RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

Modification of cellulose paper with polydopamine as a thin film microextraction phase for determination of nitrophenols in oil samples

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Cunling Ye[a*], Yujun Wu[a], Zhike Wang[b]

Cellulose papers were modified with polydopamine by a simple, efficient, and environmentally friendly approach as a novel extraction phase for thin film microextraction (TFME). The cellulose papers were characterized by Fourier transformed infrared spectroscopy (FT-IR), energy dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM). In this work, the modified cellulose papers were evaluated as a sorbent for the extraction of phenolic compounds (4-nitrophenol, 2,4-dinitrophenol) from oil samples. And various extraction parameters were optimized by selecting desorption condition, sodium hydroxide concentration and extraction time. High-performance liquid chromatography-ultraviolet and visible detection (HPLC-UV) was used for the quantification of the extracted compounds. Under optimum conditions, the calibration curves in the range of 5–1000 μg L^{-1} with a good linearity (r≥0.9982) and low limits of detection (LODs) were achieved. The limits of detection were 1.54 μg L^{-1} for 4-nitrophenol and 2.16 μg L^{-1} for 2,4-dinitrophenol, respectively. Enrichment factors (EFs) were in the range of 146-179 and relative standard deviations (RSDs) were less than 4.31% for the target analytes. The method was successfully used to investigate cooking oils. Relative recoveries were found to be ranging from 84.37% to 100.85%. The proposed method provided a simple, efficient and environmental approach for the rapid and convenient determination of nitrophenols in oil samples.

1. Introduction

Phenolic compounds can be released into the environment directly and indirectly. In recent years, phenols have been widely concerned[1,2]. Phenolic compounds are almost ubiquitous contaminants while they are widely appeared in wastewater from discharged oil refineries, the drug, paint and pesticide industries, as the intermediates of processes[3]. However, as far as we know, phenolic compounds are harmful to our body and the environment. These hazardous pollutants are harmful to organisms even at low concentrations[4]. They have potential harm to human health. For example, they may cause headache, nausea, dizziness, difficulty in swallowing, diarrhea, vomiting, shock, convulsions, and even death. What's worse, phenols can affect the central nervous system, liver, and kidneys[5-7]. Especially for nitrophenols, which belong to phenolic compounds, are listed in the US EPA for their barely biodegradable and highly toxic properties[8]. Because of the potential harm of phenolic compounds to human health and the environment, it is urgent to remove them from water, food and the environment.

To extract phenolic compounds from samples, many techniques have been developed such as liquid–liquid extraction (LLE)[9], liquid phase microextraction (LPME)[10], solid-phase extraction (SPE)[11,12], solid-phase microextraction (SPME)[13], cloud point extraction (CPE)[14], stir bar microextraction (SBME)[15] and ionic liquids extraction[16]. Among these techniques, microextraction techniques are simple, miniaturized and consume less organic solvents. SPME[17], single-drop microextraction (SDME)[18,19], dispersive liquid–liquid microextraction (DLLME)[20,21], hollow fiber liquid-phase microextraction (HF-LPME)[22], supramolecular solvent-based microextraction (SM-SBME)[23-27] and solidified floating organic drop microextraction (SFODME)[28,29] are some examples of microextraction techniques. SPME has become the most effective one of various microextraction techniques because it is simple, inexpensive, fast and low consumption of organic solvents. The principle of SPME is based on the interactions of analytes with the sample matrix and the extraction phase (coating) via adsorption and desorption (depending on the nature of the coating). The extraction selectivity and efficiency of SPME mainly depend on the coating's properties and size as well as its interactions with the analytes. In addition, it has been emphasized recently that the initial rate of SPME extraction is proportional to the surface area of the extraction phase. Extraction efficiency increases with the increase of the amount of coating. However, increasing the thickness of the

