Iranian Journal of Analytical Chemistry
Volume 5, Issue 1, March 2018 (17-24)

مجله ایرانی شیمی تجزیه
دوره ۵، شماره ۱، فروردین ماه ۱۳۹۷ (۲۴-۱۷)

اندازه‌گیری مقادیر جزئی تترانیتروکاربازول در آب‌های زیست‌محیطی با استفاده از روش کربن‌دات - ریزاستخراج مایع - مایع پخشی و اسپکتروسکوپی ماوراءبنفش - مرئی

هادی فراهانی[*و۱]، مهدی رحیمی نصرآبادی[۲]
۱. پژوهشگاه صنعت نفت، صندوق پستی ۱۴۸۵۷۳۳۱۱۱، تهران، ایران
۲. بخش شیمی، دانشگاه امام حسین (ع)، صندوق پستی ۳۴۷-۱۶۵۷۵، تهران، ایران

تاریخ دریافت: ۱۶ دی ۱۳۹۶ **تاریخ پذیرش:** ۱۲ اسفند ۱۳۹۶

Trace Determination of Tetranitrocarbazole in Aquatic Environment Using Carbon Dot-Dispersive Liquid-Liquid Microextraction Followed by UV-Vis Spectrophotometry

Hadi Farahani [1,*], Mehdi Rahimi-Nasrabadi [2]
1. Research Institute of Petroleum Industry (RIPI), P. O. Box 1485733111, Tehran, Iran
2. Department of Chemistry, Imam Hossein University, P.O. Box 16575-347, Tehran, Iran

Received: 6 January 2018 **Accepted:** 3 March 2018

چکیده

یک روش ریزاستخراج مایع – مایع پخشی بر پایه استفاده از خاصیت ذاتی رنگ سنجی کربن‌دات‌ها جفت شده با اسپکتروفتومتری فرابنفش - مرئی برای اندازه‌گیری مقادیر جزئی تترانیتروکاربازول در نمونه‌های آب زیست‌محیطی به صورت موفقیت‌آمیزی توسعه یافت. در این تکنیک بر پایه ریزاستخراج مایع – مایع پخشی، کربن دات‌های سنتز شده با کمک متیل‌تری‌اکتیل آمونیوم کلرید (آلیکوات S۳۳۶) به درون حلال کربن تتراکلرید که نقش حلال پخش کننده را ایفا می کرد، استخراج شدند. با بکارگیری خاصیت ذاتی کربن‌دات‌های غنی شده، جذبی در ناحیه ۳۰۰ نانومتر بدست آمد که در حضور تترانیتروکاربازول و به واسطه برهمکنش در سطح کلوئیدی نانوذرات سنتز شده شدت جذب افزایش معنی‌داری یافت. ابتدا پارامترهای اصلی کنترل‌کننده کارآیی ریزاستخراج مورد بررسی و ارزیابی قرار گرفتند. در شرایط بهینه فاکتور تغلیظ ۵۵/۵ به همراه کاهش اثر مزاحمت‌ها حاصل شد. گستره خطی منحنی کالیبراسیون در محدوده خطی ۲۰۰-۱ نانوگرم بر میلی‌لیتر به همراه ثابت همبستگی ۰/۹۹۹ برای آنالیت هدف بدست آمد. حد تشخیص ۰/۲ نانوگرم بر میلی‌لیتر و دقت در غلظت‌های ۲۰ و ۱۰۰ نانوگرم بر میلی لیتر (با ۱۰ بار تکرار) به ترتیب برابر با ۳/۶ و ۱/۷ حاصل شد. در پایان کارآیی روش با آنالیز تترانیتروکاربازول در نمونه‌های مختلف آب زیست‌محیطی مورد بررسی قرار گرفت و نتایج قابل قبولی بدست آمد.

واژه‌های کلیدی

ریزاستخراج مایع – مایع پخشی بر پایه کربن دات؛ آب‌های زیست محیطی؛ تترانیتروکاربازول؛ اسپکتروفوتومتری ماوراء بنفش – مرئی.

