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PAPER

Determination of nitrobenzenes and nitrochlorobenzenes in water samples using dispersive liquid-liquid microextraction and gas chromatography-mass spectrometry

Delin Zhang,[ab] Xiangying Zeng,[a] Zhiqiang Yu,*[a] Guoying Sheng[a] and Jiamo Fu[a]

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A rapid and sensitive method was developed for the determination of eight nitrobenzenes and four nitrochlorobenzenes in water. The method is based on dispersive liquid-liquid microextraction (DLLME) followed by gas chromatography-mass spectrometry (GC-MS). The key factors influencing the extraction efficiencies, including the nature and volume of the extraction and dispersion solvent and the ratios of the extraction solvent and dispersion solvent were examined and optimized. Under the optimized conditions, the method yields a linear correlation at a concentration range of 0.5 μg L^{-1}–500.0 μg L^{-1} for all the target analytes with correlation coefficients (R^2) of 0.9915 to 1.0000, and relative standard deviations (RSD, $n = 6$) of between 4.9% and 8.2%, depending on the compound analysed. In addition, good pre-concentration factors of 243 to 525 for each specific compound were achieved. These results suggest that the method presented herein is a rapid and powerful microextraction technique that is useful for the detection of these organic pollutants in water samples and is suitable for emergency monitoring.

Introduction

Nitrobenzene and nitrochlorobenzene compounds (NBs, NCBs, Table 1) are a group of chemicals that are usually used in the chemical industry in the preparation of dyes, perfumes, synthetic resins, pesticides, and drugs.[1] Of these compounds, 2-NCB and 4-NCB are possible human carcinogens that are produced in high volume worldwide. Jones *et al.* also found that hemoglobin adduct levels resulting from exposure to 2-NCB and 4-NCB in occupational workers were much higher than those detected from control workers, and that this was associated with fatigue, eye irritation, splenomegaly, and cardiovascular effects.[1] These compounds can enter into the aquatic environment *via* wastewater discharge, causing pollution of surface water. It has also been reported that the total concentration of 10 nitrobenzenes (NB, 2-NT 3-NT, 4-NT, 3-NCB, 4-NCB, 2-NCB, 2,6-DNT, 2,4-DNT, 2,4-DNCB) in the Yellow River ranged from 0.269 to 9.052 μg L^{-1}, with NB, 4-NCB and 2-NCB being the predominant contaminants.[2] Kang *et al.* detected 12.32 μg L^{-1} and 17.82 μg L^{-1} of NB in the Guanting Reservoir and the Yongding River, respectively.[3]

Several methods have been used successfully for the analysis of nitrobenzene compounds in water samples, including solid-phase extraction (SPE),[4] solid-phase microextraction (SPME),[5–9] headspace solvent microextraction (HSSME),[10] non-equilibrium liquid-phase microextraction (LPME),[10] and single drop microextraction (SDME).[11] However, there are obvious disadvantages associated with each of these methods. For example, SPE is time-consuming and has a high cost due to the expensive cartridge required, while SPME requires a longer time for equilibrium than other methods and its fiber is fragile and has a limited lifetime and desorption temperature. And HSSME, LPME and SDME require a great deal of time to transfer analytes into the micro amount of extraction solvent.

In 2006, Rezaee *et al.*[12] introduced a novel extraction method known as dispersive liquid-liquid microextraction (DLLME). This method consists of two main steps. The first step is the rapid injection of a mixture of extraction and dispersion solvents into the aqueous sample to disperse the extraction solvent into the aqueous sample, into which the analytes were enriched. Owing to the large surface area between the extraction solvent and the aqueous sample, the equilibrium state is achieved quickly, which is one of the most important advantages of DLLME. In the second step, the cloudy solution is centrifuged to achieve a sedimented phase, after which the analytes in the sedimented phase are identified by gas chromatography (GC) combined with mass spectrometry (MS) or flame ionization detection (FID).

