QUANTUM DOTS EXTRACTION COUPLED WITH HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER

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Abstract. A novel alternative method is presented for the extraction and preconcentration of polycyclic aromatic hydrocarbons (PAHs) from water samples. This new approach takes advantage of the strong affinity that exists between PAHs and N-acetyl-L-cysteine modified CdS quantum dots (NAC-CdS QDs). The NAC-CdS QDs were synthesized in our own laboratory. Twelve different PAHs in tap water samples were preconcentrated by NAC-CdS QDs before high-performance liquid chromatography with fluorescence detection (HPLC-FLD). The test results suggest that the limits of detection (LODs) for the PAHs were from 1.0 to 100 ng/L with the relative standard deviations ranging from 0.4 to 2.8% and the recoveries were varied from 74.3 to 95.9%, respectively. The entire extraction procedure with this novel pretreatment just consumes 1 mL organic solvents per sample, which makes it environmentally friendly and cost effective.
Keywords: *preconcentration; NAC-CdS quantum dots; HPLC-FLD; PAH, environmental chemistry; pollution*

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of more than 100 chemically different organic substances that are generally composed of two or more aromatic (benzene) rings (Pazos et al., 2010). They are well-known environmental pollutants originating from natural processes and human activities (Chen et al., 2008; Kobayashi et al., 2008; Gao et al., 2016; Murakami et al., 2008). Chemical analysis of PAHs is of great environmental and toxicological importance as many PAHs have been identified as potent mammary carcinogens in experimental bioassays (Elbayoumy, 1992). Exposures to PAHs have been linked to increased cancer risks in epidemiological studies (Mastrangelo et al., 1996; Maertens et al., 2008; Williams et al., 2013). The U.S. Environmental Protection Agency (EPA) lists the following 16 compounds as "Consent Decree" priority pollutants: benz [a] anthracene, benzo [b] fluoranthene, benzo [k] fluoranthene, benzo [a] pyrene, dibenzo [a, h] anthracene, indeno [1, 2, 3-cd] pyrene, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, and benzo [g, h, i] perylene (Wang and Campiglia, 2008).

Due to their hydrophobicity, PAHs are inclined to adsorb to and accumulate with particles such as dust, sediment and debris, Atmospheric PAHs may undergo photolytic and chemical (ozone) transformations or be deposited back to land (Rauscher et al., 2012; Xie and Haleegoah, 2016). A primary route of human exposure to PAHs is the ingestion of contaminated water, which is one of the indispensable materials in daily human life. Therefore, great attention was paid to the research on PAHs. Because of their low concentration in drinking water samples, the determination of PAHs in such samples often needs tedious sample preparation prior to analysis (Hawthorne et al., 2008; Wu et al. 2010).

Various instrumental methods for the analysis of PAHs have been developed which include gas chromatography (GC) with mass spectrometry (MS) detector (Tseng et al., 2014; Zhang et al., 2015), high performance liquid chromatography (HPLC) with fluorescence detector (FLD) (Capelo et al., 2005; Andrade-Eiroa et al., 2010), photodiode array (PDA) (Andrade-Eiroa et al., 2014), mass spectrometry (MS) (Zhao et al., 2013) and laser-excited time resolved Shpol'skii spectroscopy (LETRSS) (Wilson and Campiglia, 2011), respectively. Compared to other methods, HPLC is the best method for direct determination of PAHs in environmental waters due to its ability to deal with thermally unstable, high-molecular-mass organic chemicals. However, the sensitivity and selectivity of the analytical techniques are usually insufficient for direct determination of PAHs at very low concentration in complex environmental samples. Therefore, there is a crucial demand for rapid and simple preparation techniques, especially extraction techniques, for evaluating and monitoring PAHs from different environmental water samples at trace levels (Smoker et al., 2010; Pena-Pereira et al., 2012; Wang et al., 2015). Due to its enrichment and high recovery of analytes, simplicity and speed of operation, reduction of sample matrix effects, and low organic solvent consumption, solid-phase extraction (SPE) combined with HPLC or GC (Zhou et al., 2006; Pereira et al., 2009; Jin et al., 2010; Hu et al., 2014) is one of the most preferred methods for analyzing PAHs in water samples. Adsorption materials, such as stir bar, (porous metal membranes (Xie et al., 2011), silica based matrices (Krauss and Wilcke, 2001; Brown and Peake, 2003; Oleszczuk and Baran, 2004; Lesellier, 2011), functionalized magnetic nanomaterials (Zhang et al., 2010; Huo and Yan, 2012; Zou et al., 2013), carbon nanotubes (Wang et al., 2007; Bagheri et al., 2011; Kah et al., 2011), metal-organic frameworks (Pan et al., 2013), gold nanoparticles (Lin and Tseng, 2013) and immunosorbent (Perez and Barcelo, 2000) have been recently used for SPE of PAHs. However, some of these materials require multistep preparation or synthetic processes that make them not favorable in sample preparation in terms of simplicity, efficiency and cost-effectiveness.

Quantum dots (QDs) are nanoparticles with a typical size of 2-20 nanometers (nm) and are usually composed of atoms from groups II-VI or III-V of the periodic table. The applications of QDs have been reported in a medical field as the bio-markers (Bruchez et al., 1998; Chan and Nie, 1998) and in environment field as the fluorescent probe (Wu

et al., 2009; Zhao et al., 2012). To the best of our knowledge, there is no report on the use of QDs for pre-concentration purposes.

In this article, N-acetyl-L-cysteine (NAC) modified CdS quantum dots (NAC-CdS QDs) were synthesized and were used to achieve the intention of pre-concentration. Fourteen polycyclic aromatic hydrocarbons (PAHs) were selected as model compounds to examine the feasibility of this approach. What's more, our approach is based on the physicochemical affinity that exists between PAHs and QDs. Carefully optimization of experimental parameters has led to this pretreatment method and an HPLC method with fluorescence detection. To our knowledge, it is the first work to use NAC-CdS QDs for the pre-concentration of organic pollutants from environmental aqueous samples.

