Turk J Chem
36 (2012) , 614 – 623.

doi:10.3906/kim-1112-11

Determination of ultratrace amounts of dichloro-nitrobenzene and dichloro-nitroaniline in water samples using solidified floating organic drop microextraction (SFODME) and gas chromatography

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Received: 04.12.2011

Solidified floating organic drop microextraction (SFODME) in combination with gas chromatography with an electron capture detector was used for separation/enrichment and determination of 2,5-dichloro-nitrobenzene, 2,3-dichloro-nitrobenzene, and 2,6-dichloro-4-nitroaniline in water samples. The main parameters affecting the performance of SFOME, such as solvent volume, extraction time, stirring rate, extraction temperature, sample volume, nature of the solvent and ionic strength were optimized. Under the optimum experimental conditions, good relative standard deviations of 7.5%, 6.9%, and 9.3% for 7 extractions and determination of 50 ng L^{-1} of 2,5-dichloro-nitrobenzene, 2,3-dichloro-nitrobenzene and 2,6-dichloro-4-nitroaniline were obtained, respectively. Enrichment factors of 1390, 1398, and 1362 and detection limits of 1.4, 1.2, and 10 ng L^{-1} for 2,5-dichloro-nitrobenzene, 2,3-dichloro-nitrobenzene, and 2,6-dichloro-4-nitroaniline were found, respectively.

Key Words: Solidified floating organic drop microextraction, 2,5-dichloro-nitrobenzene, 2,3-dichloro-nitrobenzene, 2,6-dichloro-4-nitroaniline, gas chromatography

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Introduction

2,5-Dichloro-nitrobenzene (2,5-DCNB) and 2,3-dichloro-nitrobenzene (2,3-DCNB) are produced directly or as by-products during the synthesis of other chemicals. They are used as intermediate reagents in the chemical industry and as agricultural chemicals, because of their antibacterial and antiprotozal properties. These compounds are toxic to daphnids, fish, and algae, are stable in the environment, and are considered not readily biodegradable agents.[1,2] 2,6-Dichloro-4-nitroaniline (2,6-DC-4-NA) is a commercial fungicide that is intensively used in agriculture to control plant disease.[3] However, little is known about the environmental significant of these compounds. Thus, they deserve particular attention because of their persistence and the lack of scientific evidence on their long-term effects.[4] Therefore, evaluation and monitoring of trace levels of these analytes in water samples are important as the amounts of them that reach the water will be transferred or distributed in the environment.

Prior to determination by chromatography methods, some sample preparation techniques such as liquid-liquid extraction (LLE),[5] solid phase extraction (SPE),[6] solid phase microextraction (SPME),[7–11] and liquid phase microextraction (LPME)[12–19] were used for the separation and preconcentration of some chlorobenzene and chloroaniline compounds. However, recent research has been oriented toward efficient development of economical and miniaturized extraction methods. In this regard the liquid phase microextraction techniques have received a growing amount of attention because of their simplicity, low consumption of organic solvent, low cost, ease of operation, and possibility of obtaining a high enrichment factor.[20,21] In 2007, Khalili Zanjani and co-workers introduced a novel liquid phase microextraction called solidification of floating organic drop microextration (SFODME).[22] This method has been successfully used for the extraction of organic compounds[22–24] and metal ions from water and other matrices.[25–29]

Although there are reports on the use of liquid phase microextraction techniques for extraction of chlorobenzene and aniline derivatives from water samples, studies on the determination of dichloro-nitrobenzene compounds are rare. Thus, the main objective of this research was to examine the applicability of SFODME followed by gas chromatography-electron capture detector (GC-ECD) for simultaneous extraction and determination of 2,5-dichloro-nitrobenzene, 2,3-dichloro-nitrobenzene, and 2,6-dichloro-4-nitroaniline in water samples.