To date, this method has been successfully applied in the detection of organic compounds such as polycyclic aromatic

[a]*State Key Laboratory of Organic Geochemistry, Guangdong Provincial Key Laboratory of Utilization and Protection of Environmental resource, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China. E-mail: zhiqiang@gig.ac.cn*
[b]*Graduate School of the Chinese Academy of Sciences, Beijing, 100039, China*

Table 1 Information, ions and instrument detection limits (IDLs) for the analytes

Name	Abbreviation	M.W.	Quantitative ion (*m*/*z*)	Confirmation ions (*m*/*z*)	log*K*ow[29]	IDL (pg)
Nitrobenzene	NB	123.11	77	123, 51	1.95	10.8
2-Nitrotoluene	2-NT	137.14	120	91, 65	2.41	6.3
3-Nitrotoluene	3-NT	137.14	91	65, 137	2.41	11.1
4-Nitrotoluene	4-NT	137.14	91	65, 137	2.41	14.3
3-Nitrochlorobenzene	3-NCB	157.56	111	157, 159	2.64	8.8
2-Nitrochlorobenzene	2-NCB	157.56	75	111, 157	2.34	4.1[a]
4-Nitrochlorobenzene	4-NCB	157.56	75	111, 157	2.60	4.1[a]
2,6-Dinitrotoluene	2,6-DNT	182.14	165	63, 89	2.08	13.0
2,4-Dinitrotoluene	2,4-DNT	182.13	165	63, 89	2.08	13.4
2,4-Dinitrochlorobenzene	2,4-DNCB	202.56	75	110, 202	2.06	29.3
1,3,5-Trinitrobenzene	TNB	213.11	75	120, 213	1.22	10.6
2,4,6-Trinitrotoluene	TNT	227.13	210	63, 89	1.68	11.5

[a] IDLs were calculated based on the co-eluted peaks of 2-NCB and 4-NCB in this study.[29]

hydrocarbons (PAHs), chlorophenols, polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), organophosphorus pesticides (OPPs) and inorganic chemicals in water samples.[13,14] In 2009, Ebrahimzadeh *et al.*[15] successfully used DLLME to study NB, NTs and DNTs in water samples and achieved acceptable preconcentration factors (PFs) using carbon tetrachloride as the extraction solvent and methanol as the dispersion solvent. Sobhi *et al.*[16] also established a DLLME method to detect three mononitrotoluenes (2-NT, 3-NT and 4-NT) at trace levels in water samples and also achieved satisfactory PFs using chlorobenzene as the extraction solvent and acetonitrile as the dispersion solvent. However, to the best of our knowledge, little effort has been made to establish a rapid method for the simultaneous detection of these nitrobenzenes and nitrochlorobenzenes in water samples. Therefore, the present study was conducted to identify a rapid and simple method utilizing DLLME technique for the determination of the group of NBs and NCBs in water samples. The effects of various experimental parameters, such as the type and volume of extraction and dispersion solvent as well their ratio were studied in detail and optimum conditions were established.

Experimental

Reagents and standards

The analytes in this study (shown in Table 1) were purchased from SUPELCO, USA. All of the standard solutions were kept in the refrigerator at 4 °C. HPLC grade acetonitrile (ACN), acetone (ACE), and methanol (MeOH) were supplied by Merck, USA. Reagent grade chloroform ($CHCl_3$), carbon tetrachloride (CCl_4) and dichloromethane (CH_2Cl_2) were purchased from the Tianjin Chemical Reagent Company, China. Water was purified using a Milli-Q water purification system.

Extraction procedure

5.0 mL of Milli-Q water spiked with 5.0 μg L^{-1} of each of the NBs and NCBs was placed in a 10 mL screw-capped glass test tube with a conical bottom. A suitable volume of the mixture solvent (composed of a known amount of extraction solvent and dispersion solvent) was then added rapidly into the water using a 1000 μL syringe. A cloudy solution (water/dispersion solvent/extraction solvent) immediately formed in the test tube . The mixture was then gently shaken for 20 s by hand, after which it was centrifuged for 5 min at 810.0 × g and 25 °C. This resulted in the NBs and NCBs in the water sample being extracted efficiently into fine extraction solvent droplets and then after centrifuging, the fine particles of extraction solvent formed a sediment in the bottom of the conical test tube. The volume of the sediment was measured using a Hamilton 10 microlitre syringe. Next, 1.0 μL of the extract was obtained and analyzed by GC-MS. Each batch of samples was analyzed in triplicate.