Abstract

An efficient carbon dot-dispersive liquid-liquid microextraction followed by UV-Vis spectrophotometry (CD-DLLME-UV-Vis) has been effectively developed for the sensitive determination of 1,3,6,8-tetranitrocarbazole (TNC) in environmental water samples. In this DLLME-based method, home-made syntheses carbon dots (CDs) were directly extracted into carbon tetrachloride using trioctylmethylammonium chloride (aliquat 336), which works as a disperser agent. By applying inherent colorimetric feature, the enriched CDs exhibited an intensive absorption signal at 300 nm, which swelled up in the presence of TNC due to their interaction at the colloidal interface. Main parameters that controlling and affecting the performance of the microextraction process were evaluated and optimized in details. An enrichment factor of 55.5 beside a meaningful sample clean-up was achieved under the optimized conditions. The calibration curve was linear in the range of 1-200 ng mL^{-1} with regression coefficient corresponding to 0.999. Limit of detection (S/N = 3) was 0.2 ng mL^{-1} while the RSD% values (n = 10) for the target analyte at two concentration levels of 20 and 100 ng mL^{-1} were 3.6 and 1.7, respectively. The proposed method was ultimately exerted for the preconcentration and determination of TNC in various environmental water samples and admissible results were achieved.

Keywords

Carbon Dot-Dispersive Liquid-Liquid Microextraction; Environmental Water Samples; Tetranitrocarbazole; UV-Vis Spectrophotometry.

---

*Corresponding Author: farahaniha@ripi.ir

1. INTRODUCTION

Sample preparation is ordinarily the dominant resource-demanding section of analytical methods respecting material consumption together with the disposal requirements, and has lately received extensive attention considering the green chemistry outlook [1-2]. To ameliorate the classical sample pretreatment methodologies, researchers across the world have been orienting towards the development of microextraction techniques which consume minimal amount of extraction solvent, less time and labor, environmentally friendly and cost-effective [3-4].

Introduction of dispersive liquid-liquid microextraction (DLLME) in 2006 has significantly contributed to meeting the mentioned purposes, due to its distinction merits of simple operation, low cost, good enrichment factor and recovery along with notably curtail extraction time [5-6]. DLLME is based on a ternary component solvent system, in which extraction and disperser solvents are expeditiously introduced inside the aqueous sample to make a cloudy solution. After centrifugation, extraction solvent is sediment at the bottom of test tube and removed by a microsyringe for following instrumental analysis [7-8]. Since its convenience and quickness, DLLME has been widely applied for the extraction and preconcentration of different types of analytes from various matrices including water, biological fluids, tissues and food matrices [9-12].

Carbon dots (CDs), which are a new member of carbon nanomaterials, have recently become increasingly popular owing to their extraordinary fluorescence characteristics, high chemical stability, good biocompatibility, low toxicity, environmental friendliness and facile synthesis at large-scale with low cost [13-14]. The beneficial optical features of CDs presented a considerable potential for the applications in analytical chemistry, particularly in biological and environmental imaging and sensing [15-16].

Nitroaromatic explosives have broadly been employed with numerous industrial applications since the nineteenth century [17-18]. Discharge of contaminated manufacturing waste streams into the natural water, burial of obsolete munitions, and military exercises intensify the availability of the chemicals for migration towards water supplies [19]. Hence, their trace determination has turned an emerging and important topic of interest among with the increasing concern over the environmental issues worldwide.

High-performance liquid chromatography (HPLC) [20], gas chromatography (GC) [21], ion mobility spectrometry (IMS) [22], mass spectrometry (MS) [23], fluorescence spectroscopy [24] and electrochemical sensors [25] have been reported for the determination of the explosives materials in various matrices. Besides, the extraction techniques which are generally applied before the instrumental analysis are liquid-liquid extraction (LLE) [26] and solid phase extraction (SPE) [27]. Nevertheless, these sample pretreatment methods need either large amount of sample and toxic organic solvents while they are considered as time-consuming, labor-intensive and expensive which frequently results in strong blank values [28-29].

Recently, Larki has published a novel and efficient carbon dot-dispersive liquid-liquid microextraction (CD-DLLME) method in combination with UV-Vis spectrophotometry for the determination of fenitrothion insecticide in water samples [30]. In this DLLME-based method, CD was simply extracted through the organic phase and reveals remarkable intense of the UV-Vis absorption on account of its interaction with the target analyte at the colloidal interface. This quantitative procedure is an efficient and appropriate analytical procedure, for which magnificent accuracy and precision are demonstrated, being simpler and more sensitive than the other reported techniques for the screening intentions.

The objective of present study is to appraise the CD-DLLME-UV-Vis technique aptness for the determination of trace amount of 1,3,6,8-tetranitrocarbazole (TNC, Fig. 1) as a nitroaromatic explosive compound in aquatic environment. The factors controlling the microextraction efficiency were investigated in detail and the optimum conditions were properly set. The developing method was in the end validated for the quantitative purposes and employed to environmental water sample analysis in combination with UV-Vis spectrophotometry.

