On-Line Concentration and Fluorescence Determination HPLC for Polycyclic Aromatic Hydrocarbons in Seawater Samples and Its Application to Japan Sea

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An on-line concentration and fluorescence determination HPLC for polycyclic aromatic hydrocarbons (PAHs) in seawater was proposed. An online concentration column packed with octadecyl polyvinyl alcohol polymer, a pump and a column switching valve were introduced in the conventional HPLC with a fluorescence detector. Only 1.0–100 mL seawater sample was introduced into the concentration column at 1.0 mL min^{-1} without any other pretreatment except filtration. Then the trapped PAHs totally flew into the separation column and eluted separately to be detected fluorogenically. The proposed method had good linearity with correlation coefficients (*r*) ranged from 0.951 to 0.998, and limits of detection ranged from 0.002 to 0.50 ng L^{-1} for 15 PAHs as 100 mL seawater was loaded. The sensitivity of the method was 10 to 100 times higher than those reported by other works. The proposed method was applied to the determination of PAHs in the seawater samples collected in the Japan Sea with satisfactory results and to check the present benzo[*a*]pyrene concentration at the beaches in Noto peninsula, Japan polluted with C-heavy oil spilled from the tanker in 1997.

Key words polycyclic aromatic hydrocarbon; HPLC; seawater; Japan Sea

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants. Humans and animals are exposed to PAHs from environmental, dietary and occupational sources. Benzo[*a*]pyrene (BaP) is carcinogenic to humans, dibenz[*a*,*h*]-anthracene is probably carcinogenic to humans and benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), indeno[*1*,*2*,*3-cd*]pyrene (IDP) are possibly carcinogenic to humans.[1] Due to their potential or proven carcinogenic or mutagenic properties, some PAHs have been designated as priority pollutants for monitoring by the U.S. and European environmental agencies. It is for these reasons that the European Union has fixed very restrictive limits for these compounds in different kinds of superficial water.[2]

Many kinds of PAHs are contained in natural oil and oil spilled from tankers and wells causes serious marine contamination with PAHs. The Japan Sea is fruitful of fishery resources. In January 1997, a large amount of C-heavy oil more than 6000 kL was spilled from the Russian tanker, Nakhodka, in the central part of the Japan Sea and the spilled oil was beached on the coastlines from Shimane to Akita, Japan. This accident gave the serious damage to the fishery in Japan. The contamination of PAHs was monitored for several years after the accident.[3] Now, more than 10 years after the accident, it is believed that the Japan Sea has become clean without detailed monitoring of PAHs.

For determining PAHs in marine, specific analytical protocols have been described in detail in several reviews.[4–6] Traditional pretreatment techniques for extraction of these organic compounds from aqueous samples are liquid–liquid extraction (LLE) and solid-phase extraction (SPE).[7–10] However, these multistep techniques have disadvantages of labor-intensive, heavy usage of toxic solvents and contamination. Solid-phase microextraction with different coating materials or polymeric fiber was employed for the determination of PAHs in tap water, river water or rainwater, and these techniques provided large extraction capacity and high sensitivity ranged ng L^{-1} level when coupling with gas chromatography-mass spectrometry (GC-MS)/HPLC.[11–13] However, the evaporation of the eluate reduced the recoveries of PAHs having 2 to 3 rings which have high vapor pressures.

Compared with the PAHs concentrations in rainwater, river water, sewage and even marine sediments, the concentrations of PAHs in seawater were much lower, so the reports concerning PAHs in seawater samples were scarce until now.[8,9,14] When seawater samples were analyzed, it is necessary to collect big volume sample, *e.g.* several or several-hundred litter sample, in order to achieve the limits of detection.[5,7,8] Moreover, the recoveries of PAHs became lower with decreasing concentrations.

In this work, in order to overcome the disadvantages of traditional methods described above, an on-line concentration and fluorescence determination HPLC was proposed for determining trace levels of PAHs in seawater samples. As effective applications of the proposed method, concentrations of PAHs were also determined in seawater samples collected in the southwest part of the Japan Sea and at beaches in Noto Peninsula which were heavily damaged by the oil spill in 1997.