[a] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China.
[b] School of Environment, Henan Key Laboratory for Environmental Pollution Control, Key Laboratory for Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Normal University, Xinxiang 453007, China.
*Corresponding Author
Tel: 86-373-3326335
E-mail: ycl@htu.cn
See DOI: 10.1039/x0xx00000x

coating results in long equilibrium time[30]. In order to overcome this shortcoming, TFME possessing high surface area to volume ratio as a mode of SPME was introduced by Pawliszyn research group in 2003[31]. Thus, chemical modification of cellulose surface with suitable organic reagents makes it appropriate for extraction purposes. It is common that the extraction phases are appropriate for aqueous samples while few extraction phases are appropriate for oil samples. So, it is necessary to find a chemical modification method to make them applicable to oil samples. It is found that dopamine can be competent to the task. Dopamine, which is widely known as a catecholamine neurotransmitter, has excellent biocompatibility[32] and self-polymerizing ability[33,34]. Hong et al. reported that stable polydopamine (PDA) is formed by non-covalent self-assembly and covalent polymerization[35]. Dopamine which is inspired from the adhesive proteins of mussels can self-polymerize in alkaline aqueous media generating polymer films which adhere onto practically all material surfaces including polymers, ceramics, metals and metal oxides[36]. It is also reported that the oxidant induced polymerization of dopamine in neutral or acidic pH[33]. In this work, dopamine was used to bind the surface of cellulose papers by polymerization in alkaline aqueous solutions, the modified cellulose papers were applied for TFME. TFME parameters such as desorption condition, sodium hydroxide concentration and extraction time were studied and optimized. Under the optimized conditions, cooking oils were investigated.

2. Experimental

2.1. Chemicals and materials

Dopamine hydrochloride (98%) was obtained from Aladdin Chemistry Co., Ltd. Tris-(hydroxymethyl)aminomethane (99%) was purchased from Shanghai Xinhua Chemical Factory (Shanghai, China). Cellulose papers were purchased from Xinhua paper industry Co., Ltd (Hangzhou, China). Ethanol, dichloromethane, n-hexane, methanol (HPLC grade) and acetonitrile (HPLC grade) were obtained from Sinopharm Chemical Reagent Co., Ltd. Acetone and hydrochloric acid (36-38%) were purchased from Haohua Chemical Reagent Co., Ltd. (Luoyang, China). Sodium hydroxide was provide by Tianjin Kemiou Chemical Reagent Co., Ltd.(Tianjin, China). 4-Nitrophenol and 2,4-dinitrophenol were purchased from Sinopharm Chemical Reagent Co., Ltd. Each standard stock solution was prepared by dissolving the required amounts in HPLC grade methanol at a concentration of 1.00 mg mL^{-1} and stored at 4 ^{o}C in darkness. Working standard solutions of 4-nitrophenol and 2,4-dinitrophenol mixture were daily prepared from appropriate dilutions with HPLC grade methanol before use. All chemicals used were of analytical reagent grade, unless otherwise stated.

2.2. Instrumentation

The FT-IR spectra were obtained using a FT-IR spectrophotometer (FT-IR NEXUS, Nicolet) to identify the functional groups. Energy dispersive X-ray spectroscopy (EDS) was performed on a GENESIS system (EDAX Inc.) attached to the JEM-2100 microscope. Microstructures and morphologies were investigated using scanning electronic microscopy (SEM, JEOL JSM-6390LV). A THZ-82(A) thermostatic water-bath shaker (Jintan Scientific Analytical Instrument Co. Ltd., China) was used in the reaction and TFME process. The 1200 series high performance liquid chromatography (Agilent Technologies Inc., USA) equipped with multi-wavelength detector was used for determining the phenolic compounds (4-nitrophenol, 2,4-dinitrophenol). An Agilent ChemStation program was used to control instrument, data acquisition and analysis (Agilent, USA). The analytical column employed was a Zorbax C_{18} column (4.6 mm×250 mm, 5 μm particle size) (Agilent, USA). The components of the mobile phase were high-purity water with 2% acetic acid and methanol in the ratio of 42/58 (V/V). The flow rate was set constant at 1.0 mL min^{-1}. The detection was performed at 230 nm. The injection volume was 20 μL and the separation temperature was 25 ^{o}C.