Experimental section

Chemicals

All chemicals or reagents were of analytical grade. *All* solvents used *were* HPLC grade. Acetonitrile (≥99.9%) and N-acetyl-L-cysteine (99%) were purchased from Aladdin Industrial Corporation (Shanghai, China). Analytical grade normal-octane was from Tianjin East chemical reagent factory (Tianjin, China) while $CdCl_2·5H_2O$ (99.0%) and $Na_2S·9H_2O$ (98.0%) were purchased from Tianjin Fu Chen chemical reagent company (Tianjin, China). Water was purified using a HUMAN UP900 system (Korea). All PAHs standards were acquired from Dr. Ehrenstorfer Company (Augsburg, Germany) and used with no further purification.

Equipment and software

The equipment was composed of a Waters e2695 Series liquid chromate graph (Singapore) with a quaternary pump, a vacuum degasser, an auto sampler, a thermostatted column compartment, a Waters e2475 FLD detector and an Empower data processing system. Steady state excitation and fluorescence spectra and signal intensities were recorded via room-temperature fluorescence from undegassed solutions using Cary Eclipse fluorescence spectrophotometer (Varian, Palo Alto, CA, USA) equipped with a 1.0 cm quartz cell. The data was processed on an Empower Pro data processing system for all the analysis.

Solution preparation

Stock PAH solutions were prepared in acetonitrile and stored in the dark at 4 °C. Possible PAHs degradation was monitored via room-temperature fluorescence spectroscopy. PAHs working standard solutions for calibration were prepared by serial dilution of primary working standard solutions with the appropriate solvent. NAC-CdS QDs were stored in darkness at 4 °C. The primary working standard solutions contained 150 ng/mL for Chrysene, Phenanthrene and benzo (b) fluoranthene, 20.0 ng/mL for

Pyrene, Benzo (a) anthracene and Benzo (a) pyrene, 900 ng/mL for Anthracene, 500 ng/mL for Acenaphthene, 1000 ng/mL for Fluorene, 2000 ng/mL for Naphthalene, 400 ng/mL for Benzo (g, h, i) perylene and 500 ng/mL Dibenzo (a, h) anthracene. All working standard solutions were filtered through syringe filters (0.45 μm) before injection into the HPLC-FLD system.

Synthesis of NAC-CdS QDs

NAC-CdS QDs were synthesized via the procedures described by Koneswaran and Narayanaswamy (2009) with some modification. Briefly, $CdCl_2$ (146.5 mg, 2.5 mmol), NAC (107.3 mg, 0.7 mmol) and water (150 mL) were loaded into a 250 mL three-neck flask. The pH of the solution in the flask was adjusted to 8-9 with 1 ml of 1.0 M NaOH solution and then the solution was stirred for 0. 5h at 140 °C under N_2 flow. 10 mL $Na_2S \cdot 9H_2O$ (5 mM) aqueous solution was added by drops into the above solution under vigorous magnetic stirring. After stirring for another 0.5 h, the NAC-CdS QDs were collected by centrifugation at 13500 rpm for 10 min. The resulting NAC-CdS QDs were purified and precipitated with acetone, and finally stored in darkness at 4 °C.

Sample preparation

A amount of 500 μL water sample and appropriate amount NAC-CdS QDs (2.25 μmol/L) were mixed with an SHZ-S2 Thermostat oscillator manufactured by Changzhou AoHua Instrument Co., LTD (Changzhou, China). Centrifugation was performed with a TG16A-WS centrifuge (Shanghai, China) with a maximum rotational speed of 16000 rotations per minute (rpm).

HPLC analysis

Considering the PAHs' structure, a phenyl column, YMC-Ph column (25cm x 4mm, 5μm) from YMC Co., Ltd (Ishikawa, Japan), was used for method development. The details of LC conditions are shown in *Table 1*. Laboratory reagent blanks were run in each analytical batch to ensure the absence of contamination and carried over.

Table 1. *Gradient elution scheme for the HPLC-FLD method.*

Time (min)	Water (%, v/v)	Acetonitrile (%, v/v)	Column temperature (℃)	Flow rate (mL/min)
0	50	50	28	0.8
20	40	60	28	0.8
30	25	75	28	0.8
32	25	75	28	0.8
35	50	50	28	0.8

Results and discussion

Optimization of HPLC analysis

The strategy used to evaluate the pre-concentration of PAHs with NAC-CdS QDs included the two common features of current SPE-HPLC methodology: (a) extraction of the PAHs from drinking water samples with NAC-CdS QDs; (b) elution of PAHs from the NAC-CdS QDs precipitation with n-octane prior to chromatographic determination. PAHs recoveries were monitored via HPLC analysis. *Table 1* summarizes the settings and conditions for the complete chromatographic separation of the studied PAHs. The mobile phases are water and acetonitrile, respectively. Satisfactory resolution of the 12 PAHs was achieved with an acetonitrile /water mobile-phase gradient. The flow rate is set at 0.8 mL/min and the column temperature is held at 28 °C. The gradient elution program is initialized with 50% acetonitrile, increased to 60% acetonitrile within 20 min and increased to 75% in another 10 min, held for 2 min, and then backed to 50% acetonitrile within 3 minutes and held for 5 min to wash and recondition the column prior to the next run. The separation time was about 31 min. All sample injections were held constant at 3 µL. PAHs in the fluorescence detection mode were obtained using parameters shown in *Table 2*. In cases where contiguous PAHs elution was too fast for individual wavelength optimization, a compromise was made among the maximum excitation/emission wavelengths of the contiguous PAHs.