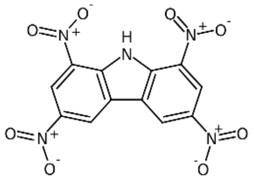

Fig. 1. Chemical structure of 1,3,6,8-tetranitrocarbazole (TNC).

2. EXPERIMENTAL

2.1. Chemicals

Ultra-pure water (Millipore, Bedford, MA, USA) was used in all experiments. All chemicals were of analytical reagent grade and exerted without extra purification. TNC (chemical formula: $C_{12}H_5N_5O_8$, CAS number: 4543-33-3 and molecular weight: 347.20 g mol^{-1}) was bought from Sigma-Aldrich (St. Louis, MO, USA). Trioctylmethylammonium chloride (aliquat 336), carbon tetrachloride (CCl_4), acetone, sodium hydroxide (NaOH), sodium acetate, hydrochloric (HCl), acetic, boric and orthophosphoric acids were obtained from Merck Company (Darmstadt, Germany). HPLC grade methanol was purchased from Riedel-de Haën Company (Seelze, Germany). Glassware applied for the experiments were formerly flooded in 0.2 mol L^{-1} nitric acid for 12 h and washed watchfully by the water.

2.2. Instrumentation

Absorption spectra were achieved with a Jenway 6320 UV-Vis spectrophotometer (England) by using a (350 µL) quartz microcell at room temperature (22 ± 0.5 ˚C). A BHG Hermle model centrifuge (Gosheim, Germany) was applied to accelerate phase separation. A Metrohm 827 pH meter (Metrohm AG, Herisau, Switzerland) equipped with a glass electrode was employed for pH measurements. Sonication was conducted with an Elmasonic S 60 H 154 (Elma, Singen am Hohentwiel, Germany) system. The fluorescence spectra were recorded by a Spectrofluorometer (Leng Guang Industrial Co., Ltd. of Shanghai, China), while the excitation and emission bandwidths were both at 10 nm. Fourier transform-infrared (FT-IR) spectra were documented utilizing a Bomem FT-IR spectrophotometer (Bomem, Canada). The morphology of the synthesis carbon dots was studying using Zeiss-EM10C-80 KV transmission electron microscopy (TEM, Oberkochen, Germany).

2.3. Preparation of solutions

A stock solution (1.0 µg mL^{-1}) of TNC was prepared in methanol. The working solutions were daily prepared by step-diluting the stock solution with the water to yield final desired concentrations. The Britton-Robinson buffer solutions of needed pH were produced in the regular manner; i.e. by addition of 0.04 mol L^{-1} acetic acid and 0.04 mol L^{-1} boric acid to a solution of 0.04 mol L^{-1} in orthophosphoric acid, with the appropriate amount of 0.2 mol L^{-1} sodium hydroxide solution. All the solutions were stored in the dark at 4 ˚C.

2.4. Preparation of real samples

The performance of the proposed method was evaluated by analyzing TNC in two environmental water samples including Karun and Bahmanshir Rivers (Ahwaz City, Iran) at three different concentration levels (in accordance with linear rang of calibration curve). The samples were collected in 1.0 L amber glass bottles. The bottles were rinsed several times with the water to be analyzed and filled till overflow. The water samples were filtered prior to the analysis using a 0.45 µm nylon membrane filter (Whatman, Maidstone, UK) to remove possible particles. All the samples were transported and stored at 4 ˚C by their analysis time.

2.5. Synthesis of the CDs

CDs were simply synthesized at 28 ± 0.5 ˚C using alkaline sugarcane juice without introduce of any additives. Briefly, 3.0 mL of NaOH 5 mol L^{-1} was dropwise added into a 50 mL filtered sugarcane juice while being agitated by a stirring bar for 15 min. The solution was sonicated for 30 min until it turns into the reddish brown color. Later on, the resulting solution was centrifuged for 15 min at 13,000 rpm and consequently, the upper clear solution (C-dots) was decanted and stored for the upcoming experiments. To evaluate the synthesized CDs, the maximum excitation and emission spectra were recorded and it was seen raising the excitation wavelength caused the CDs emission shifted to higher wavelengths accompanied with diminished fluorescence intensity. As it is clear in Fig. 2, (a) the fluorescence spectra of CDs exhibited an obvious peak around 410 nm and (b) UV–Visible spectra of CDs showed an intense peak at 300 nm. These signal intensities of CDs were magnified following preconcentration by DLLME and this aspect is instantly dependent on CDs amount in aqueous solution. Transmission electron microscopy and (TEM) and Fourier transform infrared (FT-IR) spectroscopy data of the synthesis CDs were strictly the same as previously reported by Larki [30].