2.3. Preparation of PDA modified cellulose papers

For synthesis of the PDA modified cellulose papers, we cut the cellulose filter papers into the rectangular strips (1 cm × 4 cm) with a pair of scissors. The tapes were washed with acetone and dried at room temperature. The dopamine solution was first made by dissolving dopamine hydrochloride (300 mg) in 100 mL Tris–HCl buffer (10 mM, pH 8.5). Then the tapes were immersed into the dopamine solution with shaking (120 rpm) at 30 ^{o}C under an aerobic atmosphere for 24 h. After the reaction, the PDA modified cellulose papers were thoroughly washed with deionized water and ethanol for several times to remove the non-adhered PDA. Finally, the PDA modified cellulose papers were dried under vacuum at 60 ^{o}C for 10 h before use.

2.4. TFME procedure

First, 1.00 mL of vegetable oil, 200 μL mixture of 4-nitrophenol and 2,4-dinitrophenol (10 μg mL^{-1}), 9 mL n-hexane and 5 μL sodium hydroxide (2 mol L^{-1}) were added in a 10-mL conical flask in sequence and shaken well to produce final nitrophenols concentrations equivalent to 200 μg L^{-1}. Then the tapes obtained from 2.3 were cut into two parts (1 cm×2 cm) and one of the tapes was put into the above conical flask. The conical flask was shaken in a thermostatic water-bath shaker at 150 rpm at 30 ^{o}C for 120 min. After extraction, the tape was removed from the conical flask and washed by n-hexane, and then dried at room temperature. Then, the tape was rolled into a 1.5 mL centrifuge tube containing 1.25 mL desorption solvent. After 10 min, the tape was removed from the tube and the solvent was filtered by PTFE filter. Then the solvent was evaporated under a stream of nitrogen and the final residue reconstituted in 50 μL of methanol. Finally, a 20-μL portion was injected to HPLC for chromatographic analysis.

2.5. Oil samples

Five kinds of vegetable oil were purchased from local supermarkets and investigated under optimum adsorption and desorption conditions. Particularly, one kind of the vegetable oil was used to optimize the adsorption and desorption

conditions while other kinds of the vegetable oil were used for recovery.

3. Results and discussion

3.1. PDA modified cellulose paper to act as an extraction phase

Cellulose is a linear homopolymer linked glucopyranose units aggregated to form a highly ordered structure due to its chemical constitution and spatial conformation[37]. The water-solubility of cellulose is low, but the existence of OH functional groups in its chemical structure enhances the polarity. So it is difficult to use them as reversed-phase sorbents for the extraction of non- and semi-polar compounds. In addition, water can react with OH functional groups in cellulose fibers chemical structure, and penetrate into the fibers. As a result, the network of cellulose fiber is destroyed. Cellulose paper is mainly made up of cellulose. In order to reduce the hydrophilic character of cellulose fibers and improve their adhesion properties, it is necessary to undertake a chemical modification on their surface[38]. But most of them are merely suitable for aqueous samples, so it is necessary to find a chemical modification to make them also play parts in oil samples. In this paper, cellulose paper was modified with polydopamine, which could adsorb nitrophenols in oil samples. One of the most obvious characteristics when the paper was modified with polydopamine was that the colour changed. The colour of the paper turned from white to black when the polydopamine reacted with the paper. EDS of PDA modified cellulose papers was shown in Fig. 1. Comparing Fig. 1a with Fig. 1b, N element was detected in PDA modified cellulose papers rather than cellulose papers. This result proved that the polydopamine was successfully bonded on the surface of cellulose papers. In order to further verify the result, SEM of cellulose papers (a, b, c) and PDA modified cellulose papers (d, e, f) at different magnifications were conducted (Fig. 2). From Fig. 2, obvious difference between cellulose papers and PDA modified cellulose papers could be seen. The tubes of cellulose fibers in cellulose papers were smooth while they were rough and appeared to have a compact coating with a number of small particle clusters in the higher-magnification SEM images (Fig. 2f) in PDA modified cellulose papers. The presence of these small particles is mainly attributable to aggregation of adjacent polydopamine. In addition, FT-IR analysis was introduced to test the existence of polydopamine. FT-IR analysis (Fig. S1) showed several weak peaks at 1430-1650 cm^{-1} in PDA modified cellulose papers. The weak peaks at 1430-1650 cm^{-1} resulted from benzyl functional group.