Instrumental analysis

The identification and quantification of the analytes was carried out using a Shimadzu 2010 gas chromatograph equipped with a mass spectra detector and a DB-5MS column (30 m × 0.25 mm × 0.25 μm, Agilent Technology). The temperature program was as follows: the initial temperature was 50 °C (held for 10 min), after which it was increased to 180 °C (held for 1 min) at a rate of 7 °C min^{-1}, and then to 230 °C (held for 2 min) at a rate of 3 °C min^{-1}, and finally to 300 °C at a rate of 10 °C min^{-1} (held for 5 min). The injection temperature was 250 °C. The injection port was operated in the splitless mode. The flow rate of the carrier (helium, 99.999%) was 1.1 mL min^{-1}. The mass spectrometer was operated in electroimpact (EI) and selective ion monitoring modes (SIM) with a source temperature of 200 °C, an interface temperature of 280 °C, and a solvent delay of 10 min. The *instrument detection limits* (IDLs) were calculated as 3 × (S.D./*S*),[21] where S.D. is the standard deviation of the response acquired for seven replicate injections of standard individuals (0.25 mg L^{-1}) and *S* is the slope of the calibration curve which was obtained from NBs and NCBs standard solutions in chloroform at a range of 0.005–10 mg L^{-1}. 2-NCB and 4-NCB were co-eluted under the selected GC conditions and the IDLs were calculated based on their co-eluted peaks. The retention times, selected ions and IDLs of the target compounds are shown in Table 1.

Analytical parameters

Two main parameters, extraction recovery (ER) and preconcentration factor (PF), were employed for evaluation of the

proposed method. ER was defined as the percentage of total analytes extracted in the sedimented phase (eqn (1)), while PF was defined as the ratio of the concentrations of the analytes extracted in the sedimented phase to the initial concentrations (eqn (2)):

$$\mathrm{ER} = \frac{C_{\mathrm{rec}} \times V_{\mathrm{rec}}}{C_0 \times V_{\mathrm{aq}}} \times 100\% \quad (1)$$

$$\mathrm{PF} = \frac{C_{\mathrm{rec}}}{C_0} \quad (2)$$

where, C_{rec} and C_0 were the concentrations of the analytes in the sedimented phase and the initial concentrations in the water sample, respectively. V_{rec} and V_{aq} are the volumes of the sedimented phases and the water sample, respectively.

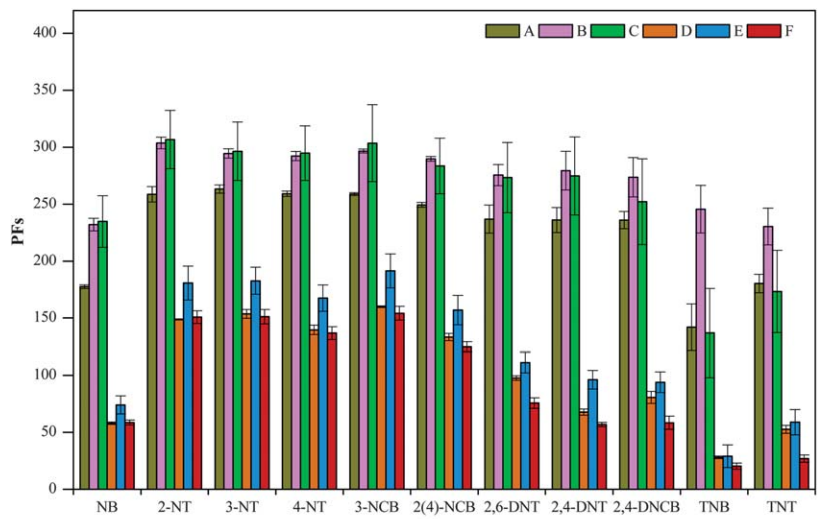
In this study, the mean values of ERs and PFs from triplicate samples were used as the index of extraction efficiency. In addition, 2-NCB and 4-NCB were co-eluted under the selected GC condition; therefore, the ERs and PFs were calculated based on their co-eluted peaks.