Experimental

Materials An EPA 610 PAHs mix containing naphthalene (Nap), acenaphthene (Ace), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), BaA, Chr, BbF, BkF, BaP, dienz[*a*,*h*]anthracene (DBA), benzo[*g*,*h*,*i*] perylene (BgPe) and IDP was purchased from Supelco

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(Bellefonte, PA, U.S.A.). Five deuterated PAHs (Nap-d_8, Ace-d_{10}, Phe-d_{10}, Pyr-d_{10} and BaP-d_{12}) were purchased from Wako Pure Chemical (Osaka, Japan) as internal standards. Both PAHs and deuterated PAHs were dissolved in acetonitrile (Kanto Chemical, Tokyo, Japan). All other chemicals used were of analytical reagent grade.

Collection and Pretreatment of Seawater Sample Seawater samples were collected at five sites (S1–5), whose latitudes and longitudes were respectively 32.8° and 129.5° (S1), 33.8° and 129.7° (S2), 34.8° and 130.5° (S3), 35.5° and 131.5° (S4), 36.0° and 132.5° (S5), in the Japan Sea in August 2008. Seawater samples were collected from the bow of Nagasaki-maru, expedition ship, moving forward, and were collected by immersing pre-cleaned borosilicate amber glass bottles (2 L) at *ca.* 0.5 m below the water surface (opening and closing it underwater). Each water sample was immediately filtered through a 0.45 μm micropore membrane (GC-50,diameter 90 mm, Advantec, Tokyo, Japan) and 10% (v/v) ethanol was added to each bottle to prevent the adsorption of PAHs on the wall. The seawater samples were stored in the refrigerator (at 4°C) no more than 1 week before analysis and no other preservatives were needed. Seawater samples collected at two beaches in Noto Peninsula, Japan damaged by the oil spill in 1997 were also used for comparison.

Artificial seawater was prepared by dissolving 32 g of NaCl, 14 g of $MgSO_4 \cdot 7H_2O$ and 0.2 g $NaHCO_3$ in 1 L of Milli-Q water.

On-line Concentration and Determination HPLC System for PAHs in Seawater The proposed HPLC system was shown in Fig. 1. The system consisted of three Hitachi L-2130 pumps (Tokyo, Japan), a Hitachi degasser, a Hitachi L-2485 fluorescence detector and a Hitachi organizer. An Asahipak ODP-50G column (4.6 mm i.d.×10 mm, Shodex, Tokyo, Japan) was used as the concentrator column. An Inertsil ODS-P column (4.6 mm i.d.×250 mm, GL-Science Company, Tokyo, Japan) and an Inertsil ODS-P column (4.6 mm i.d.×33 mm) were used as the separator and guard columns, respectively. PAHs were concentrated on the concentrator column by loading seawater sample through the solid-line in Fig. 1.

The on-line concentration and elution were operated as follows with the Teflon tubing. After seawater sample (with 10% ethanol) was added with internal standards of Nap-d_8, Ace-d_{10}, Phe-d_{10}, Pyr-d_{10} and BaP-d_{12}, an aliquot (1.0–100 mL) of the mixture was introduced into the HPLC system through the HPLC pump 1. The inlet tubing was rinsed with the sample