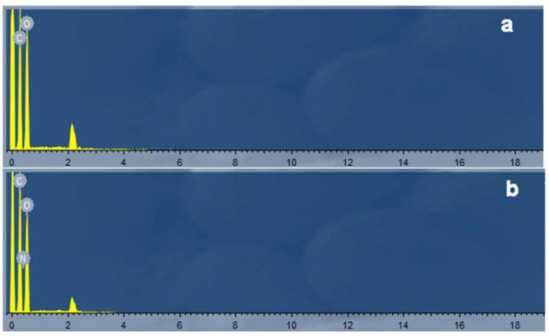

Fig. 1 EDS of cellulose filter papers (a) and PDA modified cellulose papers (b).

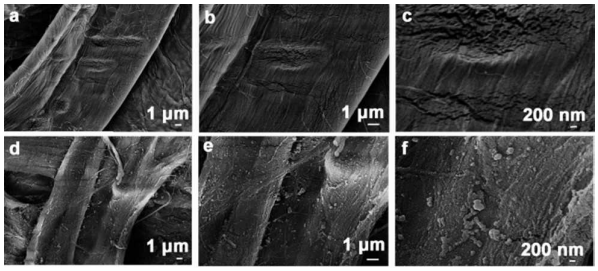

Fig. 2 SEM of cellulose filter papers at (a) 10k ×, (b) 20k × and (c) 50k × magnifications, PDA modified cellulose papers at (d) 10k ×, (e) 20k × and (f) 50k × magnifications.

3.2. Optimization of TFME

The PDA modified cellulose papers were used as an extraction phase, and the TFME parameters such as desorption condition, sodium hydroxide concentration and extraction time were studied and optimized. The type of desorption solvent was an important factor on sample recovery. According to literature[11], some organic solvent such as methanol, dichloromethane and acetonitrile were often used to elute the adsorbed phenols. However, in this work, these solvents showed poor eluting capability towards the studied phenols. As suggested in the literature[39], elution of phenols was also performed with the mixture of ethanol and hydrochloric acid (HCl). Thus, methanol/HCl, dichloromethane/HCl and acetonitrile/HCl were tried. The results indicated that acidification of these organic solvent by HCl significantly increased the recoveries of the two analytes. As shown in Fig. 3, we could find that the eluent of acetonitrile/HCl (especially 25 μL HCl in 2.5 mL acetonitrile) gave better elution performance for the two analytes. This phenomenon may be attributed to ion exchange phenomena between the presence of free chloride ions and the adsorbed phenol anions[39]. So, a mixture of 25 μL HCl and 2.5 mL acetonitrile was chosen as the desorption solvent for the next experiments.

In order to ensure that the two phenols were eluted from the PDA modified cellulose papers completely and no carryover occurred, different volumes of the solvent mixture from 250 to 1500 μL were examined. As can be seen in Fig. S2, 1250 μL was sufficient for the highest extraction amount of the two analytes. However, when the volume of desorption solvent was more than 1250 μL, the peak areas of the two analytes decreased obviously. Thus, 1250 μL was used in the further study.