Results and discussion

Various parameters influence DLLME performance and efficiency, including the nature and volume of the extraction and the dispersion solvents, the volume of the mixed solvent, the extraction time, and salt addition.[12] Because an equilibrium state can be achieved very quickly in DLLME, the extraction time required is short and has a limited impact on the ERs and PFs.[17–19,22–24] Accordingly, the extraction time was not investigated in our study and a five minute extraction time was selected according to Ebrahimzadehet *et al.*[15] Additionally, because the goal of this study was to identify NBs and NCBs in surface water the effect of salinity was not taken into consideration.[11] Much effort has been paid to selection of a suitable extraction solvent and dispersion solvent, as well as an appropriate volume and ratio of these two kinds of solvents. In the present study, 5.0 mL of Milli-Q water spiked with 5.0 μg L^{-1} of each of the NBs and NCBs was used to study the extraction performance. All experiments were conducted in triplicate and the means of the results were used for optimization.

Selection of extraction and dispersion solvent

Selection of the extraction solvent was a key step in the DLLME method. The extraction solvent should have a higher density than water, low solubility in water and a high extraction capability for the target analytes. The dispersion solvent should be miscible with both water and the extraction solvents, promoting the dispersion of the extraction solvent when the mixed solvents (dispersion and extraction) are injected into water.[12,16,17] Based on the above criteria, five widely used solvents, CH_2Cl_2 (density: 1.33 g mL^{-1}), $CHCl_3$ (density: 1.47 g mL^{-1}), CCl_4 (density: 1.59 g mL^{-1}), CS_2 (density: 1.26 g mL^{-1}), and C_6H_5Cl (density: 1.11 g mL^{-1}) were investigated as extraction solvents, while MeOH, ACE and ACN were selected as dispersion solvents. A series of experiments was carried out, using mixtures of extraction solvents and dispersion solvents at different ratios and volumes, to achieve a sedimented phase of approximately 10.0 ± 0.5 μL, and then the corresponding ERs and PFs were calculated.[12,16] When less than 90.0 μL of CH_2Cl_2 was used as the extraction solvent, almost no two-phase systems were observed regardless of the dispersion solvent that it was combined with. This observation is was similar to that reported in previous studies.[23,25] Similarly, CS_2 and C_6H_5Cl also exhibited significantly lower extract efficiency than $CHCl_3$ and



A: Acetone-$CHCl_3$, B: Acetonitrile-$CHCl_3$, C: MeOH-$CHCl_3$, D: Acetone-CCl_4, E: Aectonitrile-CCl_4, F: MeOH-CCl_4

Fig. 1 Pre-concentration factor of the NBs and NCBs; samples spiked to 5.0 μg L^{-1} of each analyte. Extraction conditions: aqueous sample volume 5.0 mL; extraction time: 2 min; sedimented phase controlled to 10.0 ± 0.5 μL.

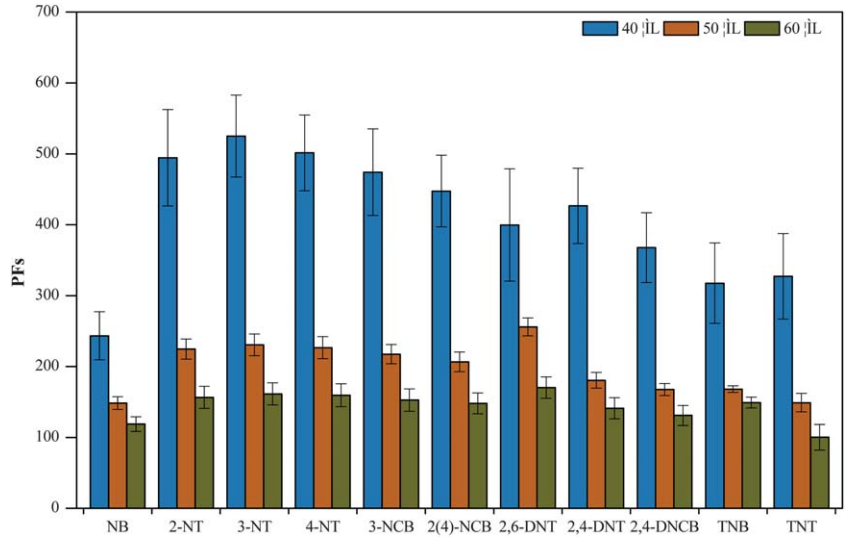


Fig. 2 Effect of the volume of the extraction solvent ($CHCl_3$) on PFs of the NBs and NCBs. Extraction conditions: sample volume: 5.0 mL; dispersion solvent: 500.0 μL acetonitrile.