Experimental

Reagents and samples

All reagents used were of the highest purity available and at least of analytical reagent grade. Stock solutions (1000 mg L^{-1}) of 2,5-dichloro-nitrobenzene, 2,3-dichloro-nitrobenzene, and 2,6-dichloro-4-nitroaniline were prepared by dissolving an accurate mass of 0.1 g of each compound into a 100 mL flask and diluting to the mark with methanol. Standard solutions were prepared daily from the stock solutions by serial dilution with water. Deionized water was used throughout the sample preparation and all solutions were stored in pre-cleaned polypropylene (Nalgene, Lima, OH, USA) containers. 2,5-Dichloro-nitrobenzene ($C_6H_3Cl_2NO_2$), 2,3-dichloro-nitrobenzene ($C_6H_3Cl_2NO_2$), 2,6-dichloro-4-nitroaniline ($C_6H_4Cl_2N_2O_2$), 1-undecanol, 1-dodecanol, 1,10-dicolorodecan, and n-hexadecane were obtained from Merck (Darmstadt, Germany). 1-Undecanol was used as the selected extracting solvent.

Instrumentation

Experiments were carried out using a gas chromatography Aligent (Wilmington, DE, USA) 6890N-ECD equipped with a split/spiltless injector, electronic pressure control in the injector, and an electron capture detector. A capillary column DB1701 (30 m × 0.32 mm I.D., 0.25 μm film thickness) from Agilent company (Wilmington, DE, USA) was used. Nitrogen gas (purity 99.999%) at a flow rate of 1.4 mL min^{-1} was used as the carrier and makeup gas. Oven temperature was programmed as follows: 40 °C for 5 min, heated at 40 °C min^{-1} to 180 °C and kept for 5 min, and finally raised at 20 °C min^{-1} to 280 °C and held for 5 min. The injection was performed in the splitless mode. The ECD was held at 260 °C.

Extraction procedure

To 14 mL of a sample or standard solution containing the analytes was added 0.8 g of sodium chloride and the solution was transferred into ∼15 mL vial containing a stirrer bar. Then 10 μL of 1-undecanol was added, the magnetic stirrer was turned on, and the solution was mixed for 25 min at 1000 rpm. In this step the analytes were extracted into 1-undecanol. After the extraction time was up, the sample vial was kept in an ice bath until the organic solvent was solidified (∼5 min). The solidified solvent was then transferred into a conical vial with a glass spatula where it melted immediately and 2 μL of it was injected into the gas chromatograph for analysis.

Results and discussion

In order to optimize the SFODME procedure for the simultaneous extraction and determination of analytes, the effects of different conditions were explored. These factors included the type and volume of extraction solvent, the temperature of extraction, the volume of the sample, stirring rate, salt addition, and extraction time. The optimization was performed using 14 mL of solution containing 50 ng L^{-1} of each analyte.

In the SFODME method, the enrichment factor and the percent of extraction were calculated as described before.[27,29]

$$\text{Percent of extraction} = \left(\frac{C_o V_o}{C_{aq} V_{aq}}\right) \times 100 \quad (1)$$

$$\text{Enhancement Factor} = \frac{C_0}{C_{aq}} \quad (2)$$

where V and C are the volume and concentration, and the suffixes o and aq stand for the organic and initial aqueous phases, respectively. C_o was calculated from the calibration curve.

The choice of organic solvent is a critical factor in the development of an efficient SFODME procedure, as the physico-chemical properties of the solvent govern the distribution ratio and consequently the extraction efficiency of analytes. Thus, the extraction solvent must satisfy several requirements: it should be stable during the extraction period; have low water solubility, low toxicity, a melting point near room temperature (10-30 °C), and high affinity for the target analyte; and its peak must be separated from the analyte peaks in the chromatogram. According to these criteria, several extracting solvents, including 1-undecanol (mp 13-15 °C),

1-dodecanol (mp 22-24 °C), 1, 10-dichlorodecane (mp 14-16 °C), 1-bromohexadecane (mp 17-18 °C), and n-hexadecane (mp 18 °C) were investigated. The chromatographic peak of 1-bromohexadecane, 1-dodecanol, and 1,10-dichlorodecane overlapped with the analyte peaks and was not resolved, so these solvents were ruled out for further consideration. The peaks of 1-undecanol and n-hexadecane were easily separated from the analytes; however, as the extraction efficiency of all analytes was higher with 1-undecanol, it was selected as extracting solvent for subsequent experiments. The chromatogram of analytes in 1-undecanol at optimum temperature program of GC is demonstrated in Figure 1.