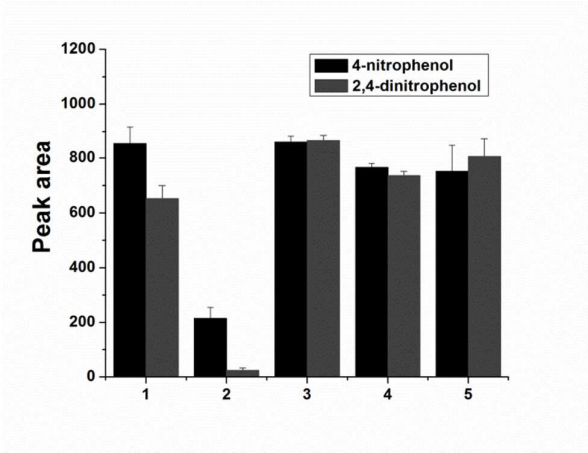

Fig. 3 Effect of desorption solvent type on the extracted amounts of the phenolic compounds (1000 μL oil; concentration of phenolic compounds, 200 μg L^{-1}; 9 mL n-hexane; 10 μL 2 mol L^{-1} NaOH; shaking rate, 150 rpm; extraction temperature, 30 ℃; time of extraction, 150 min; volume of desorption, 1000 μL; time of desorption, 10 min). (1) 25 μL hydrochloric acid in 2.5 mL methanol, (2) 25 μL hydrochloric acid in 2.5 mL dichloromethane, (3) 25 μL hydrochloric acid in 2.5 mL acetonitrile, (4) 10 μL hydrochloric acid in 2.5 mL acetonitrile, (5) 50 μL hydrochloric acid in 2.5 mL acetonitrile.

Effect of desorption time was also investigated in the rang of 10-50 min. As shown in Fig. S3, with the increasing of the desorption time, the desorption effects were almost the same, and 10 min was enough to elute the two phenols from the PDA modified cellulose paper.

In general, NaOH aqueous solutions are used to separate phenols from oils. In this work, preliminary extraction experiments were carried out in the presence of small amounts of NaOH aqueous solutions. It was found that the peak areas of the two analytes were improved significantly with respect to those obtained in the absence of NaOH. Hence, the extraction was done by changing the volume of 2 mol L^{-1} NaOH from 0 to 70 μL and Fig. 4 showed the volume of NaOH profiled with a peak area. The results indicated that the highest analytical signals were observed in the case of 5 μL. The presence of NaOH can promote ionization of phenols as weak acids in oils. The phenol anions have the strong affinity to the binding sites of the PDA modified cellulose papers, which may further improve enrichment capacities of the PDA modified cellulose papers for the two analytes. However, when the volume of NaOH aqueous solutions was over 5 μL, the peak areas of the two analytes decreased rapidly. This happened because the larger volume of NaOH aqueous solutions could form tiny water droplets depositing in the bottom of conical flasks. A great amount of strong polar phenol anions should enter into alkaline water droplets easily like the reverse DLLME[40] leading to the much lower extraction efficiency. To get a high analytical sensitivity, 5 μL of 2 mol L^{-1} NaOH was used.

In addition, extraction time plays a very important role in the TFME process because the adsorbed amount of analytes always increases with the extraction time until reaching the adsorption equilibrium[31]. Different extraction times from 20 to 150 min were evaluated in this work (Fig. S4). The peak area of each analyte greatly increased with the increase of extraction time and reached the maximum adsorption amount at 120 min, so 120 min was chosen as the optimum time for the extraction of the nitrophenols.

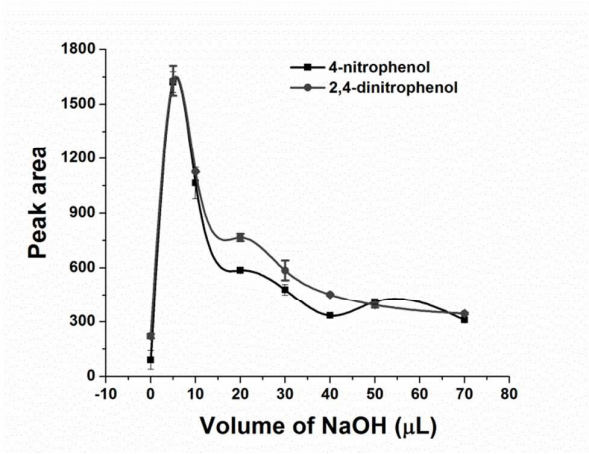

Fig. 4 Effect of volume of sodium hydroxide on the extracted amounts of the phenolic compounds (1000 μL oil; concentration of phenolic compounds, 200 μg L^{-1}; 9 mL n-hexane; shaking rate, 150 rpm; extraction temperature, 30 ℃; time of extraction, 150 min; desorption solvent, 25 μL hydrochloric acid in 2.5 mL acetonitrile; volume of desorption, 1250 μL; time of desorption, 10 min).