CCl_4, and were not used as an extraction solvent in the subsequent analyses.

The results obtained using 500.0 μL of ACN, ACE, and MeOH as the dispersion solvent in conjunction with different volumes of extraction solvent ($CHCl_3$ or CCl_4) are shown in Fig. 1. When $CHCl_3$ was selected as the extraction solvent, the PFs were 178–263, 232–304 and 173–307 when ACE, ACN and MeOH were used as the dispersion solvent, respectively. When CCl_4 was used as the extraction solvent, the PFs were 28–160, 29–191 and 20–154 for ACE, ACN and MeOH, respectively. These results indicate that better PFs could be achieved using $CHCl_3$ as the extraction solvent in combination with any of the dispersion solvents. In addition, better repeatability was also obtained using ACN (RSDs = 0.6% to 8.5%, $n = 3$) than MeOH (RSDs = 8.1 to 28.6%, $n = 3$) and ACE (RSDs = 0.9 to 14.4%, $n = 3$) when $CHCl_3$ was used as the extraction solvent. Based on these findings, ACN was selected as the dispersion solvent and $CHCl_3$ as the extraction solvent for subsequent studies.

Effect of extraction solvent volume

The volume of extraction solvent is a critical issue for the ERs and PFs. As the $CHCl_3$ volume increased in the appropriate range, many more analytes were enriched into the extraction solvent, resulting in better ERs and PFs. Conversely, the concentrations of the analytes were decreased when excess extraction solvent was applied, thereby causing lower ERs and PFs. To achieve acceptable ERs and PFs, the volume of the extraction solvent was optimized. We fixed the dispersion solvent ACN at 500.0 μL, the volume of extraction solvent ($CHCl_3$) was tested at a range of 20.0–60.0 μL at 10.0 μL intervals. No sedimented phase was obtained when less than 40.0 μL $CHCl_3$ was

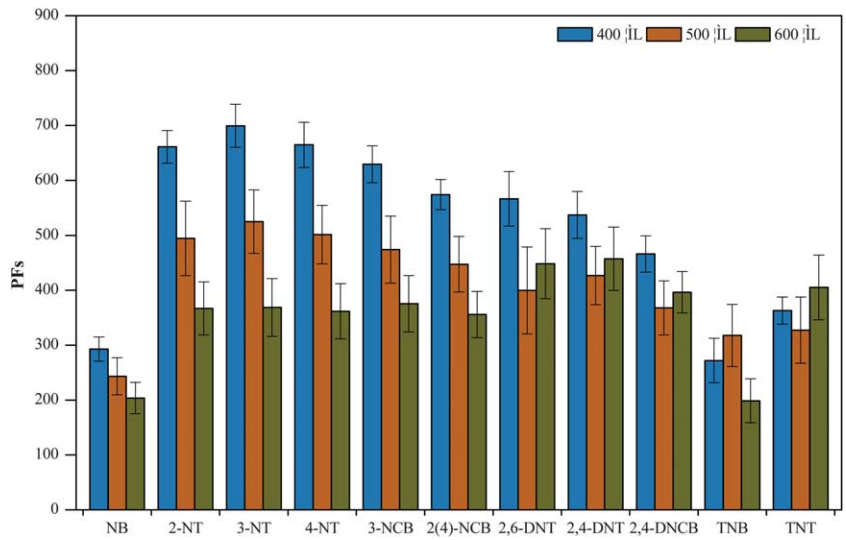


Fig. 3 Effect of the volume of the dispersiion solvent (acetonitrile) on the PFs of the NBs and NCBs. Extraction conditions: sample volume, 5.0 mL; extraction solvent, 40.0 μL $CHCl_3$.

