river water sample spiked at 10 pg/ml using external calibration curve also are shown in Table 3 and the SIM chromatogram of this sample is shown in Fig. 4, respectively. The error of experimental results for the true results was within 20% except for fluoranthene and no significant interference peaks were observed. For testing the method, this system has been used to analyze at least 25 river water samples per day and over 10 days but no maintenance was required with obstruction of the system by clogging of the glass capillary tube with silver nitrate. This result indicates that the method is reliable and robust and is therefore applicable to routine analysis.

4. Conclusion

The the coupling of SPE using the blue-chitin cartridges together with LC–ESI-MS using silver

Table 3
Limit of detection (LODs), linearity, precision of PAHs in LC–ESI-MS

Compound	r^{2} [a]	LOD [b] (pg/ml)	Quantitative [c] results (pg/ml)	Instrument precision (RSD, %)	
				Repeatability [d]	Reproducibility [e]
Fluoranthene	0.999	30	6	6.3	9.3
Pyrene	0.999	10	9	4.3	6.2
Benzo[*a*]anthracene	0.999	2	11	4.9	6.3
Chrysene	0.999	4	8	5.5	8.1
Benzo[*b*]fluoranthene	0.999	5	11	6.8	9.5
Benzo[*k*]fluoranthene	0.998	3	12	4.9	7.1
Benzo[*a*]pyrene	0.999	1	11	5.1	7.8
Dibenzo[*ah*]anthracene	0.998	3	9	6.4	7.1
Benzo[*ghi*]perylene	0.999	2	10	5.8	8.3
Indeno[1,2,3-*cd*]pyrene	0.999	2	11	6.1	7.7

[a] r^2 is the correlation coefficient of calibration equation ranged from 2 to 1000 pg/ml except for fluoranthene, pyrene and benzo[*a*]fluoranthene. The concentration ranges of these compounds are from 5, 10 and 50 to 1000 pg/ml, respectively.
[b] Limit of detection is defined as $S/N=3$ for the spiked river water.
[c] Calculated for river water spiked at 0.01 ng/ml level except fluoranthene which was spiked at 0.05 ng/ml into river water.
[d] Repeatability was calculated on the basis of five replicates at 100 pg/ml within 1 day.
[e] Reproducibility was calculated on the basis of single analysis per 1 day for 3 days at 100 pg/ml.