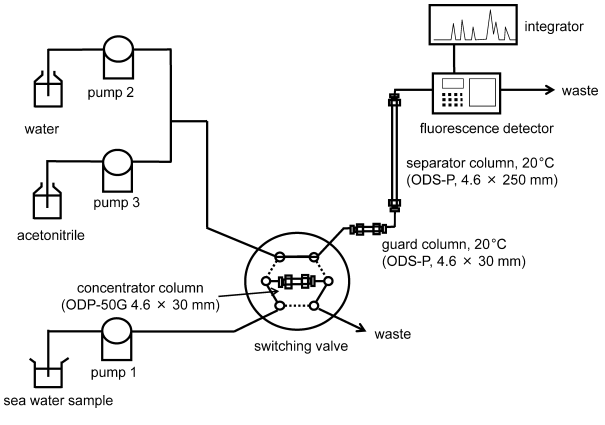

Fig. 1. Schematic Diagram of the Proposed System

for 10 min before loading. The loading volume depended on the concentrations of PAHs in the samples. PAHs in the sample were adsorbed and concentrated on the concentrator column (ODP-50G). The column was washed with 15 mL of distilled water to remove the interfering compounds and salts. The volume of samples and washing solutions was controlled by the loading time when the optimized flow rate of pump 1 was 1.0 mL min^{-1}. After the valve was switched (from the solid line to the dotted line in Fig. 1), PAHs were eluted from the concentrator column and separated on the separator column (ODS-P) with the HPLC mobile phase. Then, PAHs were determined fluorogenically under the following conditions according to our previous report[15] with minor modification as follows. The mobile phase consisted of acetonitrile and Milli-Q water and the flow rate of mobile phase was kept constant at 1.0 mL min^{-1}.

The gradient time program of pumps 2 and 3 was controlled by the Hatachi organizer. Initially, the content of acetonitrile in the mobile phase was 55% (v/v) for the first 20 min, and then was changed from 70 to 80% (20–35 min), after that, it was kept at 90% (35–45 min), then was increased to 100% (45–60 min) and kept for 20 min. The excitation and emission wavelengths were set at 280 and 340 nm (0–31.5 min) for Nap, Nap-d_8, Ace, Ace-d_{10}, Fle, Phe, Phe-d_{10}, 250 and 400 nm (31.5–34 min) for Ant, 286 and 433 nm (34–36 min) for Flu, 331 and 392 nm (36–41 min) for Pyr and Pyr-d_{10}, 264 and 407 nm (41–68.9 min) for BaA, Chr, BbF, BkF, BaP, BaP-d_{12}, DBA, BgPe and 294 and 482 nm (68.9–80 min) for IDP, respectively.

The whole system was checked routinely with blank samples for preventing from contamination.

Results and Discussion

Optimization of On-line Concentration As the solid-phase extraction sorbent for the on-line determination of PAHs in natural water, a kind of fluorocarbon polymer was used. In the system, only PAHs with high concentration, *e.g.* Nap, Ant, and Pyr, were determined.[14] In the present work, an octadecyl polyvinyl alcohol polymer (ODP) column, which was made of porous vinyl alcohol copolymer modified with octadecyl groups on the surface, was used as the concentrator column for enrichment of PAHs having 2 to 6 rings in seawater samples. The polymeric ODP column was more resistant to strong acid and basic solutions than commonly used silica-based octadecyl silyl (ODS) columns. Moreover, the polymeric ODP column showed selective retention power for PAHs compounds due to the existence of π-electron interaction between PAHs molecule and ODP polymer.[16] Therefore, we first compared the PAHs retention abilities on ODP and ODS columns. The recoveries of PAHs were higher on the polymeric ODP column than on the ODS column, indicating that the ODP column had stronger retention of PAHs and greater selectivity for PAHs. The elution profiles showed that PAHs were more stable on the ODP column than on the ODS column when the columns were loaded with PAHs and stored for several days before elution respectively. The higher stability on the ODP column might be because octadecyl polyvinyl alcohol polymers was more resistant to water than silica. For these reasons, an ODP column was selected for the concentrator column. The new ODP concentrator column was conditioned with 20 mL methanol and distilled water, respectively, at the flow rate of 0.5 mL min^{-1}.

The recoveries of PAHs depend on the flow rate of seawater, although a short time concentration is better. The peak heights were measured at flow rates from 0.5 to 2.0 mL min^{-1}, and the maximum peak heights were observed at flow rates of 0.5 and 1.0 mL min^{-1} for most PAHs. At flow rates over 1.0 mL min^{-1}, the peak heights decreased with the increase in the flow rate (Fig. 2). So, the flow rate was set at 1.0 mL min^{-1} for the following experiments.

The recoveries of PAHs were lower without the addition of ethanol. This might be attributed to the absorption of PAHs on the bottle walls due to the high hydrophobic property.[17,18] Here, methanol and ethanol were added to the water samples respectively. We found that 10% ethanol was just as effective as 10% methanol to decrease the adsorption of PAHs and that the recoveries of PAHs were constant at the concentrations over 10%. Considering that ethanol was nontoxic and safe to bring it on the ships, 10% ethanol was immediately added to the collected seawater samples after filtration. The seawater sample containing 10% ethanol was loaded on the column at 1.0 mL min^{-1}. The column was washed with 15 mL distilled water after trapping the PAHs in order to remove the adsorbed interfering compounds and prevent salts out from the column.