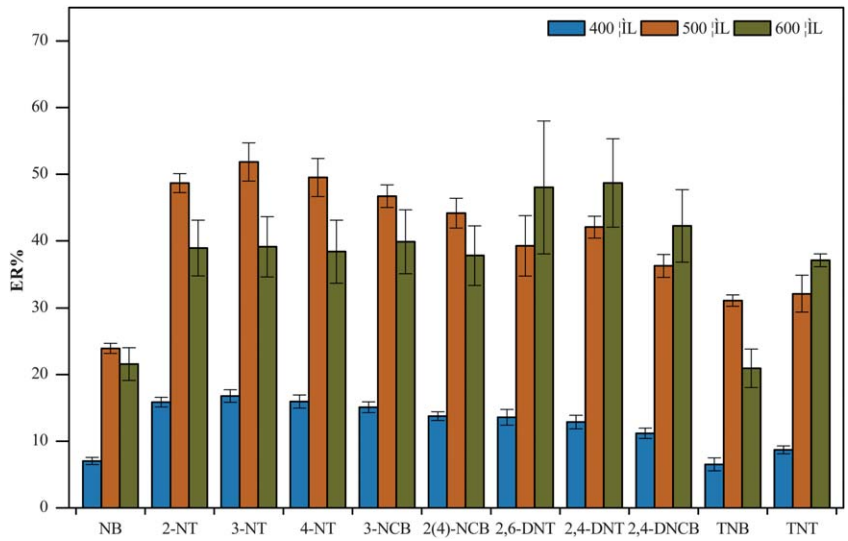


Fig. 4 Effect of the volume of the dispersive solvent (acetonitrile) on the ERs of the NBs and NCBs. Extraction conditions: sample volume, 5.0 mL; extraction solvent, 40.0 μL $CHCl_3$.

used. However, when the $CHCl_3$ level increased from 40.0 to 60.0 μL, the volume of the sedimented phase increased from 5.0 ± 0.9 to 10.5 ± 0.6 and 16.0 ± 1.0 μL, while the PFs decreased obviously from 243–525 (40.0 μL) to 148–256 (50.0 μL), and then to 101–176 (60.0 μL) (Fig. 2). No significant differences in the ERs were observed (average value of 12 NBs and NCBs) when 40.0 μL (average value 40.5%), 50.0 μL (40.7%) or 60.0 μL (45.8%) of $CHCl_3$ were used. This phenomenon agrees with the results of previously conducted studies.[12,16,20,26,27] Based on these findings, 40.0 μL of $CHCl_3$ was selected as the optimal volume for the following studies.

Effect of the dispersion solvent volume

The volume of the dispersion solvent is an important influence factor for DLLME because it can significantly influence the droplet size of the extraction solvent, which can result in remarkable variation in the volume of the sedimented phase.[12,28] Several experiments were conducted using dispersion solvent volumes of 400.0, 500.0 and 600.0 μL while the volume of the extraction solvent ($CHCl_3$) was fixed at 40.0 μL. The results indicated that better PFs (272–700) were achieved using 400.0 μL ACN, and that acceptable PFs (243–525) were obtained from 500.0 μL ACN, while poor PFs (177–427) were obtained from 600.0 μL ACN (Fig. 3). Better ERs and reproducibility (low RSD) were also acquired from 500.0 μL ACN (Fig. 4). This phenomenon could be explained by the distribution coefficient being affected remarkably by the volume of the dispersion solvent, while at a low volume, the mixture of the extraction solvent and dispersion solvent could not be dispersed well in the water, causing lower extraction recoveries of these analytes. Conversely, superfluous dispersion solvent can augment the solubility of NBs and NCBs in water, leading to a decrease in ERs. These results are similar to those reported by Sobhi *et al.*[16] Taking the ERs and PFs into account, 500.0μL ACN was selected as the optimum volume of dispersion solvent.

Evaluation of the method performance

Under the above optimum conditions, a series of experiments were conducted to test the performance of the method developed herein, including the determination of the method detection limits (MDLs), linear range (LR) and repeatability. The method detection limits, which were defined as 3.143σ (EPASW-846), were calculated from seven replicates of water samples spiked with NBs and NCBs at 0.5 μg L^{-1}, where σ is the standard deviation. The repeatability was examined by conducting six parallel experiments at a concentration of 5.0 μg L^{-1} for each of the NBs and NCBs, and the average PFs were also calculated.