Table 2. *Excitation and emission wavelength program for HPLC fluorescence detection.*

PAHs	Time (min)	Excitation (nm)	Emission (nm)
Naphthalene	13.6	217	330
Acenaphthene	16.9	247	400
Fluorene	17.5	260	310
Phenanthrene	18.6	245	365
Anthracene	19.3	355	400
Pyrene	21.4	332	391
Chrysene	25.0	262	381
Benzo(a)anthracene	25.5	282	388
Benzo(b)fluoranthene	27.6	255	435
Benzo(a)pyrene	27.9	260	406
Benzo(g,h,i)perylene	29.8	295	411
Dibenzo(a,h)anthracene	30.8	294	396

Fig. 1 shows a typical chromatogram with the complete separation of the twelve PAHs. Three chromatographic runs of the same standard mixture recorded from three independent injections provided the following average retention times (min): 13.6 (naphthalene), 16.9 (acenaphthene), 17.5 (fluorene), 18.6 (phenanthrene), 19.3

(anthracene), 21.4 (pyrene), 25.0 (chrysene), 25.5 (benz [a] anthracene), 27.6 (benzo [b] fluoranthene), 27.9 (benzo [a] pyrene), 29.8 benzo [g, h, i] perylene) and 30.8 (dibenzo [a, h] anthracene). The distinct values of the experimental averages show the possibility to identify the twelve PAHs from their retention times. As can be seen, the resolution of benzo [b] fluoranthene and benzo [a] pyrene was not very well (R=0.9). In fact, such low resolution between benzo [b] fluoranthene and benzo [a] pyrene did not have significant impacts on our analysis of the sample investigated.
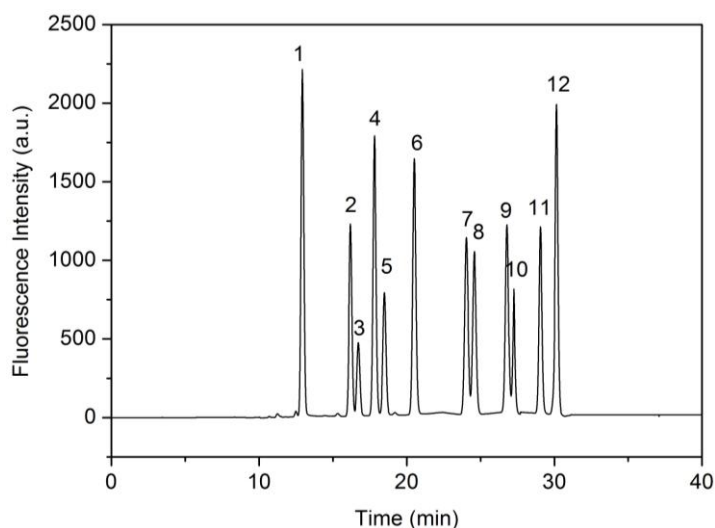

Figure 1. *Typical HPLC chromatogram of 12 PAHs stand mixture containing 75.0 ng/mL Chrysene, Phenanthrene and Benzo(b)fluoranthene, 10.0 ng/mL Pyrene, Benzo(a)anthracene and Benzo(a)pyrene, 450 ng/mL Anthracene, 250 ng/mL Acenaphthene, 500 ng/mL Fluorene, 1000 ng/mL Naphthalene, 20.0 ng/mL Benzo(g,h,i)perylene and 25.0 ng/mL Dibenzo(a,h)anthracene at selected operational conditions. Peaks: (1) Naphthalene, (2) Acenaphthene, (3) Fluorene, (4) Phenanthrene, (5) Anthracene, (6) Pyrene, (7) Chrysene, (8) Benzo(a)anthracene, (9) Benzo(b)fluoranthene, (10) Benzo(a)pyrene, (11) Benzo(g,h,i)perylene, (12) Dibenzo(a,h)anthracene.*

Preliminary studies on the interaction of PAHs with QDs

To conduct the interaction of PAHs with QDs, three different QDs were synthesized in our lab including NAC-CdS, Gold Nanoparticles protected by 1H-1,2,4-Triazole-3-thiol (TRO-AuNCs) as well as Bovine serum albumin modified Gold Nanoparticles (BSA-AuNCs). PAHs extraction was immediately tested using benzo[a]pyrene as the model compound. The 500 µL QDs were mixed with 500 µL of 2.0 µg/mL benzo [a] pyrene acetonitrile solution, respectively. After shaking for 30 min and centrifugation for additional 10 min, the NAC-CdS can be precipitated obviously, the precipitate was separated by carefully removing and collecting the supernatant with a micropipette. TRO-AuNCs and BSA-AuNCs did not have obvious changes. Room-temperature

fluorescence spectra of the NAC-CdS and CdS liquid solutions confirmed the reduction of benzo [a] pyrene in the supernatant, therefore, it may be adsorbed to the surface of NAC-CdS precipitation. Furthermore, the reduction observed in NAC-CdS supernatant was more obviously than that of CdS supernatant. Therefore, all further studies were carried out with NAC-CdS QDs.

The concentration of the NAC-CdS QDs

The concentration of the NAC-CdS QDs generated in our lab was 3.7×10^{-4} M. 1.0 μg/mL benzo [a] pyrene in acetonitrile was used as a model compound to study the relationship between the concentration of NAC-CdS QDs and extraction efficiency of PAHs. The extraction procedure consisted of shaking 1.0 μg/mL benzo [a] pyrene acetonitrile solution spiked with different concentration of NAC-CdS QDs for 30 min followed by centrifugation for 10 min. The shaking time was found to be long enough to achieve maximum PAHs extraction at 300 rpm. The signal intensities from the supernatants were measured by room-temperature fluorescence. As shown in *Fig. 2*, the fluorescence intensity of benzo [a] pyrene in supernatants decreased with adding the higher concentration of the NAC-CdS. The concentration of the NAC-CdS and F/F_0 (F is the intensities of NAC-CdS and benzo [a] pyrene in supernatants; F_0 is the intensity of benzo [a] pyrene in acetonitrile solution.) are in good linear relationship. When NAC-CdS concentration was up to 2.25 μmol/L, 1 mL 1.0 μg/mL benzo[a]pyrene can be complete extracted. Thus, 2.25 μmol/L NAC-CdS QDs solution was selected in our further studies.