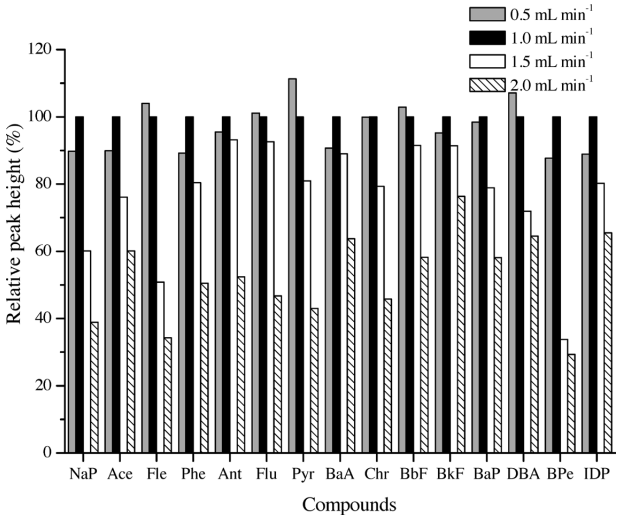

Fig. 2. Effect of Flow Rate of Pump 1 on the Relative Peak Height of PAHs

The samples were the spiked artificial seawater samples and the spiked concentration was shown in the text. The loading volume was 100 mL. The peak height at flow rate of 1.0 mL/min was defined as 100%.

The breakthrough volume was tested to evaluate the maximum sample volume which can be applied with a theoretical 100% recovery. The different volume of artificial seawater samples containing a constant concentration of analyte were treated as described in 'On-line Concentration and Determination HPLC System for PAHs in Seawater.' When the breakthrough volume of analyte began, this relationship started to deviate from linearity.[19] There was no deviation from linearity observed when the tested volume was changed from 100 to 1000 mL. The relationships between the peak height ratios of PAHs and their respective internal standards against the sample volume were linear. This result suggested that the concentrator column (ODP) had enough capacity for concentrating PAHs in seawater samples and the breakthrough volume of the column was larger than 1000 mL of the polluted seawater such as samples collected in harbors.

Performance of the Proposed Method In order to evaluate the practical applicability of the proposed system, performance parameters such as linearity, precision, limits of detection (LODs) and limits of quantization (LOQs) were measured under optimum analytical conditions using 100 mL artificial seawater samples spiked with PAHs. Results were given in Table 1. Concentrations of PAHs in the artificial seawater samples were as follows: Nap and Ace, 20 ng L^{-1}; Fle, Flu, BbF, DBA and BgPe, 4 ng L^{-1}; IDP, 3.2 ng L^{-1}; Phe, Ant, Pyr, BaA, Chr, BkF and BaP, 2.0 ng L^{-1}. All the PAHs showed good linearity with correlation coefficients (r) ranging from 0.951 to 0.998 (Table 1). Recoveries ranged from 74% (IDP) to 110% (Ant) with relative standard deviation (R.S.D.) of 1.5–9.4%. R.S.D.s were between 0.4–5.0% for repeatability (n=3) and 1.8–9.8% for reproducibility (n=5).

Limits of detection (LODs) (concentrations giving a signal-to-noise ratio of 3) ranged from 0.002 (Ant) to 0.50 ng L^{-1} (IDP) as the loading sample volume was 100 mL. LODs by the proposed method were smaller than those by GC-MS/MS

Table 1. Linearity, Recovery, Repeatability and Reproducibility of the Proposed Method[a]