As shown in Table 2, the MDLs ranged from 24.1 pg mL^{-1} to 107.4 pg mL^{-1} depending on the compound dertermined. These values were lower than those reported in previously conducted studies.[15,16,29] Good linearity was found at a range of 0.5–500.0 μg L^{-1} (0.5, 10.0, 25.0, 100.0, and 500.0 μg L^{-1}), exhibiting correlation coefficients (R^2) ranging from 0.9915 to 1.0000 depending on the compounds investigated. The results also indicated that the average PFs of the replicate spiked samples

Table 2 Analytical performance data for NBs and NCBs by the DLLME method

Compounds	LR[a] (μg L^{-1})	R^2	RSD (%; $n = 6$)	PFs[b]	MDL (pg mL^{-1})[c]
NB	0.5–500.0	0.9915	5.4	243	34.5
2-NT	0.5–500.0	0.9960	5.1	494	72.9
3-NT	0.5–500.0	0.9963	6.3	525	83.3
4-NT	0.5–500.0	0.9953	4.9	501	76.8
3-NCB	0.5–500.0	0.9967	5.4	474	78.5
2(4)-NCB	0.5–500.0	0.9959	7.1	447	60.6
2,6-DNT	0.5–500.0	1.0000	7.6	400	107.4
2,4-DNT	0.5–500.0	1.0000	5.8	427	75.7
2,4-DNCB	0.5–500.0	0.9999	6.2	368	99.5
TNB	0.5–500.0	0.9990	7.8	318	24.1
TNT	0.5–500.0	0.9943	8.2	327	81.9

[a] Linear range. [b] Pre-concentration factor. [c] Method detection limits.

Table 3 PFs, recoveries obtained in the determination of NBs and NCBs in spiked bottle, tap and river water samples

	Bottle water		Tap water		River water	
Compounds	RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)
NB	58.3	4.1	60.2	5.2	60.6	3.9
2-NT	69.2	5.3	71.5	6.2	71.8	5.6
3-NT	71.2	7.1	73.2	6.3	73.3	7.9
4-NT	70.6	6.9	72.8	7.2	72.7	8.6
3-NCB	76.4	7.5	77.8	6.2	78.4	7.3
2(4)-NCB	93.2	6.7	94.6	5.1	95.1	6.4
2,6-DNT	97.9	6.7	95.2	9.4	83.2	9.5
2,4-DNT	84.1	7.9	85.9	8.3	86.8	7.5
2,4-DNCB	87.3	6.7	96.6	7.6	81.4	8.1
TNB	25.9	8.1	26.5	7.3	26.2	7.6
TNT	30.7	9.0	29.7	8.5	27.3	9.7

ranged from 243–525, showing excellent repeatability with RSDs that ranged from 4.9% to 8.2% for different compounds.

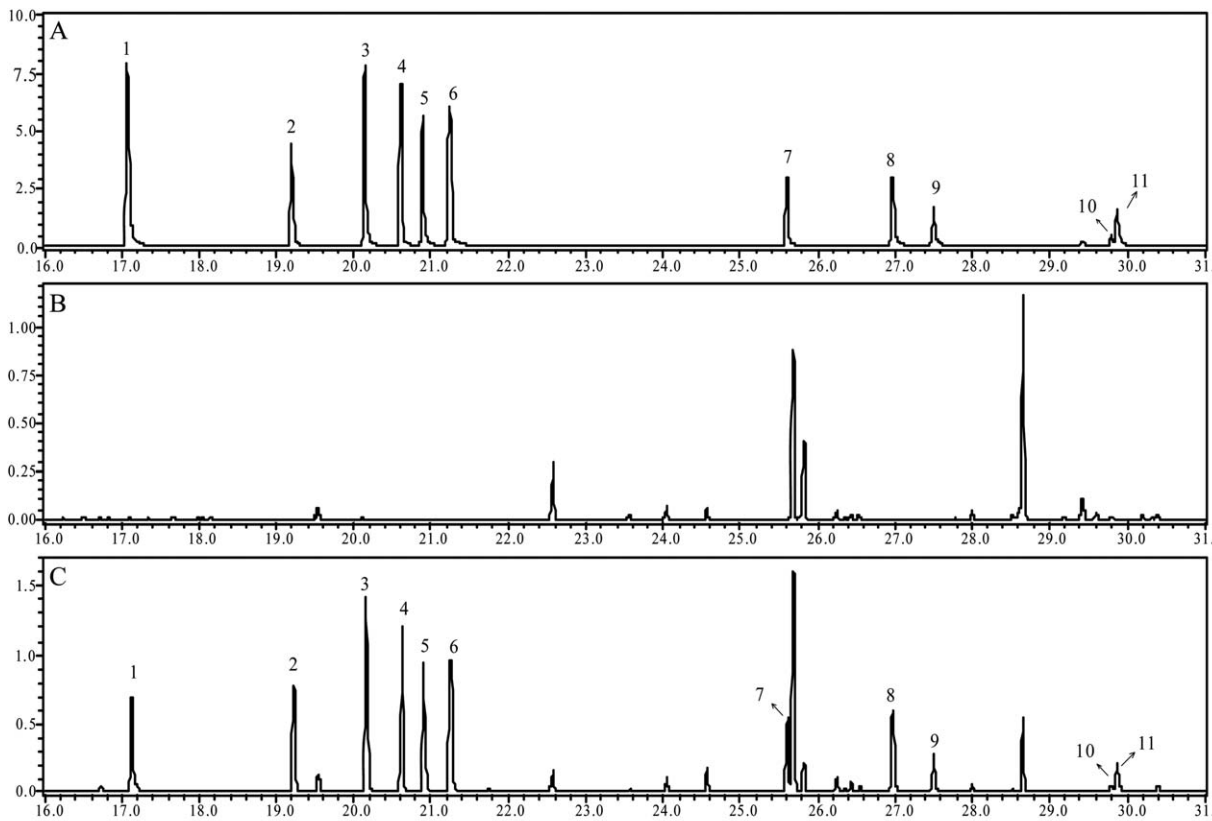
Application in real samples and matrix effect