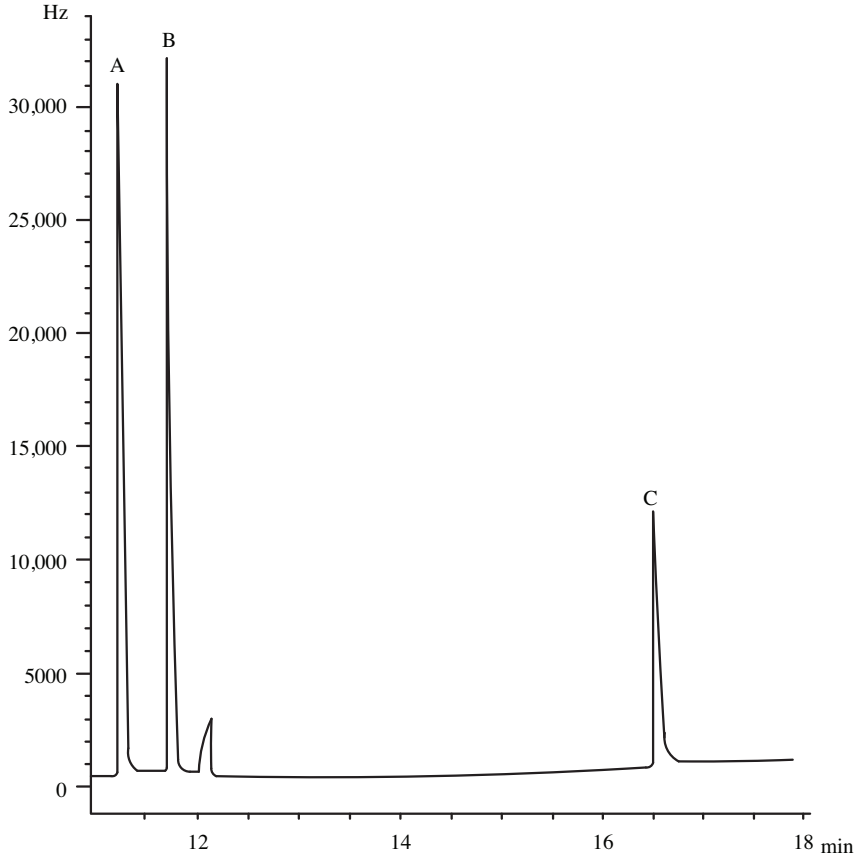

Figure 1. Chromatogram of investigated analytes in 1-undecanol under optimum temperature conditions of GC. (A) 2,5-dichloro-nitrobenzene, (B) 2,3-dichloro-nitrobenzene, (C) 2,6-dichloro-4-nitroaniline; Conditions: sample volume 14 mL, analytes concentration 50 ng L^{-1}, salt concentration 1 mol L^{-1}, sample temperature 50 °C, organic phase volume 10 μL, stirring rate 1000 rpm, extraction time 30 min.