PAHs	Linearity (r)	LOD (ng L^{-1})	LOQ (ng L^{-1})	Recovery±R.S.D. (%, n=5)	Repeatability (R.S.D., %, n=3)	Reproducibility (R.S.D., %, n=5)
Nap	0.951	0.042	0.14	98±1.5	0.9	5.6
Ace	0.970	0.013	0.042	95±1.5	1.6	7.7
Fle	0.984	0.020	0.067	101±2.4	0.4	8.4
Phe	0.976	0.011	0.036	93±4.2	4.7	5.8
Ant	0.998	0.002	0.007	110±6.8	2.4	5.3
Flu	0.988	0.030	0.10	88±9.4	4.9	9.8
Pyr	0.994	0.012	0.040	95±9.3	2.5	7.3
B*a*A	0.990	0.012	0.040	92±6.5	1.1	3.8
Chr	0.990	0.018	0.061	88±5.3	1.2	1.8
B*b*F	0.996	0.060	0.20	84±5.2	4.1	9.6
B*k*F	0.988	0.013	0.044	89±5.6	2.6	5.1
B*a*P	0.988	0.012	0.039	80±7.4	1.3	8.9
DBA	0.990	0.20	0.67	75±8.2	5.0	7.1
BgPe	0.986	0.22	0.73	79±7.3	2.3	9.1
IDP	0.986	0.50	1.7	74±7.7	1.8	8.9

a) Loading sample volume, 100 mL.

method coupled with solid phase microextraction and HPLC-fluorescence detection method coupled with nanoextraction recently reported.[8–12,17,20] Especially LODs of Ace, Ant, Pyr, BaA, Chr, BkF and BaP by the proposed method were 1/10 to 1/100 of the reported values.

On the other hand, artificial seawater samples spiked with 100 times higher concentrations of PAHs were prepared and 1.0 mL of the solution was loaded to the system. The slopes of the calibration curves and LOQs of PAHs were almost the same as those obtained above, suggesting that the proposed method is useful for both highly polluted and clean seawater samples.

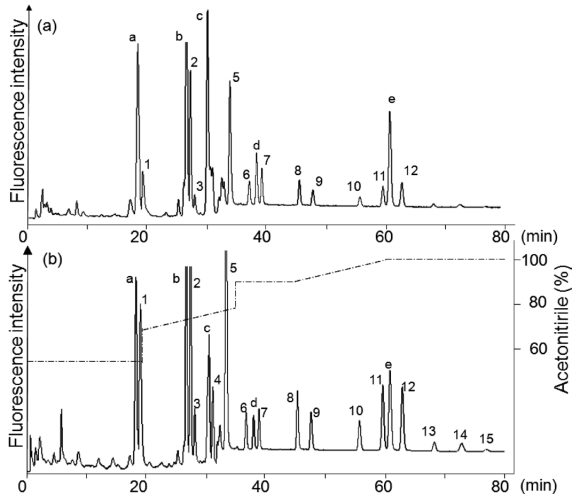

Fig. 3. Typical Chromatograms of (a) Real Japan Sea Water Sample and (b) Artificial Seawater Sample Spiked with PAHs

The sampling site of (a), S1. The spiked PAH concentrations, seen text; the dotted line in (b) indicated the acetonitrile concentration (%) in the mobile phase. Peaks: 1, Nap; 2, Ace; 3, Fle; 4, Phe; 5, Ant; 6, Flu; 7, Pyr; 8, BaA; 9, Chr; 10, BbF; 11, BkF; 12, BaP; 13, DBA; 14, BgPe; 15, IDP; a, Nap-d_8; b, Ace-d_{10}; c, Phe-d_{10}; d, Pyr-d_{10}; e, BaP-d_{12}.

PAHs Concentrations in Japan Sea Samples The proposed method was applied to seawater samples collected from the Japan Sea to investigate the stage. Figure 3 showed representative chromatograms of the Japan Sea water and a spiked artificial seawater sample obtained by the proposed method under the optimized conditions. The loading volume was 100 mL. Table 2 showed the concentrations of PAHs at the five sampling sites. Average concentrations ranged from 0.1 (Ant) to 22.9 (Nap) ng L^{-1} in the southwest part of the Japan Sea. Nap, a 2-ring PAH, was the predominant compound. BaA, BbF and BkF, whose concentrations were lower than LODs the reported in traditional methods, were quantified by the proposed method. DBA, BgPe and IDP showed trace peaks in Fig. 3, although they were lower than the LODs. The recoveries of PAHs spiked to the Japan Sea samples showed similar result as that of the spiked artifical seawater samples. These results suggested that the proposed method could determine PAHs at sub ppt (ng L^{-1}) in marine water.