3.3. Analytical characteristics

In order to investigate the oil samples, the analytical characteristics of the proposed method were determined in terms of linearity, precision (expressed as the relative standard deviation), enrichment factor and limit of detection. All of the obtained results were summarized in Table 1. Calibration curves for 4-nitrophenol and 2,4-dinitrophenol were obtained in the concentration range of 5-1000 μg L^{-1}. A good linearity with correlation coefficients (r) greater than 0.9982 was obtained for the analytes. Precision was investigated by performing intraday and interday precision studies. The intra-day RSDs of the method varied from 3.07 % to 3.37 % and the inter-day RSDs were obtained in the range of 4.18-4.31 % (n=8). Enrichment factors were obtained by comparing the peak areas of the target analytes after pre-concentration with the peak areas of the target analytes for calibration curves without pre-concentration directly. The enrichment factors were obtained by eight replicate extractions of oil samples spiked with 200 μg L^{-1} of the analytes (Table 1). Based on a signal-to-noise ratio of 3 (S/N = 3), the LODs could reach 1.54 μg L^{-1} for 4-nitrophenol and 2.16 μg L^{-1} for 2,4-dinitrophenol, respectively. Compared with previous works for the determination of the phenolic compounds[41,42], this work exhibited an acceptable analytical performance.

Journal Name

ARTICLE

Table 1

Analytical performance of the method

Compound	Linear range (μg L^{-1})	Correlation coefficient(r)	Precision [a] (%)		EFs [b]	LODs (μg L^{-1})
			Intra-day	Inter-day		
4-nitrophenol	5-1000	0.9998	3.37	4.18	157.41	1.54
2,4-dinitrophenol	5-1000	0.9982	3.07	4.31	170.97	2.16

[a] Relative standard deviation (n=8)

[b] The mean values of the enrichment factors (n=8)

Table 2

Relative recoveries for oil sample analysis

Sample		Relative recovery (%) ⁎	
		4-nitrophenol	2,4-dinitrophenol
1 #	80 μg L^{-1}	94.85±8.00	84.37±7.25
	200 μg L^{-1}	98.65±6.29	90.88±5.62
2 #	80 μg L^{-1}	89.17±3.51	85.07±3.39
	200 μg L^{-1}	97.69±3.11	98.66±1.03
3 #	80 μg L^{-1}	87.93±2.86	100.47±3.89
	200 μg L^{-1}	94.29±0.85	100.85±3.90
4 #	80 μg L^{-1}	87.33±3.99	99.37±13.18
	200 μg L^{-1}	99.72±1.28	93.07±4.63

⁎ Mean values ± standard deviation (n=3)

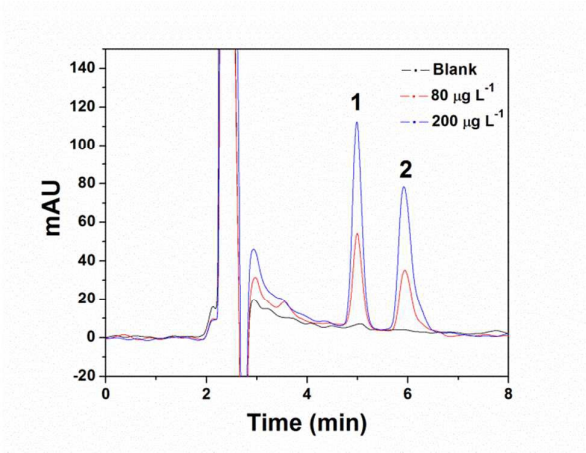

Fig. 5 The chromatograms of a vegetable oil sample and spiked sample from the bottom up: blank, 80 μg L^{-1} and 200 μg L^{-1}. (1) 4-nitrophenol; (2) 2,4-dinitrophenol.