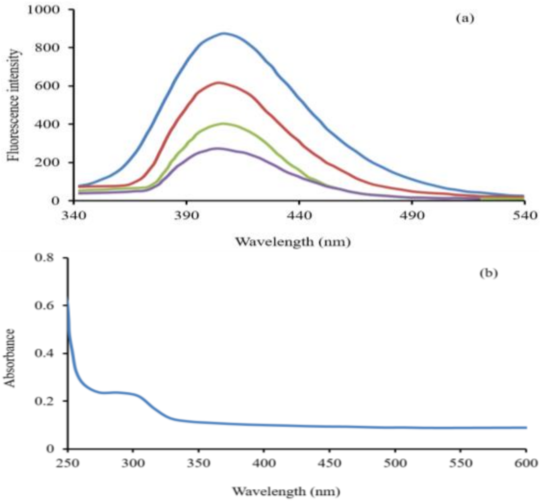

Fig. 2. (a) Fluorescence emission spectra and (b) UV-visible absorbance spectra of the CDs.

2.6. DLLME procedure

A 1.0 mL of CDs solution (1:10 ratio), a 1.0 mL of Britton-Robinson buffer (pH 7.0) and a fractional standard solution of TNC were added to a volumetric flask and diluted up to 10 mL. Then, the solution was moved to a conical glass test tube and 180 µL of CCl_4 (as extracting solvent) containing 1.5% (w/v) aliquat 336 (as disperser solvent) was quickly injected into the solution by a microsyringe. Herein, a cloudy solution was formed and TNC was extracted into the fine droplets of CCl_4. The mixture was thereafter centrifuged at 5000 rpm for 5 min to fully settle down the extracting solvent. The above aqueous phase was ejected and the enriched CDs with volume of 170 ± 5 µL were warily removed by a microsyringe, located inside the quartz microcell and its absorbance was measured at 300 nm. Blank samples were systematically run with the mentioned procedure.

3. RESULTS AND DISCUSSION

All quantifications developed in this study were made by calculating the UV-Vis absorbance from the average of three replicate measurements. In an effort to optimize the main parameters controlling the performance of this work, a one at a time approach was applied while a 100 ng mL^{-1} of TNC was used in all experiments.

3.1. The effect of sample pH

As quantum dots are recognized to be pH sensitive, their optical features can come up from particle surface states and presumably, the energy transfer among CDs and analyte [30]. Herein, two pH adjustments are presented. Britton-Robinson buffer was used for enhancing carbon dots efficiency and the other one (sample pH) was used for analyte extraction (by applying HCl and NaOH). For this reason and to achieve the highest analytical signals, the effect of sample pH on the absorption intensity of the enriched CDs was assessed in the range of 2-10 by applying HCl and NaOH (10^{-2} mol L^{-1} of each, using a micropipette). Since it is obvious in Fig. 3, absorbance jumps by raising the pH to 5.5 and drops significantly afterwards. On that account, pH value of 5.5 was selected as the optimum. In order to avoid fluctuations of acidity during the following experiments especially in real applications, 1.0 mL of sodium acetate buffer (pH 5.5) was added into all the sample solutions.

3.2. The effect of CDs quantity

The amount of the CDs is one of the major parameter affecting the microextraction performance and it was investigated by applying their different ratio in the range of 1:1 to 1:20 into the final aqueous solution. As depicted in Fig. 4, absorbance climbs by increasing the ratio to 1:10 and decline meaningfully, thereafter. Hence, the ratio of 1:10 was chosen as the optimum value for the rest of the task.

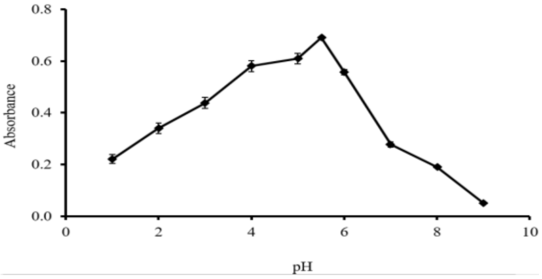

Fig. 3. The effect of pH on the extraction efficiency.