To increase the sensitivity of the SFODME, the effect of solvent volume on extraction efficiency was investigated. The volume of extracting solvent is an important factor that affects the enrichment factor. An increase in the ratio of the volume of the aqueous phase to the organic phase will increase the preconcentration factor, but it may reduce the extraction efficiency in a given extraction time. For this purpose different volumes of 1-undecanol (7-13 μL) were subjected to SFODME under the constant condition of other variables. The results, shown in Figure 2, indicate that by increasing the volume of 1-undecanol up to 10 μL the peak areas

are slightly increased and reach their maximum. This observation can be explained by the fact that in LLE the rate of analyte transport into the microdrop is directly related to the interfacial area between the aqueous and organic phase and inversely related to the volume of the organic phase.[22] Thus, at low volume of organic phase the effect of interfacial area predominates and the analytical signal increases with an increase in solvent volume. A further increase in microdrop volume causes the solvent volume effect to predominate and the analytical signal is decreased. Therefore, an organic volume of 10 μL was selected as the optimum volume of organic solvent.

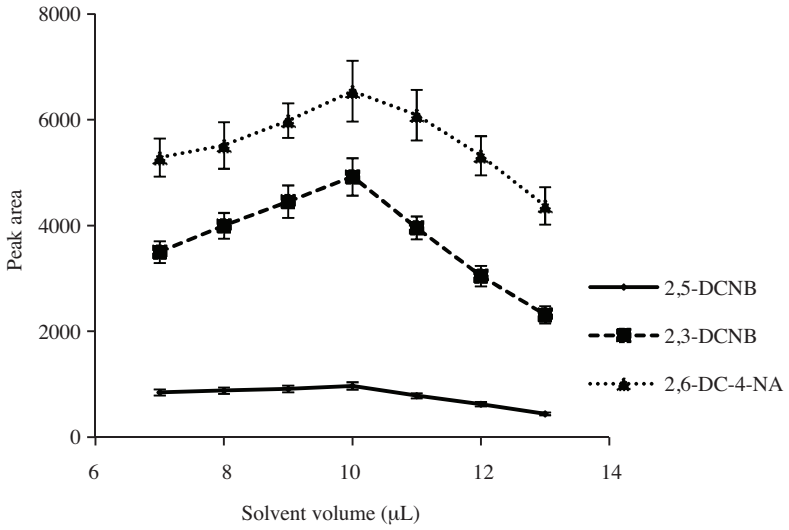

Figure 2. Effect of solvent volume on extraction of analytes; Conditions: sample volume 14 mL, analytes concentration 50 ng L^{-1}, salt concentration 1 mol L^{-1}, sample temperature 50 °C, stirring rate 1000 rpm, extraction time 30 min, each point is the average of 3 independent measurements.

The temperature of solution is a factor that can affect the kinetics of extraction through the diffusion coefficients and mass transfer of the analytes from the aqueous to the organic phase. Thus, the higher the temperature, the faster the kinetics of reaction and the equilibrium will be reached in a shorter extraction time. The effect of temperature on the extraction efficiency was studied in the range of 17-80 °C at constant extraction time (Figure 3). The results showed that under these conditions by increasing the temperature up to 50 °C the extraction efficiency was increased. However, at higher temperature the extraction system was unstable, which may be due to the increase in the solubility of organic phase in aqueous sample phase or over-pressurization of the sample vial. Therefore, in further experiments the sample vial temperature was held at 50 °C.

In order to explore the possibility of extraction of low concentrations of analytes from the large sample volume, the effect of sample volume, which influences the enrichment factor, was considered. For this purpose different volumes (10-18 mL) of sample solution containing 0.7 ng of each analyte were extracted at optimum conditions in the proper size vial. The results showed that the quantitative recovery ($>95\%$) was obtained for sample volume up to 14 mL. Thus, based on the organic phase volume (10 μL) and the maximum sample volume for which the extraction was quantitative (14 mL) a preconcentration factor of 1400 was determined.