To check possible matrix effects and investigate the applicability of this method for field sample analysis, three different water samples were analyzed for the occurrence and levels of NBs. Commercial bottle drinking water was purchased from Guangzhou Watercup Water Purification Technology Co., Ltd, tap water samples were collected from our laboratory, and surface water was taken from the Dongjiang River in the Pearl River Delta. In addition, corresponding spiked samples (50.0 μg L^{-1}, $n = 7$) of these water samples were also analyzed to assess the matrix effects *via* the relative recovery (RR). The relative recovery was calculated using eqn (3):

$$RR = \frac{C_f - C_r}{C_o} \times 100\% \quad (3)$$

where C_f and C_r were the concentrations of the analytes found in the spiked sample and corresponding real sample, and C_0 was the initial spiked concentrations in the water sample, respectively. The results are given in Table 3. GC-MS chromatograms of standards (A), blank river water (B) and spiked river water with NBs and NCBs at 50 μg L^{-1} (C) are presented in Fig. 5.

As shown in Table 3, for most target compounds except for TNB and TNT, the corresponding RRs ranged from 58.3–97.9%, 60.2–96.6% and 60.6–95.1% for bottle, tap and river water, respectively. These results demonstrate that the different matrices had no significant effect on RRs of NBs and NCBs using the developed DLLME method. Conversely, lower RRs



(1) NB,(2) 2-NT,(3) 3-NT,(4) 4-NT,(5) 3-NCB,(6) 2(4)-NCB,(7) 2,6-DNT,(8) 2,4-DNT,(9) 2,4-DNCB,(10) TNB,(11)TNT

Fig. 5 GC-MS chromatogram of (A) standard (concentration: 5000 μg L^{-1}); (B) blank river water; (C) spiked water with NBs and NCBs at 50 μg L^{-1} obtained by DLLME, conditions: water sample volume, 5.0 mL; 500 μL of mixed solvent (ACN : $CHCl_3$ = 500 : 40); extraction time: 2 min.

(<35.0%) were found for TNB and TNT, which might be due to their lower log*K*ow value (see Table 1), which is similar to the results of a previous study.[7]

Conclusions

In this study, a rapid, simple and sensitive DLLME extraction technique was established for the determination of eight nitrobenzenes and four nitrochlorobenzenes exhibiting large differences in their polarities. The results disclosed that good linearity in the range 0.5–500.0 μg L^{-1}, lower MDLs, acceptable PFs and good repeatability were achieved using the developed method. Under the optimum conditions, NBs in water samples could be extracted and analyzed in a short time using a limited amount of organic solvent. This method is especially well suited for rapid identification and quantification of analogous contaminants in emergency water pollution situations.

Acknowledgements

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