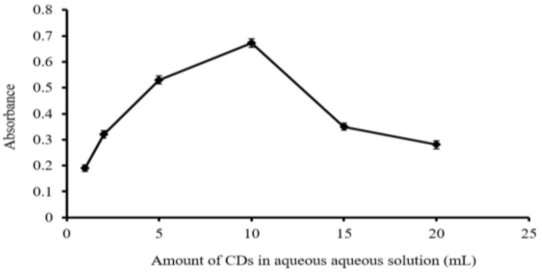

Fig. 4. The effect of CDs amount on the extraction efficiency.

3.3. The selection of extracting solvent

The selection of an appropriate extraction solvent has a primary role in the developed method for the purpose of gaining satisfactory recovery, worthy enrichment factor and sufficient selectivity of the target analyte. Moreover, the absorbance of the enriched CDs considerably relies on the kind of the extracting solvent. In accordance with the DLLME bases, the extraction solvent has to meet the following demands: (a) higher density than water, (b) proper extraction ability for the analyte and (c) low solubility in water. In this step, dichloromethane, carbon tetrachloride and chloroform were evaluated as the extraction solvents. Among various well-known solvents and according to our various laboratory experiences in the regard [31-33], the best results were obtained by employing carbon tetrachloride and so, it was selected as the extraction solvent. In this study, carbon tetrachloride along with aliquat 336 was injected into the aqueous solution of CDs which caused to improve the dispersion of extraction solvent in the aqueous sample. As it is well documented, the injection of this mixture in the presence of common disperser solvent (such as methanol, ethanol, acetonitrile and acetone) caused dissolution of a portion of CCl_4 into the aqueous phase and as a result, decreased the volume of the sedimented phase and extraction efficiency [34]. Hence, this procedure was done without addition of disperser solvent since aliquat 336 acts as disperser agent.

3.4. Effect of extraction solvent volume

The volume of the extraction solvent has a direct effect on the volume of sedimented phase and therefore, affects the enrichment factor. In order to assess the effect of extraction solvent volume, different amounts of carbon tetrachloride (180, 190, 200, 250, 300 and 350 µL) including 1.5% w/v of aliquat 336 were subjected to the DLLME procedure. In accordance with the obtained results, it was obvious that the absorbance of organic phase boosted by declining the volume of CCl_4. However, in fewer volumes, the sedimented phase is not sufficient to introduce for the analytical instrument (Fig. 5). So, 180 µL of carbon tetrachloride was used out as an optimum volume with regard to the mentioned practical limitation.

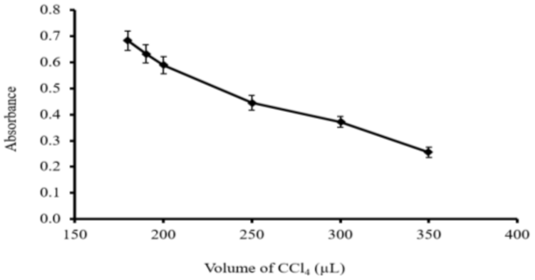

Fig. 5. The effect of CCl_4 volume on the extraction efficiency.

3.5. Effect of aliquat 336 concentration

The aliquat 336 concentration in carbon tetrachloride is noticeably affecting the analytical signals and so, it was evaluated. In these circumstances, a fixed volume of carbon tetrachloride containing different concentration levels of aliquat 336 (0 to 2.5% w/v) was injected into the solutions of TNC. The results indicated that raising aliquat 336 concentrations up to 1.0% cause an increase in the absorbance of organic phase and then hold steady (Fig. 6). For this reason, 1.5% of aliquat 336 was selected as the optimum value as it gave higher reproducibility.

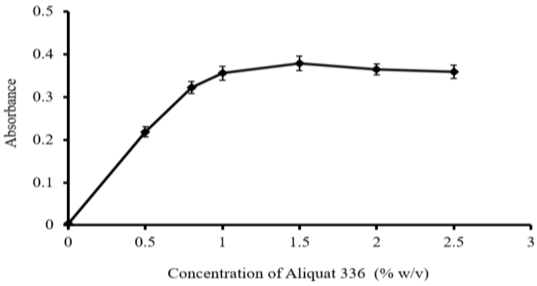

Fig. 6. The effect of Aliquat 336 concentration on the extraction efficiency.