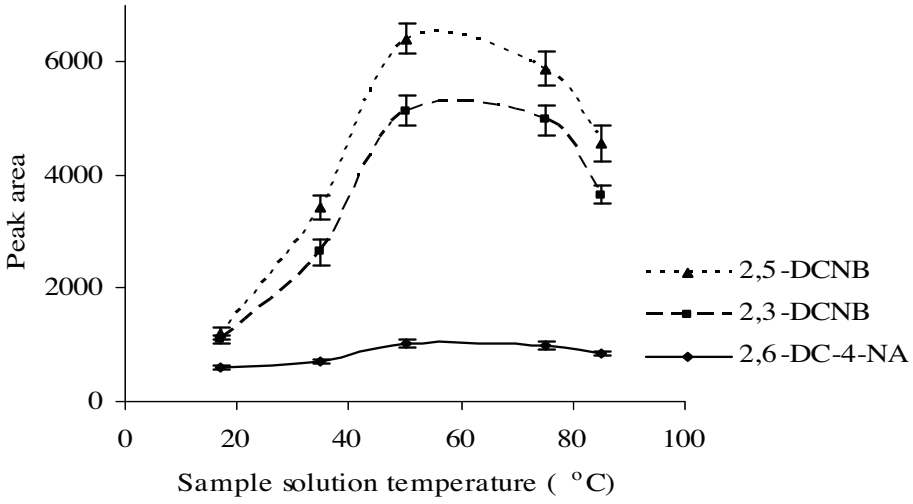

Figure 3. Effect of sample temperature extraction of analytes; Conditions: sample volume 14 mL, analytes concentration 50 ng L^{-1}, salt concentration 1 mol L^{-1}, organic phase volume 10 μL, stirring rate 1000 rpm, extraction time 30 min, each point is the average of 3 independent measurements.

Extraction time is an important factor influencing extraction efficiency and speed of analysis. In order to have good precision, sensitivity, and speed, it is necessary to select an extraction time that guarantees the achievement of equilibrium between aqueous and organic phases. The effect of extraction time on extraction efficiency was examined by varying the extraction time from 5 to 40 min in the constant experimental conditions. The results showed that (Figure 4) the extraction was relatively fast and after 25 min the peak areas of analytes were independent of extraction time. An optimum stirring period of 25 min was selected.

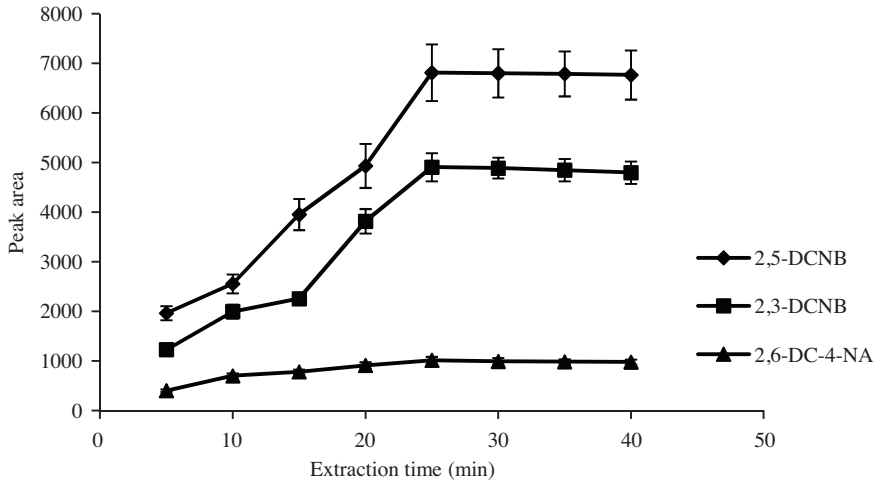

Figure 4. Effect of extraction time; Conditions: sample volume 14 mL, analytes concentration 50 ng L^{-1}, salt concentration 1 mol L^{-1}, sample temperature 50 °C, organic phase volume 10 μL, stirring rate 1000 rpm, each point is the average of 3 independent measurements.