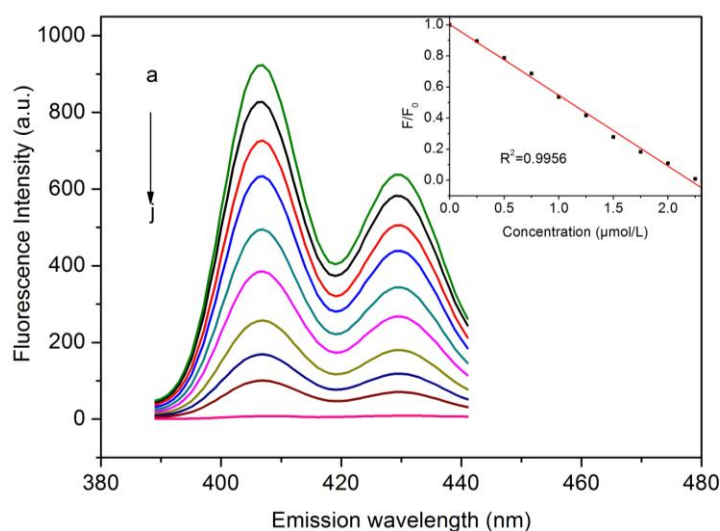*Figure 2. Relationship between the concentration of NAC-CdS QDs and decresed fluorescence intensity of 1.0 μg/mL Benzo(a)pyrene standard solution, F is the intensities of NAC-CdS and benzo[a]pyrene supernatants; F0 is the intensity of benzo[a]pyrene acetonitrile solution. a: 0.00, b: 0.25, c: 0.50, d: 0.75, e: 1.00, f: 1.25, g: 1.50, h:1.75, i: 2.00 and j: 2.25 μmol/L. Inset: the linear plot.*

Maximum amount of extractable PAHs

The extraction steps were the same as the described before. In addition to the blank samples, the concentration of NAC-CdS QDs was held invariable in all extraction steps (2.25 µmol/L) while PAHs concentrations were varied within their respective linear ranges. PAHs extraction was supervised via room-temperature fluorescence spectroscopy by comparing the intensities of supernatants to PAHs standard solutions with the same experimental procedure but in the absence of NAC-CdS QDs.
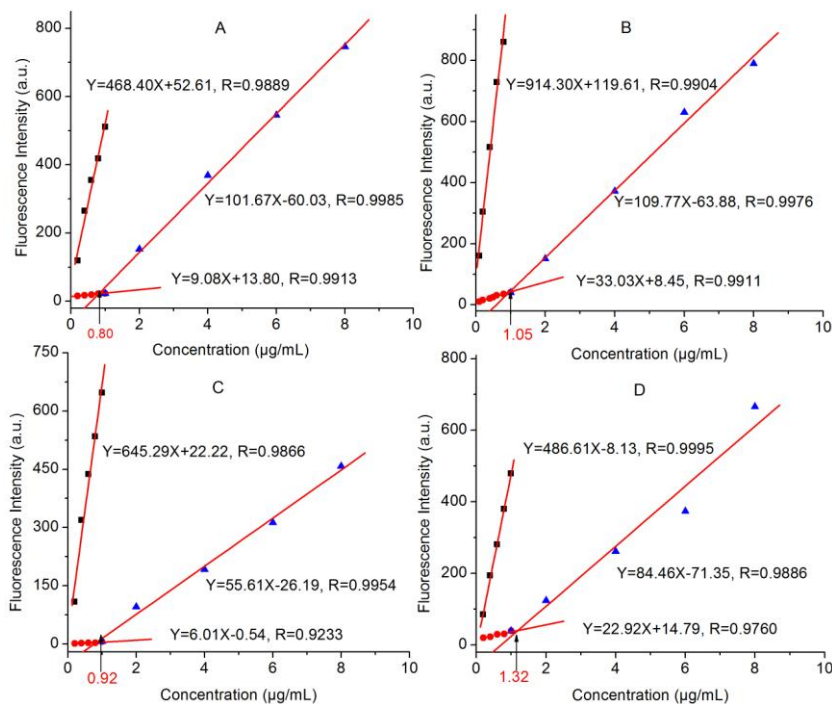

Figure 3. *Fluorescence intensity as a function of PAHs concentration (µg/mL): (A) Phenanthrene, (B) Benzo(a)pyrene, (C) Chrysene, (D) Naphthalene. Signal intensity were recorded from PAHs standard solution (■) and from supernatants of PAHs standards previously extracted with 2.25 µmol/L NAC-CdS QDs (▲) and (●).*

Four model PAHs, namely, naphthalene, phenanthrene, chrysene and benzo [a] pyrene, were selected as representative compounds of PAHs containing 2, 3, 4, and 5 rings, respectively. *Fig. 3* shows the experimental results obtained for the model PAHs studied in this work. All linear fittings were made with concentration and fluorescence intensities. The straight lines associated the data points marked as (■) correspond to the fluorescence intensities of PAHs standard solutions in the lack of NAC-CdS QDs. The straight lines correlating the data points marked as (▲) and (●) represent the fluorescence intensities of supernatants after centrifugation with 600 µL 2.25 µmol/L NAC-CdS QDs. As can be seen in *Fig. 3*, the fluorescence intensities within the (●) segments were almost equivalent to the blank signals in a concentration ranging from 0

to 1.0 µg/mL. This fact may be caused by the absence of PAHs in the supernatants, but the disappeared PAHs may be completely adsorbed on the surface of NAC-CdS QDs. Fluorescence intensities within the (▲) data points were obviously higher than the intensities in blank signals (●) and increased linearly with the nominal PAHs concentrations. After extraction, the majority of PAHs were adsorbed on the surface of NAC-CdS QDs and the PAHs concentration was decreased dramatically. Therefore, the signal intensities in the (▲) segments were much lower than the intensities in the (■) segments. The maximum concentration of extracted PAHs can be estimated by the intercepts of (▲) and (●) segments. Except the four model PAHs, other PAHs were also tested in the same way. *Table 3* lists the maximum PAHs concentration that 2.25 µmol/L NAC-CdS QDs solution can extract from individual PAHs standard solutions. Those concentrations tested are well above PAHs concentrations usually encountered in tap water samples.

Table 3. Maximum amount of PAHs extracted with 2.25 µmol/L NAC-CdS QDs.