3.6. The effect of time

Similar to other methods, extraction time is a key parameter in DLLME that controlling the extraction performance and should be as short as possible [35, 36]. Herein, it is defined as interval time between injection the mixture of disperser and extraction solvent into the aqueous sample and starting to centrifuge [37]. It is remarkable that following the formation of the cloudy solution, the contact area between extraction solvent and aqueous phase is extremely large. Consequently, transition of the analyte from aqueous phase to the extraction solvent is highly prompt. The effect of extraction time was examined in the range of 0 to 10 min and results demonstrated that the variations of absorbance signal against the extraction time were not substantial. Furthermore, the influence of centrifugation time was examined. The results imply that the most time-consuming step in this procedure is centrifugation of cloudy solution for a complete separation of organic and aqueous phase, which was 5 min at 5000 rpm while there was no need to spend time on the interval step and it was done immediately.

3.7. The analytical performance

To ascertain the applicability of the method, calibration curve was plotted at the optimum conditions. The limit of detection (LOD) based on the signal-to-noise ratio (S/N) of three, the coefficient constant (r^2), the linear dynamic range (LDR), enrichment factor (EF) and the relative standard deviations (RSDs) were calculated. The LDR (1-200 ng mL^{-1}, $r^2 = 0.999$) is fair enough to cover any probable concentration of the analyte in different real samples while LOD of 0.2 ng mL^{-1} imply an acceptable sensitivity of the developed method. The precision of the method was calculated at concentration of 20 and 100 ng L^{-1} of TNC standard solution and the RSDs for ten replications were 3.6 and 1.7%, respectively. In addition, EF determined as the ratio of TNC concentrations in the settled phase and the aqueous sample solution (volumes after and before enrichment) was 55.5.

3.8. Interference study

The potential interfering effects of some foreign species which are commonly encountered in environmental water samples were examined. For assessing the influences, solutions with 100 ng mL^{-1} of TNC including various amounts of individual interfering ions were treated in accordance with the optimized procedure. The tolerance level was explained as the maximum concentration of interfering ions causing a change in the analytical signal less than 5% when it was compared with the signal of TNC standard solution. In reference to Table 1, there is no interference from the co-existing ions in the environmental water samples for TNC monitoring.

Table 1. The effect of interfering species on the analysis of TNC.

Interfering species	Tolerance ratio (w/w)
Na^+, NH_4^+, NO_3^-, SO_4^{2-}, Ca^{2+}	1000
Pb^{2+}, Ni^{2+}, CO_3^{2-}, Mg^{2+}, Ag^+	500
Cu^{2+}, Cd^{2+}, Hg^{2+}	100
Co^{2+}, Cr^{3+}, Mn^{2+}	50
Al^{3+}, $H_2C_2O_4$	5

3.9. Environmental real sample analysis

At the optimum conditions, the method performance was verified by analyzing the analyte in the two environmental water samples. The results showed that the real samples were free of TNC contamination. To appraise the matrix effects, all the real samples were spiked with TNC standards at three different concentration levels. It should be noted that DLLME is a non-exhaustive extraction procedure and the relative recovery (determined using the ratio of the concentrations found in the real environmental sample and reagent water sample, spiked with the same amount of the analyte), instead of the absolute recovery (used in exhaustive extraction procedures), was performed. The relative recovery experiments of the analyte are disposed in Table 2. The attained recoveries were between 95.2-105.2%, demonstrating that the method is not affected by the matrix in actual applications. Moreover, satisfactory RSD% values (below than 3.0%, n=6) were obtained in the real sample analysis.

Table 2. The results obtained from analysis of environmental water samples.

Sample	Added (ng mL^{-1})	Found[a] (ng mL^{-1})	Relative recovery%
Karoon river	0	ND[b]	---
	25.0	23.8 ± 0.9	95.2
	75.0	74.1 ± 2.8	98.8
Bahmashir river	0	ND	---
	25.0	26.3 ± 1.0	105.2
	75.0	78.0 ± 3.0	104.0

[a] Mean ± standard deviation (*n* = 3).

[b] Not detected.

4. CONCLUSION

The intention of present study was to develop and validate a rapid, sensitive, robust and reliable DLLME-based method applying CDs, combined with UV-Vis spectrophotometry for the quantitative determination of TNC in the aquatic environment. Herein, without employing any disperser agents, the label free CDs can be quickly extracted to organic phase just by assistance of aliquat 336. The results obtained from the method approved that it is a good alternative extraction and determination technique for nitroaromatic explosives screening and offers interesting advantages such as simplicity, low cost and considerably concise analysis time. Good linearity and precisions were also achieved in real matrixes. Hence, considering all the profits together, the method possesses great potential to be employed in the further applications.