Sample stirring rate is another important factor in extractions that affects the mass transfer and enhances the kinetic of extraction. According to the film theory of convective-diffusive mass transfer in the LPME system, the faster the sample agitation, the lower the thickness of diffusion film in the aqueous phase and consequently the higher the mass-transfer coefficient in the aqueous phase.[30] In this study, the stirring rate was varied between 250 and 1125 rpm at a constant extraction time of 25 min. The extraction efficiency was found to increase with increasing stirring rate up to 1000 rpm and then remained constant. Hence, a stirring rate of 1000 rpm was adopted for further study.

In order to investigate the effect of ionic strength on the SFODME performance, several experiments were performed with different NaCl concentration (0.0-2.74 mol L^{-1}) while keeping the other experimental parameters constant. Addition of salt to the sample usually enhances the extraction efficiency due to the salting out effect. On the other hand, the presence of a high concentration of salt may change the physical properties of the Nernst diffusion film and thus reduce the rate of diffusion of the analytes into the microdrop of organic solvent.[23,31] The results confirmed that salt addition up to a concentration of 1 mol L^{-1} causes an increase in extraction efficiency. However, a further increase in NaCl causes a decrease in the extraction efficiency, possibly due to the decrease in analyte mass transfer from the aqueous solution into the organic drop. Therefore, in all the further experiments the NaCl concentration was adjusted to 1 mol L^{-1}.

Analytical performance

The calibration curves were constructed by extracting the analytes from 14 mL sample standard solutions. Under the optimum conditions the calibration curves were linear in the concentration range of 5-100 ng L^{-1}, 5-170 ng L^{-1}, and 20-1400 ng L^{-1} for 2,5-dichloro-nitrobenzene, 2,3-dichloro-nitrobenzene, and 2,6-dichloro-4-nitroaniline, respectively. The equations of calibration graphs were $A = 126.4C + 199.5$ ($R^2 = 0.995$, $S_{A/C} = 340.3$, $S_b = 3.4$, $S_a = 174.4$), $A = 87.8\,C + 593.9$ ($R^2 = 0.998$, $S_{A/C} = 226{,}1$ $S_b = 1.2$, $S_a = 115.4$), and $A = 29.5\,C - 499.5$ ($R^2 = 0.997$, $S_{A/C} = 3366.4$, $S_b = 2.64$, $S_a = 1642$) for 2,5-dichloro-nitrobenzene, 2,3-dichloro-nitrobenzene, and 2,6-dichloro-4-nitroaniline, respectively (where A is the peak area and C is the concentration of analytes (ng L^{-1}) in aqueous phase, $S_{A/C}$ is the random error in Y direction, S_b is the standard deviation of slope, and S_a is the standard deviation of intercept). The enhancement factors determined as the ratio of the slope of calibration curves with and without preconcentration were found to be 1390, 1398, and 1362 for 2,5-dichloro-nitrobenzene, 2,3-dichloro-nitrobenzene, and 2,6-dichloro-4-nitroaniline, respectively. The relative standard deviations (R.S.D.) for 7 replicate measurements at 50 ng L^{-1} were $\pm 7.5\%$, $\pm 6.9\%$, and $\pm 9.3\%$, and the limits of detection (LOD), defined as 3 times the standard deviation of the blank measurements to the slope of calibration curve, were 1.4, 1.2, and 10 ng L^{-1} for 2,5-dichloro-nitrobenzene, 2,3-dichloro-nitrobenzene, and 2,6-dichloro-4-nitroaniline, respectively.

Application

The reliability of the recommended procedure was examined through determination of analytes in well water, river water, seawater, and the effluent of a pigment producing factory. The concentrations of analytes in all samples were found to be less than the limits that threaten the life of daphnids, fish, and algae.[1–3] The accuracy of the method was examined by analysis of the samples spiked with 2 different levels of analytes. The result of

Table 1. Determination of analytes in real samples.