PAHs[a]	Max Concentration (ng/L)[b]
Naphthalene	1.3×10^6
Acenaphthene	0.9×10^6
Fluorene	0.6×10^6
Phenanthrene	0.8×10^6
Anthracene	1.0×10^6
Pyrene	0.9×10^6
Chrysene	0.6×10^6
Benzo(a)anthracene	0.8×10^6
Benzo(b)fluoranthene	2.7×10^6
Benzo(a)pyrene	1.0×10^6
Benzo(g,h,i)perylene	1.0×10^6
Dibenzo(a,h)anthracene	1.6×10^6

Releasing PAHs for HPLC analysis

The forethought strategy to recover PAHs molecules from the surface of NAC-CdS QDs was to use an organic solvent with strong binding affinity for PAHs, which would release PAHs to the surrounding medium. Several solvents were attempted for this purpose including alcohols (methanol, ethanol, isopropyl alcohol), alkanes (toluene, cyclohexane, n-hexane).

PAHs extractions were implemented from 500 µL deionized water previously spiked with PAHs standards to make 75.0 ng/mL for Chrysene, Phenanthrene and Benzo (b) fluoranthene each, 10.0 ng/mL for Pyrene, Benzo (a anthracene and Benzo (a) pyrene each, 450 ng/mL for Anthracene, 250 ng/mL for Acenaphthene, 500 ng/mL for

Fluorene, 1000 ng/mL for Naphthalene, 20.0 ng/mL for Benzo (g, h, i) perylene and 25.0 ng/mL Dibenzo (a, h) anthracene. These concentrations (C_{PAHs}) are many times higher than the highest maximum contaminant level (200 ng/L) of regulated PAHs. After sample centrifugation, the supernatant (supernatant A) was separated from the centrifuge tube and collected for HPLC analysis. 1 mL n-hexane was added to the precipitate and the resulting mixture was shaken for 30 min at the 300 rpm and centrifuged for 10 min at 12000 rpm. And the supernatant (supernatant B) was separated from the precipitate and collected for HPLC analysis.

PAHs concentrations in supernatants A ($[PAHs]_A$) and B ($[PAHs]_B$) were determined via the calibration curve method. The calculated the overall recovery (OR), the extraction efficiency (E) and the releasing efficiencies (RE). The best releasing efficiencies were obtained with n-hexane. *Table 4* summaries the OR, E, and RE values obtained with n-hexane.

Table 4. *Recoveries for the NAC-CdS QDs extraction procedure.*

PAHs[a]	OR (%)[b]	E (%)[c]	RE (%)[d]
Naphthalene	73.0	85.3	85.6
Acenaphthene	77.1	85.8	89.8
Fluorene	75.0	69.6	79.0
Phenanthrene	91.0	98.8	92.1
Anthracene	74.1	92.1	80.4
Pyrene	73.0	99.7	73.1
Chrysene	72.6	95.1	76.3
Benzo(a)anthracene	79.0	87.7	90.1
Benzo(b)fluoranthene	75.7	84.8	89.2
Benzo(a)pyrene	82.8	88.8	93.2
Benzo(g,h,i)perylene	75.0	95.2	78.8
Dibenzo(a,h)anthracene	75.1	97.9	76.6

Comparison of SPE to the NAC-CdS QDs procedure

To compare the evaporation step to the NAC-CdS procedure, a traditional SPE procedure was also conducted in our study. Neutral alumina was chosen as the adsorbent, and the elution solvent was methylene chloride. After SPE, the elution solvent was dried in a rotary evaporation instrument and then the residue was reconstituted in 1 mL acetonitrile. The acetonitrile solution was filtered through a syringe filter (0.45 μm) prior to injection into the HPLC-FLD. *Table 5* summarizes the PAHs recoveries obtained via the SPE procedure and those obtained with the NAC-CdS QDs procedure. Standard mixtures of the PAHs were prepared in pure acetonitrile and spiked in 500 μL tap water samples to provide three different concentration levels. In

Table 5, some of the PAHs spiked concentrations exceed their solubility in water, but the appropriate percent of acetonitrile in spiked water samples can solve this problem. The water samples were collected in our lab. The PAHs concentration in the SPE eluting solvent (acetonitrile) and the final extract of the NAC-CdS procedure were monitored via HPLC analysis using calibration curves built with a minimum of six standard solutions. As compared to SPE procedure, a remarkable improvement of the recoveries is observed with the NAC-CdS procedure at low and high spiked levels as shown in *Table 5*. A better precision was achieved as well when using NAC-CdS procedure at both medium and high spiked levels. Such results indicate our methods for sample preparation is superior to conventional SPE.

Table 5. *PAHs recoveries from tap water samples via SPE-HPLC and NAC-CdS-HPLC analysis.*

PAHs[a]	Spiked, ng/L	SPE[b]		NAC-CdS[c] Extraction	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Naphthalene	600	34.2	1.5	75.5	2.8
	1200	64.6	1.9	80.3	1.9
	6000	16.1	2.1	85.8	1.3
Acenaphthene	150	43.5	0.4	74.3	2.1
	300	71.0	1.5	76.3	1.0
	1500	27.4	1.3	81.4	1.2
Fluorene	300	53.6	0.2	75.1	2.6
	600	94.6	2.0	76.7	1.4
	3000	54.8	1.0	78.7	1.6
Phenanthrene	45.0	52.7	0.2	74.4	2.7
	90.0	90.9	1.3	71.2	1.9
	450	57.6	0.8	84.8	1.4
Anthracene	150	45.3	0.3	72.6	2.4
	300	72.3	4.9	79.3	1.0
	1500	28.4	3.4	76.9	1.3
Pyrene	6.0	57.8	0.5	75.1	0.7
	12.0	98.0	1.3	77.2	0.8
	60.0	85.3	3.2	72.8	0.9
Chrysene	45.0	43.7	1.5	88.8	1.2
	90.0	71.7	0.8	85.3	0.4
	450	22.8	2.0	79.7	0.5
Benzo(a)anthracene	6.0	64.1	0.4	79.2	1.5
	12.0	87.5	1.3	80.5	0.5
	60.0	74.7	2.3	84.3	0.4
Benzo(b)fluoranthene	45.0	38.0	1.5	80.6	1.9
	90.0	58.9	2.2	90.2	0.9
	450	75.1	4.1	89.6	1.0
Benzo(a)pyrene	6.0	70.2	1.0	92.4	1.9
	12.0	79.5	4.8	92.5	1.4
	60.0	50.5	0.8	95.9	1.4
Benzo(g,h,i)perylene	12.0	46.5	0.2	82.7	1.7
	24.0	78.3	3.2	81.6	1.6
	120	63.8	1.3	90.1	1.6
Dibenzo(a,h)anthracene	15.0	48.5	0.8	77.0	1.6
	30.0	69.8	1.8	84.3	1.1
	150	59.8	3.3	87.7	1.4