DISCLOSURE STATEMENT

The authors declare no conflict of interests.

REFERENCES

[1] R. Costa, Newly introduced sample preparation techniques: towards miniaturization, *Crit. Rev. Anal. Chem.* 44 (2014) 299-310.

[2] J. Pan, C. Zhang, Z. Zhang and G. Li, Review of online coupling of sample preparation techniques with liquid chromatography, *Anal.* Chim. Acta 815 (2014) 1-15.

[3] Z.H. Liu, G.N. Lu, H. Yin, Z. Dang, H. Littier and Y. Liu, Sample-preparation methods for direct and indirect analysis of natural estrogens, Trends Anal. Chem. 64 (2015) 149-164.

[4] K.M. Dimpe and P.N. Nomngongo, Current sample preparation methodologies for analysis of emerging pollutants in different environmental matrices, *Trends Analyt. Chem.* 82 (2016) 199-207.

[5] M.I. Leong, M.R. Fuh and S.D. Huang, Beyond dispersive liquid-liquid microextraction, *J. Chromatog. A* 1335 (2014) 2-14.

[6] N. Campillo, P. Viñas, J. Šandrejová and V. Andruch, Ten years of dispersive liquid–liquid microextraction and derived techniques, *Appl. Spectrosc. Rev.* 52 (2017) 267-415.

[7] H. Yan and H. Wang, Recent development and applications of dispersive liquid–liquid microextraction, *J. Chromatog. A* 1295 (2013) 1-15.

[8] J. Šandrejová, N. Campillo, P. Viñas and V. Andruch, Classification and terminology in dispersive liquid–liquid microextraction." *Microchem. J.* 127 (2016) 184-186.

[9] C.V. Ramos-Dorta, V. Pino and A.M. Afonso, Monitoring polycyclic aromatic hydrocarbons in seawaters and wastewaters using a dispersive liquid–liquid microextraction

method, *Environ. Technol.* 34 (2013) 607-616.

[10] Y. Du and S. Guo, Chemically doped fluorescent carbon and graphene quantum dots for bioimaging, sensor, catalytic and photoelectronic applications, *Nanoscale* 8 (2016) 2532-2543.

[11] X. Wang, L. Wu, J. Cao, X. Hong, R. Ye, W. Chen and T. Yuan, Magnetic effervescent tablet-assisted ionic liquid dispersive liquid–liquid microextraction of selenium for speciation in foods and beverages, *Food Addit. Contam. A* 33 (2016) 1190-1199.

[12] C. Vakh, E. Evdokimova, A. Pochivalov, L. Moskvin and A. Bulatov, Effervescence assisted dispersive liquid–liquid microextraction followed by microvolume UV-Vis spectrophotometric determination of surfactants in water, *Toxicol. Environ. Chem.* 99 (2017) 613-623.

[13] K. Hola, . Zhang, Y. Wang, E.P. Giannelis, R. Zboril and A.L. Rogach, Carbon dots-Emerging light emitters for bioimaging, cancer therapy and optoelectronics, *Nano Today* 9 (2014) 590-603.

[14] Y. Du and S. Guo, Chemically doped fluorescent carbon and graphene quantum dots for bioimaging, sensor, catalytic and photoelectronic applications, *Nanoscale* 8 (2016) 2532-2543.

[15] S.Y. Lim, W. Shen and Z. Gao, Carbon quantum dots and their applications, *Chem. Soc. Rev.* 44 (2015) 362-381.

[16] P. Zuo, P., X. Lu, Z. Sun, Y. Guo and H. He, A review on syntheses, properties, characterization and bioanalytical applications of fluorescent carbon dots, *Microchim. Acta* 183 (2016) 519-542.

[17] J.D. Rodgers and N.J. Bunce, Treatment methods for the remediation of nitroaromatic explosives, *Water Res.* 35 (2001) 2101-2111.

[18] K.S. Ju and R.E. Parales, Nitroaromatic compounds, from synthesis to biodegradation, *Microbiol. Mol. Biol. Rev.* 74 (2010) 250-272.

[19] P. Kovacic and R. Somanathan, Nitroaromatic compounds: Environmental toxicity, carcinogenicity, mutagenicity, therapy and mechanism, *J. Appl. Toxicol.* 34 (2014) 810-824.