Recovery of Beaches Damaged by Oil Spilled from Nakhodka from the View Point of BaP Finally the BaP concentration was determined in seawater samples collected at two beaches (Kaiso and Hagahashi) in Noto Peninsula, which were heavily damaged by the beached oil from the Nakhodka in January 1997, in Table 3. The BaP concentrations at Kaiso (8.1 ng L^{-1}) and Nagahashi (7.4 ng L^{-1}) were very high one month after the accident and decreased with time. Then the concentrations at 3 years after the accident (April, 2000) became to the normal level of the Japan Sea (0.2–0.3 ng L^{-1}).

Conclusion

An on-line HPLC system for concentrating and determining PAHs in small volume seawater samples was proposed with the advantages of automatic, simple and on-line sampling pretreatment. The polymeric ODP column concentrated PAHs in the samples with excellent matrix removal, and on-line elution and determination through switching valve guaranteed the

Table 2. Concentrations (ng L^{-1}) of PAHs Collected at Different Sampling Sites in the Japan Sea

Method	Proposed work						MASE[a]-GCMS[21]	LLE-GCMS[8]	SPE-HPLC[9]
Sampling site	Japan Sea						Bilbao, Spain	Alexandria Coast, Egypt	Saronikos Gulf, Greece
	S1[b]	S2	S3	S4	S5	Ave.±S.D.			
NaP	23.9	26.0	23.9	23.7	16.8	22.9±3.5	166	n.d.[c]	160
Ace	1.5	1.7	1.5	1.2	1.3	1.4±0.2	110	n.d.	41
Fle	1.6	1.6	1.6	1.2	1.3	1.5±0.2	37	2.1	42
Phe	i.p.[d]	i.p.	i.p.	i.p.	i.p.	—	118	14.8	54
Ant	0.1	0.1	0.1	0.1	0.1	0.1±0	76	3.8	30
Flu	1.5	1.6	1.5	1.6	1.4	1.5±0.1	21	6.7	34
Pyr	0.8	1.0	0.8	0.7	0.9	0.8±0.1	30	5.6	18
BaA	0.1	0.2	0.1	0.1	0.3	0.2±0.1	n.d.	n.d.	—
Chr	0.2	0.2	0.2	0.2	0.4	0.3±0.1	n.d.	5.1	—
BbF	0.6	0.6	0.6	0.5	0.5	0.6±0.1	9	n.d.	55
BkF	0.3	0.4	0.3	0.2	0.2	0.3±0.1	10.1	n.d.	—
BaP	0.2	0.3	0.2	0.2	0.2	0.2±0.1	9.7	9.0	25
DBA	n.q.[e]	n.q.	n.q.	n.q.	n.q.	—	n.d.	n.d.	—
BgPe	n.q.	n.q.	n.q.	n.q.	n.q.	—	n.d.	n.d.	—
IDP	n.q.	n.q.	n.q.	n.q.	n.q.	—	n.d.	n.d.	—
Total	30.8	33.7	30.8	29.7	23.4	29.7±3.8	679	47.0	459

a) MASE, membrane-associated solvent extraction; *b*) sampling site (locations of each sampling site seen text); *c*) not detected; *d*) not quantified because of the interfering peaks; *e*) detected but not quantified because lower than LOD.

Table 3. BaP Concentrations ($ng\,L^{-1}$) in Seawater Samples Collected at Beaches in Noto Peninsula Damaged by Nakhodka Spilled Oil in 1997 and South Part of the Japan Sea

Sampling date	Noto peninsula		Japan Sea (ave. of S1–5)
	Kaiso	Nagahashi	
Feb., 1997	8.1[a)]	7.4[a)]	—[b)]
Jan., 1998	1.6[a)]	—	—
April, 2000	0.3[a)]	0.2[a)]	—
April, 2008	0.2	0.2	0.2

a) Cited from ref. 3. *b*) Sample was not collected.

higher sensitivity than currently available systems. Thus the proposed method which required a small volume sample was successfully applied for the determination of PAHs in not only polluted seawater but also clean background seawater. This is the first report to determine the normal levels of PAHs. This method also found that the BaP concentration in seawater at beaches in Noto Peninsula which were damaged by the oil spill in 1997 had become to the normal level.

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