Method validation

Table 6 summarizes the analytical figures of merit obtained via NAC-CdS –HPLC analysis. All linear dynamic ranges are based on the average intensities of at least six PAHs concentrations. The LODs for each analyte was estimated at a concentration level at which the S/N reached 3:1. The concentration level accepted as the LOQs was the one giving a peak with an S/N of at least 10:1. The excellent correlation coefficients (R) demonstrate the good linear relationships in all cases. The limits of detection varied from 1.0 to 100 ng/L. Although a straightforward LODs comparison to those reported in the literature via HPLC is challenge as different instrumental setups, experimental and mathematical approaches have been used for their calculation, our LODs (1.0 to 100 ng/L) are comparable to those (0.9-58 ng/L) of Wang and Campiglia who developed a method for the determination of polycyclic aromatic hydrocarbons in drinking water samples by solid-phase nano extraction and high-performance liquid chromatography (Wang and Campiglia 2008). All LODs in our study are well below maximum contaminant level of regulated PAHs (10-200 ng/L) (Winslow et al., 2001). The relative standard deviations (RSD) demonstrate a excellent precision of measurements in our study at the trace concentration level.

Table 6. *Analytical figures of merit via NAC-CdS-HPLC.*

| | **Parameters** | | | | | | |
| | Method sensitivity | | | Regression equation data, Y(EU)=A × concentration ±B | | | |
Analyst	LOD, ng/L	LOQ, ng/L	Concentration range, ng/L	Slope (A)	Intercept(B)	Standard Deviation of residuals	Residual sum of squares	Correlation coefficient (R^2)
Naphthalene	50.0	150.0	150.0-20× 10^5	1.938e+006	4.716e+005	2.303e+013	2.122e+013	0.9997
Acenaphthene	25.0	75.0	750.0-5× 10^5	2.207e+006	6.255e+006	2.565e+013	2.633e+013	0.9994
Fluorene	100.0	300.0	300.0-10× 10^5	4.361e+006	3.015e+005	2.325e+006	2.704e+013	0.9989
Phenanthrene	3.7	10.0	10.0-1.5× 10^5	2.640e+004	1.562e+007	6.131e+005	1.503e+012	0.9999
Anthracene	90.0	200.0	200.0-90× 10^5	6.493e+005	2.424e+006	2.092e+005	1.312e+011	0.9999
Pyrene	1.0	3.0	3.0-0.2× 10^5	4.654e+006	1.490e+008	5.480e+006	1.201e+014	0.9981
Chrysene	7.5	25.0	25.0-1.5× 10^5	6.215e+005	2.525e+007	1.541e+006	9.509e+012	0.9996
Benzo(a) anthracene	1.0	3.0	3.0-0.2× 10^5	5.907e+006	2.480e+008	2.138e+006	1.828e+013	0.9995
Benzo(b) fluoranthene	15.0	45.0	45.0-1.5× 10^5	3.622e+006	1.260e+007	2.162e+006	1.870e+013	0.9998
Benzo(a)pyrene	1.0	3.0	3.0-0.2× 10^5	4.487e+007	2.638e+008	1.029e+007	4.239e+014	0.9917
Benzo(g,h,i) perylene	2.0	6.0	6.0-0.4× 10^5	7.638e+007	8.754e+007	8.988e+006	3.231e+014	0.9984
Dibenzo(a,h) anthracene	1.2	3.0	3.0-0.5× 10^5	8.338e+007	7.292e+007	6.548e+006	1.715e+014	0.9982

PAHs detection in water samples

The applicability to detect PAHs in tap water was investigated with the tap water in our lab in Nanchong. Milliliter volumes of tap water were spiked with microliter volumes of PAHs standard solutions to provide three final concentrations levels listed in *Table 5*. NAC-CdS QDs extraction analysis was carried out with 500 µL tap water. *Table 5* summaries the average recoveries and their standard deviations for the tested sample. The relative standard deviations varied from 0.4 to 2.8%. The recoveries of the twelve regulated PAHs from tap water samples of unknown composition varied from 74.3 to 95.9%.

Conclusions

This study has found a approach to improving the analytical figures of merit of SPE-HPLC for the analysis of PAHs in tap water samples was developed via the use of NAC-CdS QDs synthesized by ourselves to pre-concentrate PAHs. Our procedure is simple and fast as there is no SPE involved but shaking, centrifugation, separation and reconstitution. The reason for the adsorption between PAHs and NAC-CdS QDs is not clear yet and further studies may be needed to understand the interaction between them.

REFERENCES

[1]   Andrade-Eiroa, A., Leroy, V., Dagaut, P., Bedjanian, Y. (2010): Determination of polycyclic aromatic hydrocarbons in kerosene and bio-kerosene soot. - Chemosphere 78: 1342-1349.

[2]   Andrade-Eiroa, A., Shahla, R., Romanias, M. N., Dagaut, P. (2014): Correction: An alternative to trial and error methodology in solid phase extraction: an original automated solid phase extraction procedure for analysing PAHs and PAH-derivatives in soot. - RSC Advances 4: 42271-42271.

[3]   Bagheri, H., Ayazi, Z., Aghakhani, A. (2011): A novel needle trap sorbent based on carbon nanotube-sol–gel for microextraction of polycyclic aromatic hydrocarbons from aquatic media. - Analytica Chimica Acta 683: 212-220.

[4]   Brown, J. N., Peake, B. M. (2003): Determination of colloidally-associated polycyclic aromatic hydrocarbons (PAHs) in fresh water using C18 solid phase extraction disks. - Analytica Chimica Acta 486: 159-169.