[20] U. Ochsenbein, M. Zeh and J.D. Berset, Comparing solid phase extraction and direct injection for the analysis of ultra-trace levels of relevant explosives in lake water and tributaries using liquid chromatography-electrospray tandem mass spectrometry, Chemosphere 72 (2008) 974-980.

[21] M. Berg, J. Bolotin and T.B. Hofstetter, Compound-specific nitrogen and carbon isotope analysis of nitroaromatic compounds in aqueous samples using solid-phase microextraction coupled to GC/IRMS, Anal. Chem. 79 (2007) 2386-2393.

[22] J. Lee, S. Park, S.G. Cho, E.M. Goh, S. Lee, S.S. Koh and J. Kim, Analysis of explosives using corona discharge ionization combined with ion mobility spectrometry–mass spectrometry, *Talanta* 120 (2014) 64-70.

[23] K. Badjagbo and S. Sauvé, Mass spectrometry for trace analysis of explosives in water, *Crit. Rev. Anal. Chem.* 42 (2012) 257-271.

[24] R.C. Stringer, S. Gangopadhyay and S.A. Grant, Detection of nitroaromatic explosives using a fluorescent-labeled imprinted polymer, *Anal. Chem.* 82 (2010) 4015-4019.

[25] T. Gan and S. Hu, Electrochemical sensors based on graphene materials, *Microchim. Acta* 175 (2011) 1-19.

[26] J. Feltes, K. Levsen, D. Volmer and M. Spiekermann, Gas chromatographic and mass spectrometric determination of nitroaromatics in water, *J. Chromatogr. A* 518 (1990) 21-40.

[27] R. Tachon, V. Pichon, M.B. Le Borgne and J.J. Minet, Comparison of solid-phase extraction sorbents for sample clean-up in the analysis of organic explosives, *J. Chromatogr. A* 1185 (2008) 1-8.

[28] J. Pawliszyn and S. Pedersen-Bjergaard, Analytical microextraction: current status and future trends**,** *J. Chromatogr. Sci.* 44 (2006) 291-307.

[29] J. Moreda-Piñeiro and A. Moreda-Piñeiro, Recent advances in combining microextraction techniques for sample pre-treatment, *Trends Analyt. Chem.* 71 (2015) 265-274.

[30] A. Larki, A novel application of carbon dots for colorimetric determination of fenitrothion insecticide based on the microextraction method, *Spectrochim. Acta A* 173 (2017) 1-5.

[31] C. Carrillo-Carrión, B.M. Simonet and M. Valcárcel, Carbon nanotube–quantum dot nanocomposites as new fluorescence nanoparticles for the determination of trace levels of PAHs in water, *Anal. Chim. Acta* 652 (2009) 278-284.

[32] H. Farahani, P. Norouzi, R. Dinarvand and M.R. Ganjali, Development of dispersive liquid–liquid microextraction combined with gas chromatography–mass spectrometry as a simple, rapid and highly sensitive method for the determination of phthalate esters in water samples, *J. Chromatogr. A* 1172 (2007) 105-112.

[33] M. Rahimi-Nasrabadi, M.M. Zahedi, S.M. Pourmortazavi, R. Heydari, H. Rai, J. Jazayeri and A. Javidan, Simultaneous determination

of carbazole-based explosives in environmental waters by dispersive liquid-liquid microextraction coupled to HPLC with UV-Vis detection, *Microchim. Acta* 177 (2012) 145-152.

[34] N. Pourreza, S. Rastegarzadeh and A. Larki, Determination of fungicide carbendazim in water and soil samples using dispersive liquid-liquid microextraction and microvolume UV-Vis spectrophotometry, *Talanta* 134 (2015) 24-29.

[35] H. Farahani, M. Shokouhi, M. Rahimi-Nasrabadi and R. Zare-Dorabei, Green chemistry approach to analysis of formic acid and acetic acid in aquatic environment by headspace water-based liquid-phase microextraction and high-performance liquid chromatography, *Toxicol. Environ. Chem.* 98 (2016) 714-726.

[36] J.A. Ocaña-González, R. Fernández-Torres, M.Á. Bello-López and M. Ramos-Payán, New developments in microextraction techniques in bioanalysis: a review, *Anal. Chim. Acta* 905 (2016) 8-23.

[37] A. Zgoła-Grześkowiak and T. Grześkowiak, Dispersive liquid-liquid microextraction, *Trends Analyt. Chem.* 30 (2011) 1382-1399.