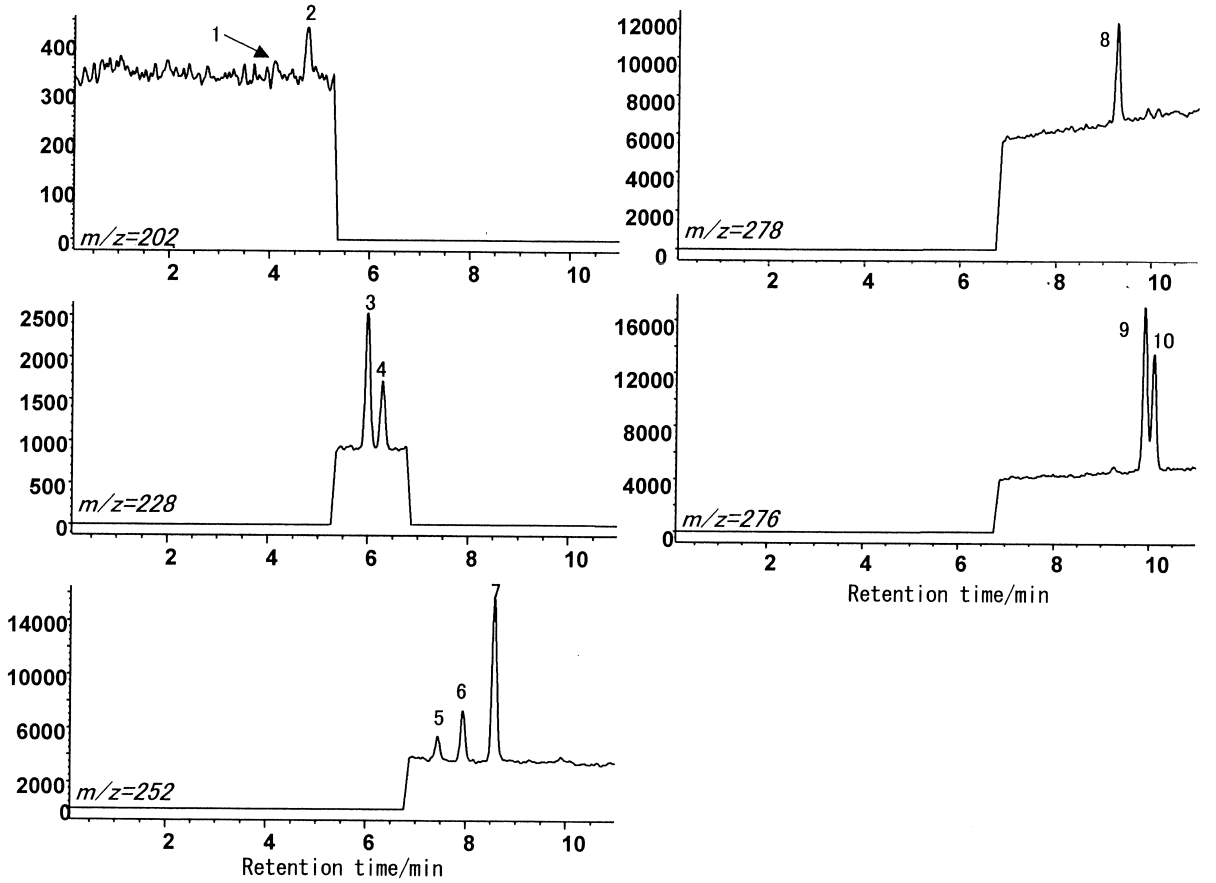

Fig. 4. Typical SIM chromatogram obtained by LC–ESI-MS with silver nitrate of river water spiked at 0.01 ng/ml. 1: Fluoranthene, 2: pyrene, 3: benzo[*a*]anthracene, 4: chrysene, 5: benzo[*b*]fluoranthene, 6: benzo[*k*]fluoranthene, 7: benzo[*a*]pyrene, 8: dibenzo[*ah*]anthracene, 9: benzo[*ghi*]perylene, 10: indeno[1,2,3-*cd*]pyrene.

nitrate as post-column reagent is powerful technique for the determination of four-, five- and six-ring PAHs in river water at the low pg/ml level without the need of additional clean-up steps. Very low detection limits could be reached due to the enhanced selective enrichment of the blue-chitin cartridge and high sensitivity obtained with ESI-MS detection using silver nitrate.

The next step of this work is to expand the analytical method to apply the procedure to the determination of PAHs in various media, such as diesel exhaust particulates. Furthermore, the coupling of SPE using the blue-chitin cartridges together with LC–ESI-MS using silver nitrate will have applicability in a wide range of research for the compounds having non-polar polycyclic planar structures.

References

[1] R.D. Voyksner, Environ. Sci. Technol. 28 (1994) 118A.
[2] A.P. Bruins, Trends Anal. Chem. 13 (1994) 37.
[3] Y. Hua, W. Lu, M.S. Henry, R.H. Pierce, R.B. Cole, J. Chromatogr. A 750 (1996).
[4] R.B. Cole (Ed.), Electrospray Ionization Mass Spectrometry, Wiley, New York, 1997.
[5] M.T. Galceran, E. Moyano, J. Chromatogr. A 683 (1994) 9.
[6] B. Casetta, R. Cozzani, A.L. Cinquina, S. di Marzio, Rapid Commun. Mass Spectrom. 10 (1996) 1497.

[7] G.J. Mol, R.C.J. van Dam, R.J. Vreeken, O.M. Steijger, J. Chromatogr. A 833 (1999) 53.
[8] T. Lacker, S. Strohschein, K. Albert, J. Chromatogr. A 854 (1999) 37.
[9] P. Eichhorn, T.P. Knepper, J. Chromatogr. A 854 (1999) 221.
[10] D. Baglio, D. Kotzias, B.R. Larsen, J. Chromatogr. A 854 (1999) 207.
[11] J.B. Plomley, P.W. Crozier, V.Y. Taguchi, J. Chromatogr. A 854 (1999) 245.
[12] M. Takino, S. Daishima, K. Yamaguchi, J. Chrmatogr. A 857 (1999) 220.
[13] M. Takino, S. Daishima, K. Yamaguchi, Anal. Sci. 16 (2000) 707.
[14] H. Moriwaki, Annu. Rep. City Inst. Public Health Environ. Sci. 61 (1999) 77.
[15] W. Linder, W. Posch, O.S. Wolfbeiis, P. Tritthast, Chromatographia 20 (1985) 213.
[16] G.K. Low, G.E. Batley, R.O. Lidgard, A.M. Duffield, Biochem. Environ. Mass Spectrom. 13 (1986) 95.
[17] P. Wu, T. Chiang, L. Wang, C. Chang, Y. Ko, Mutat. Res. 403 (1998) 29.
[18] D.R. Doerge, J. Clayton, P.P. Fu, D.A. Wolfe, Biol. Mass Spectrom. 22 (1993) 654.
[19] M.T. Galceran, E. Moyano, J. Chromatogr. A 731 (1996) 75.
[20] C.H. Marvin, B.E. McCarry, J. Villella, D.W. Bryant, R.W. Smith, J. Polycyclic Aromatic Comp. 9 (1996) 193.
[21] H. Moriwaki, A. Imaeda, R. Arakawa, Anal. Commun. 36 (1999) 53.
[22] H. Moriwaki, Analyst 125 (2000) 417.
[23] C.H. Marvin, M. Tessaro, B.E. McCarry, D.W. Bryant, Sci. Total. Environ. 156 (1994) 119.
[24] A.E. Legzdins, B.E. McCarry, C.H. Marvin, D.W. Bryant, Int. J. Environ. Anal. Chem. 60 (1994) 79.
[25] H. Hayatsu, T. Oka, A. Wakata, Y. Ohara, T. Hayatsu, H. Kobayashi, S. Arimoto, Mutagenesis Res. 119 (1983) 233.
[26] S. Kira, K. Taketa, Y. Nogami, H. Hayatsu, Environ. Toxicol. Water Qual. 10 (1995) 167.
[27] S. Kira, Y. Nogami, T. Ito, H. Hayatsu, Mar. Environ. Res. 46 (1998) 267.
[28] H. Hayastu, T. Hayatsu, S. Arimoto, H. Sakamoto, Anal. Biochem. 235 (1996) 185.
[29] H. Sakamoto, T. Ohe, T. Hayatsu, H. Hayatsu, Mutagenesis Res. 371 (1996) 79.