3.4. Analysis of oil samples

The TFME-HPLC method proposed in this work was applied to quantitatively measure the phenolic compounds in oil samples. The proposed extraction method was combined with HPLC-UV and the extraction procedure of the oil samples was the same as the analysis of the standard solution. The oil samples spiked at a concentration of 80 μg L^{-1} and a concentration of 200 μg L^{-1} with the target analytes were investigated, and the analytical results were summarized in Table 2. Relative recoveries obtained for oil samples varied from 84.37% to 100.85%. Fig. 5 showed the liquid chromatogram of the phenolic compounds in a vegetable oil before and after spiking at 80 μg L^{-1} and 200 μg L^{-1}.

4. Conclusions

In this study, cellulose papers were successfully modified with polydopamine by a simple, efficient and environmentally friendly approach for the first time. The PDA modified cellulose papers were introduced as a novel extracting phase for TFME. The cellulose papers modified before and after were characterized by EDS, FT-IR and SEM. The results demonstrated that the papers were modified by polydopamine successfully. The proposed extraction method was combined with HPLC-UV to determine the phenolic compounds (4-nitrophenol, 2,4-dinitrophenol) in oil samples, which showed that the PDA modified cellulose papers have great potential applications in the pre-concentration of phenolic compounds from vegetable oil systems.

Acknowledgments

The financial support provided by National Natural Science Foundation of China (No. 21107022) and the Key Scientific Research Project of Higher Education of Henan Province of China (No. 15A610007) are gratefully acknowledged.