[5]   Bruchez, M., Jr., Moronne, M., Gin, P., Weiss, S., Alivisatos, A. P. (1998): Semiconductor nanocrystals as fluorescent biological labels. - Science 281: 2013-2016.

[6]   Capelo, J. L., Galesio, M. M., Felisberto, G. M., Vaz, C., Pessoa, J. C. (2005): Micro-focused ultrasonic solid–liquid extraction (µFUSLE) combined with HPLC and fluorescence detection for PAHs determination in sediments: optimization and linking with the analytical minimalism concept. - Talanta 66: 1272-1280.

[7]   Chan, W. C., Nie, S. (1998): Quantum dot bioconjugates for ultrasensitive nonisotopic detection. - Science 281: 2016-2018.

[8]   Chen, J. C., Huang, J. S., Chen, C. M., Guo, J. S. (2008): Emission characteristics of PAHs, benzene and phenol group hydrocarbons in O2/RFG waste incineration processes. - Fuel 87: 2787-2797.

[9]   Elbayoumy, K. (1992): Environmental carcinogens that may be involved in human breast-cancer etiology. - Chemical Research in Toxicology 5: 585-590.

[10]   Gao, Y., Han, J., Li, L. H., Liu, L., Lv, F. G. (2016): Research on the internal power gear honing processing technology for hard tooth surface. - Journal of Mechanical Engineering Research and Developments 39(2): 500-512.

[11]   Hawthorne, S. B., St Germain, R. W., Azzolina, N. A. (2008): Laser-induced fluorescence coupled with solid-phase microextraction for in situ determination of pahs in sediment pore water. - Environmental Science & Technology 42: 8021-8026.

[12]   Hu, H., Liu, S., Chen, C., Wang, J., Zou, Y., Lin, L., Yao, S. (2014): Two novel zeolitic imidazolate frameworks (ZIFs) as sorbents for solid-phase extraction (SPE) of polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. - Analyst 139: 5818-5826.

[13]   Huo, S. H., Yan, X. P. (2012): Facile magnetization of metal-organic framework MIL-101 for magnetic solid-phase extraction of polycyclic aromatic hydrocarbons in environmental water samples. - Analyst 137: 3445-3451.

[14]   Jin, J., Zhang, Z., Li, Y., Qi, P., Lu, X., Wang, J., Chen, J., Su, F. (2010): Enrichment of polycyclic aromatic hydrocarbons in seawater with magnesium oxide microspheres as a solid-phase extraction sorbent. - Analytica Chimica Acta 678: 183-188.

[15]   Kah, M., Zhang, X., Jonker, M. T. O., Hofmann, T. (2011): Measuring and modeling adsorption of PAHs to carbon nanotubes over a six order of magnitude wide concentration range. - Environmental Science & Technology 45: 6011-6017.

[16]   Kobayashi, R., Okamoto, R. A., Maddalena, R. L., Kado, N. Y. (2008): Polycyclic aromatic hydrocarbons in edible grain: A pilot study of agricultural crops as a human exposure pathway for environmental contaminants using wheat as a model crop. - Environmental Research 107: 145-151.

[17]   Koneswaran, M., Narayanaswamy, R. (2009): Mercaptoacetic acid capped CdS quantum dots as fluorescence single shot probe for mercury(II). - Sensors and Actuators B 139: 91-96.

[18]   Krauss, M., Wilcke, W. (2001): Biomimetic extraction of PAHs and PCBs from soil with octadecyl-modified silica disks to predict their availability to earthworms. - Environmental Science & Technology 35: 3931-3935.

[19]   Lesellier, E. (2011): Additional studies on shape selectivity by using the carotenoid test to classify C18 bonded silica. - Journal of Chromatography A 1218: 251-257.

[20]   Lin, J. H., Tseng, W. L. (2013): Gold nanoparticles for specific extraction and enrichment of biomolecules and environmental pollutants. - Rev. Anal. Chem. 31: 153-162.

[21]   Maertens, R. M., Yang, X., Zhu, J., Gagne, R. W., Douglas, G. R., White, P. A. (2008): Mutagenic and carcinogenic hazards of settled house dust I: Polycyclic aromatic hydrocarbon content and excess lifetime cancer risk from preschool exposure. - Environmental Science & Technology 42: 1747-1753.

[22]   Mastrangelo, G., Fadda, E., Marzia, V. (1996): Polycyclic aromatic hydrocarbons and cancer in man. - Environmental Health Perspectives 104: 1166-1170.

[23]   Murakami, M., Sato, N., Anegawa, A., Nakada, N., Harada, A., Komatsu, T., Takada H., Tanaka, H., Ono, Y., Furumai, H. (2008): Multiple evaluations of the removal of pollutants in road runoff by soil infiltration. - Water Research 42: 2745-2755.

[24] Oleszczuk, P., Baran, S. (2004): Application of solid-phase extraction to determination of polycyclic aromatic hydrocarbons in sewage sludge extracts. - Journal of Hazardous Materials 113: 237-245.

[25] Pan, D., Wang, J., Chen, C., Huang, C., Cai, Q., Yao, S. (2013): Ultrasonic assisted extraction combined with titanium-plate based solid phase extraction for the analysis of PAHs in soil samples by HPLC-FLD. - Talanta 108: 117-122.

[26] Pazos, M., Rosales, E., Alcántara, T., Gómez, J., Sanromán, M. A. (2010): Decontamination of soils containing PAHs by electroremediation: A review. - Journal of Hazardous Materials 177: 1-11.

[27] Pena-Pereira, F., Costas-Mora, I., Lavilla, I., Bendicho, C. (2012): Rapid screening of polycyclic aromatic hydrocarbons (PAHs) in waters by directly suspended droplet microextraction-microvolume fluorospectrometry. - Talanta 89: 217-222.

[28] Pereira, M. G., Walker, L. A., Wright, J., Best, J., Shore, R. F. (2009): Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in the eggs of predatory birds in britain. - Environmental Science & Technology 43: 9010-9015.