	Amount added (ng L^{-1})			Amount found* (ng L^{-1})			Recovery (%)		
Sample	2,5-DCNB	2,3-DCNB	2,6-DC-4-NA	2,5-DCNB	2,3-DCNB	2,6-DC-4-NA	2,5- DCNB	2,3-DCNB	2,6-DC-4-NA
Well water	-	-	-	ND	ND	90 ± 4	-	-	-
	50	50	50	52 ± 3	47 ± 3	135 ± 9	104	94	90
	100	100	100	105 ± 7	109 ± 6	184 ± 10	105	109	94
Effluent	-	-	-	8 ± 0.5	40 ± 3	47 ± 2	-	-	-
	50	50	50	60 ± 4	85 ± 6	100 ± 6	104	90	106
	100	100	100	102 ± 5	148 ± 10	150 ± 7	94	108	103
River water	-	-	-	12 ± 1	22 ± 0.9	56 ± 3	-	-	-
	50	50	50	65 ± 3	70 ± 5	103 ± 5	106	96	94
	100	100	100	116 ± 6	119 ± 8	159 ± 10	104	97	103
Seawater	-	-	-	20 ± 1	45 ± 4	60 ± 5	-	-	-
	50	50	50	74 ± 4	99 ± 5	108 ± 9	108	108	96
	100	100	100	125 ± 7	140 ± 9	153 ± 8	105	95	93

Table 2. Comparison of the developed method with other microextraction techniques.

Method of analysis	Species	Limit of detection (ng L^{-1})	Enhancement factor	RSD (%)	Ref.
SFODME-GC/ECD	2,5-dichloro-nitrobenzene	1.2-10	1362-1398		This work
	2,3-dichloro-nitrobenzene			6.9-9.3	
	2,6-dichloro-4-nitroaniline				
DLLME-GC/MS	Aniline	40-90	212-645	5.8-11.5	15
	4-chloroaniline				
	3-chloro-2-methylaniline				
	3,5-dichloroaniline				
DLLME-SFO-GC/ECD	1,2- dichlorobenzene	5-50	174-246	2.6-8.7	16
	1,2,4- trichlorobenzene				
	tetrachloroethylene				
	hexachlorobutadiene				
	4-bromodiphenyl ether				
LLLME-HPLC-UV	3-nitoaniline	1000	148.6	4.9	17
SDME-GC/ECD	1,2-dichlorobenzene	4-8	-	<6	13
	1,3- dichlorobenzene				
	1,4- dichlorobenzene				
	1,2,3- trichlorobenzene			1.27-8.20	
HFLPME-HPLC	2-nitroaniline	30-250	6092-17,094		12
	4-nitroaniline				
	3-chloroaniline				
	4-bromoaniline				
SPME-HPLC/UV	2-nitroaniline	40-130	88-307	1.3-6.1	10
	4-nitroaniline				
	2-chloroaniline				
	2,4-dichloroaniline				

this investigation is given in Table 1 and illustrates that the recovery of added analytes is good (90%-108%). Thus the method is capable of measurement of analytes from complex matrices such as effluents.

Comparison with other methods

The preconcentration and determination of analytes by the developed SFODME-GC method were compared with those of other microextraction methods used for their extraction and determination. The results are shown in Table 2 and indicate that, with the exception of the HFLPME-HPLC method,[12] the enhancement factors of the developed method are higher. The detection limit of the proposed method is also lower than that of most of the reported methods[10,12,15–17] and its precision is comparable to that of the others.

Conclusion

In the present study a SFODME method combined with GC-ECD was developed for the extraction and determination of trace amounts of 2,5-dichloro-nitrobenzene, 2,3-dichloro-nitrobenzene, and 2,6-dichloro-4-nitroaniline in complex matrices such as effluents. The method has high enhancement factor and low detection limit. Other advantages of the method are minimum consumption of toxic organic solvents, low cost, and no need for sophisticated extraction apparatus. Future work will be directed toward the comparison of the capability of different liquid phase microextraction methods for separation and preconcentration of these compounds from various matrices.

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