Notes and references

1 H. Tahermansouri, Z. Dehghan and F. Kiani, *RSC Adv.*, 2015, **5**, 44263-44273.
2 P. Xu, G. M. Zeng, D. L. Huang, L. Liu, C. Lai, M. Chen, C. Zhang, X. X. He, M. Y. Lai and Y. B He, *RSC Adv.*, 2014, **4**, 40828-40836.
3 D.M. Nevskaia, E. Castillejos-Lopez, V. Munoz and A. Guerrero-Ruiz, *Environ. Sci. Technol.*, 2004, **38**, 5786–5796.
4 B. H. Hameed and A. A. Rahman, *J. Hazard. Mater.*, 2008, **160**, 576–581.
5 G. Favaro, D. De Leo, P. Pastore, F. Magno and A. Ballardin, *J. Chromatogr. A*, 2008, **1177**, 36–42.
6 C. J. Liao, C. P. Chen, M. K. Wang, P. N. Chiang and C. W. Pai, *Environ. Toxicol.*, 2006, **21**, 71–79.
7 F. E. O. Suliman, S. S. Al-Kindi, S. M. Z. Al-Kindy and H. A. J. Al-Lawati, *J. Chromatogr. A*, 2006, **1101**, 179–184.
8 Toxic Substance Control Act, US Environmental Protection Agency, Washington, DC, 1979.
9 Y. Wang, D. Wei, H. Yang, Y. Yang, W. Xing, Y. Li and A. Deng, *Talanta*, 2009, **77**, 1783–1789.
10 F. J. López-Jiménez, S. Rubio and D. Pérez-Bendito, *Food Chem.*, 2010, **121**, 763–769.
11 M. Raoov, S. Mohamad, M. R. bin Abas and H. Surikumaran, *Talanta*, 2014, **130**, 155-163.
12 Z. Zhang, H. Zhang, Y. Hu and S. Yao, Anal. *Chim. Acta*, 2010, **661**, 173–180.
13 J. Regueiro, E. Becerril, C. Garcia-Jares and M. Llompart, *J. Chromatogr. A*, 2009, **1216**, 4693–4702.
14 W. Liu, W. Zhao, J. Chen and M. Yang, *Anal. Chim. Acta*, 2007, **605**, 41–45.
15 C. Yu, Q. Liu, L. Lan and B. Hu, *J. Chromatogr. A*, 2008, **1188**, 124–131.
16 Y. Fan, M. Chen, C. Shentu, F. El-Sepai, K. Wang, Y. Zhu and M. Ye, *Anal. Chim. Acta*, 2009, **650**, 65–69.
17 M. M. Tian, D. X. Chen, Y. L. Sun, Y. W. Yang and Q. Jia, *RSC Adv.*, 2013, **3**, 22111-22119.
18 A. Jain and K. K. Verma, *Anal. Chim. Acta*, 2011, **706**, 37–65.
19 L. Pelit, İlknur Bağatır, Füsun Okçu Pelit and F. Nil Ertaş, *RSC Adv.*, 2014, **4**, 32189-32196.
20 F. Aydin, E. Yilmaz and M. Soylak, *RSC Adv.*, 2015, **5**, 40422-40428.
21 M. Shamsipur and B. Hashemi, *RSC Adv.*, 2015, **5**, 20339-20345.
22 H. Jiang, B. Hu, B. Chen and W. Zu, *Spectrochim. Acta, Part B*, 2008, **63**, 770–776.
23 S. Jafarvand and F. Shemirani, *J. Sep. Sci.*, 2011, **34**, 455–461.
24 A. Ballesteros-Gomez, S. Rubio and D. Perez-Bendito, *J. Chromatogr. A*, 2009, **1216**, 530–539.
25 S. Jafarvand and F. Shemirani, *Anal. Methods*, 2011, **3**, 1552–1559.
26 A. Moral, M. D. Sicilia and S. Rubio, *J. Chromatogr. A*, 2009, **1216**, 3740–3745.
27 F. Rezaei, Y. Yaminia, M. Moradi and B. Daraei, *Anal. Chim. Acta*, 2013, **804**, 135–142.
28 M. R. Moghadam, S. Dadfarnia and A. M. H. Shabani, *J. Hazard. Mater.*, 2011, **186**, 169–174.
29 S. Dadfarnia and A. M. H. Shabani, *Anal. Chim. Acta*, 2010, **658**, 107–119.
30 J. Pawliszyn, Handbook of Solid Phase Microextraction, *Chemical Industry Press of China, Beijing, China*, 2009.
31 I. Bruheim, X. Liu and *J. Pawliszyn, Anal. Chem.*, 2003, **75**, 1002–1010.
32 S. Hong, K. Y. Kim and H. J. Wook, S. Y. Park, K. D. Lee, D. Y. Lee and H. Lee, *Nanomedicine*, 2011, **6**, 793–801.
33 H. Lee, S. M. Dellatore, W. M. Miller and P.B. Messersmith, *Science*, 2007, **318**, 426–430.
34 H. Lee, J. Rho and P. B. Messersmith, *Adv. Mater.*, 2009, **21**, 431–434.
35 S. Hong, Y. S. Na and S. Choi, I. T. Song, W. Y. Kim and H. Lee, *Adv. Funct. Mater.*, 2012, **22**, 4711–4717.
36 Q. Wei, F. Zhang, J. Li, B. Li and C. Zhao, *Polym. Chem.*, 2010, **1**, 1430–1433.
37 Y. Gu and J. Huang, *J. Mater. Chem.,* 2009, **19**, 3764-3770.
38 M. Abdelmouleh, S. Boufi, A. Ben Salah, M. N. Belgacem and A. Gandini, *Langmuir*, 2002, **18**, 3203–3208.
39 F. Ferri, L. Bertin, A. Scoma, L. Marchetti and F. Fava, *Chem. Eng. J.*, 2011, **166**, 994–1001.
40 A. Spietelun, Ł. Marcinkowski, M. de la Guardia and J. Namieśnik, *Talanta*, 2014, **119**, 34-45.
41 J. N. Sun, J. Chen, Y. P. Shi, *Talanta*, 2014, **125**, 329–335.
42 Q. Z. Feng, L. X. Zhao, J. M. Lin, *Anal. Chim. Acta*, 2009, **650**, 70–76.

Polydopamine cellulose papers were used to detect the nitrophenols in oil samples as a novel extraction phase.