[29] Perez, S., Barcelo, D. (2000): Evaluation of anti-pyrene and anti-fluorene immunosorbent clean-up for PAHs from sludge and sediment reference materials followed by liquid chromatography and diode array detection. - Analyst 125: 1273-1279.

[30] Rauscher, L., Sakulthaew, C., Comfort, S. (2012): Using slow-release permanganate candles to remediate PAH-contaminated water. - Journal of Hazardous Materials 241: 441-449.

[31] Shamsipur, M., Hashemi, B. (2015): Extraction and determination of polycyclic aromatic hydrocarbons in water samples using stir bar sorptive extraction (SBSE) combined with dispersive liquid-liquid microextraction based on the solidification of floating organic drop (DLLME-SFO) followed by HPLC-UV. - RSC Advances 5: 20339-20345.

[32] Smoker, M., Tran, K., Smith, R. E. (2010): Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Shrimp. - Journal of Agricultural and Food Chemistry 58: 12101-12104.

[33] Tseng, W. C., Chen, P. S., Huang, S. D. (2014): Optimization of two different dispersive liquid–liquid microextraction methods followed by gas chromatography–mass spectrometry determination for polycyclic aromatic hydrocarbons (PAHs) analysis in water. - Talanta 120: 425-432.

[34] Wang, H., Campiglia, A. D. (2008): Determination of polycyclic aromatic hydrocarbons in drinking water samples by solid-phase nanoextraction and high-performance liquid chromatography. - Analytical Chemistry 80: 8202-8209.

[35] Wang, H., Zhao, X., Meng, W., Wang, P., Wu, F., Tang, Z., Han, X., Giesy, J. P. (2015): Cetyltrimethylammonium Bromide-Coated Fe3O4 Magnetic Nanoparticles for Analysis of 15 Trace Polycyclic Aromatic Hydrocarbons in Aquatic Environments by Ultraperformance, Liquid Chromatography With Fluorescence Detection. - Analytical Chemistry 87: 7667-7675.

[36] Wang, W. D., Huang, Y. M., Shu, W. Q., Cao, J. (2007): Multiwalled carbon nanotubes as adsorbents of solid-phase extraction for determination of polycyclic aromatic hydrocarbons in environmental waters coupled with high-performance liquid chromatography. - Journal of Chromatography A 1173: 27-36.

[37] Williams, E. S., Mahler, B. J., Van Metre, P. C. (2013): Cancer risk from incidental ingestion exposures to PAHs associated with Coal-Tar-Sealed pavement. - Environmental Science & Technology 47: 1101-1109.

[38] Wilson, W. B., Campiglia, A. D. (2011): Determination of polycyclic aromatic hydrocarbons with molecular weight 302 in water samples by solid-phase nano-extraction and laser excited time-resolved shpol'skii spectroscopy. - Analyst 136: 3366-3374.

[39] Winslow, S. D., Pepich, B. V., Bassett, M. V., Wendelken, S. C., Munch, D. J., Sinclair J. L. (2001): Microbial inhibitors for U.S. EPA drinking water methods for the determination of organic compounds. - Environmental Science & Technology 35: 4103-4110.

[40] Wu, H., Wang, X., Liu, B., Lu, J., Du, B., Zhang, L., Ji, J., Yue, Q. Han, B. (2010): Flow injection solid-phase extraction using multi-walled carbon nanotubes packed micro-column for the determination of polycyclic aromatic hydrocarbons in water by gas chromatography-mass spectrometry. - Journal of Chromatography A 1217: 2911-2917.

[41] Wu, P., Li, Y., Yan, X. P. (2009): CdTe Quantum Dots (QDs) Based Kinetic Discrimination of Fe2+ and Fe3+, and CdTe QDs-Fenton Hybrid System for Sensitive Photoluminescent Detection of Fe2+. - Analytical Chemistry 81: 6252-6257.

[42] Xie, P. J., Haleegoah, J. (2016): Research on vision-based underwater robot positioning and map building technology. – Journal of Mechanical Engineering Research and Developments 39(1): 211-216.

[43] Xie, S. M., Zhang, M., Wang, Z. Y., Yuan, L. M. (2011): Porous metal membranes for solid-phase extraction of polycyclic aromatic hydrocarbons. - Analyst 136: 3988-3996.

[44] Zhang, J., Zhang, L., Li, R., Hu, D., Ma, N., Shuang, S., Cai, Z., Dong, C. (2015): Magnetic graphene composites as both an adsorbent for sample enrichment and a MALDI-TOF MS matrix for the detection of nitropolycyclic aromatic hydrocarbons in PM2.5. - Analyst 140: 1711-1716.

[45] Zhang, S., Niu, H., Hu, Z., Cai, Y., Shi, Y. (2010): Preparation of carbon coated Fe3O4 nanoparticles and their application for solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples. - Journal of Chromatography A 1217: 4757-4764.

[46] Zhao, G., Chen, Y., Wang, S., Yu, J., Wang, X., Xie, F., Liu, H., Xie J. (2013): Simultaneous determination of 11 monohydroxylated PAHs in human urine by stir bar sorptive extraction and liquid chromatography/tandem mass spectrometry. - Talanta 116: 822-826.

[47] Zhao, Y., Ma, Y., Li, H. Wang, L. (2012): Composite QDs@MIP Nanospheres for Specific Recognition and Direct Fluorescent Quantification of Pesticides in Aqueous Media. - Analytical Chemistry 84: 386-395.

[48] Zhou, Y. Y., Yan, X. P., Kim, K. N., Wang, S. W., Liu, M. G. (2006): Exploration of coordination polymer as sorbent for flow injection solid-phase extraction on-line coupled with high-performance liquid chromatography for determination of polycyclic aromatic hydrocarbons in environmental materials. - Journal of Chromatography A 1116: 172-178.

[49] Zou, Y., Chen, Y., Yan, Z., Chen, C., Wang, J., Yao, S. (2013): Magnetic solid-phase extraction based on tetrabenzyl modified Fe3O4 nanoparticles for the analysis of trace polycyclic aromatic hydrocarbons in environmental water samples. - Analyst 138: 5904-5912.