

Quantitation of mononitrotoluenes in aquatic environment using dispersive liquid–liquid microextraction followed by gas chromatography–flame ionization detection

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ABSTRACT

A simple and efficient method (known as dispersive liquid–liquid microextraction (DLLME)) combined with gas chromatography–flame ionization detector (GC–FID) has been successfully developed for the extraction and determination of mononitrotoluenes (MNTs) in aquatic samples. The effects of parameters such as the nature and volume of the extracting and disperser solvents on the microextraction efficiency were also investigated. The volume of the extracting solvent (chlorobenzene) and that of the disperser solvent (acetonitrile) were obtained to be equal to 10.0 μL and 0.5 mL, respectively, in the optimal microextraction conditions established. Under the optimal conditions, the detection limit of the method was 0.5 $\mu\text{g L}^{-1}$ and the relative standard deviations (RSDs%) for determination of the MNTs were in the range of 8.0–9.4. Linearity was found to be in the range of 1–1000 $\mu\text{g L}^{-1}$; also, the pre-concentration factors were in the range of 351–357. Finally, the method was applied to determine the trace amounts of the MNTs in several real aquatic samples and satisfactory results were obtained.

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1. Introduction

Sample preparation is a tedious and yet unavoidable procedure in analytical chemistry [1]. The objective of this challenging and critical step is to transfer the analyte into a form that is pre-purified, concentrated, and compatible with the analytical system [2,3]. The extracted and enriched analytes of interest from the sample matrix are often accomplished by procedures, such as liquid–liquid extraction (LLE) [4,5] and solid-phase extraction (SPE) [6,7]. The invention of solid-phase microextraction (SPME) by Pawliszyn and Arthur [8], basically initiated the interest for microextraction techniques in analytical chemistry. SPME satisfies most of the requirements of a good sample preparation technique, including simplicity of use, automation, and low consumption of materials [9]. Thus, it has been applied to determine a broad range of organic compounds in numerous types of samples [10].

An alternative solvent-minimized sample preparation approach to complement SPME appeared in the middle-to-late 1990s [11–13]; liquid-phase microextraction (LPME) utilizes only a small amount of solvent (low microliter range) for concentrating analytes from aqueous samples. It is simply a miniaturized format of

LLE and overcomes many of its disadvantages as well as some of those of SPME (e.g. non-dependence on a commercial supplier and sample carryover). LPME is simple to implement and use, generally fast, and is characterized by its affordability and reliance on widely-available apparatus or materials [14]. The applications of LPME in environmental and biological analysis have been described in several papers [15–17].

Recently, Assadi et al. have developed a simple and rapid pre-concentration and microextraction method, named dispersive liquid–liquid microextraction (DLLME), which was initially applied for the determination of polycyclic aromatic hydrocarbons (PAHs) in water samples [18]. This method consists of two steps: (1) the injection of an appropriate mixture of extracting and disperser solvents into the aqueous sample. In this step, the extracting solvent is dispersed into the aqueous sample as very fine droplets and the analytes are enriched into it. Owing to the infinitely large surface area between the extracting solvent and the aqueous sample, the equilibrium state is achieved quickly and the extraction is independent of time. This is the most important advantage of this method. (2) The centrifugation of cloudy solution. After centrifugation, the determination of analytes in the sedimented phase can be performed by a proper instrumental analysis. This quantitative microextraction method is an efficient and satisfactory analytical procedure, because excellent accuracy and precision are demonstrated.

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Mononitrotoluenes (MNTs) are a group of explosive compounds, being widely present in aquatic environments due to their broad spread applications [19]. MNTs are used in the synthesis of intermediates for production of dyes, rubber chemicals, pesticides and several industrial applications [20]. These compounds are highly toxic, substances in low concentrations, and formed by biodegradation are suspected to be carcinogenic [21]. Therefore, MNTs determination in various matrices at trace level is of great importance [22–26]. It is noteworthy that the maximum allowable concentration of MNTs is 5 ppm [27].

The aim of the present study is to assess the suitability of DLLME technique for the determination of MNTs in water samples. The factors affecting the microextraction efficiency were studied in details and the optimal conditions were established. The resulting method was validated for quantitative purposes and then was applied to real sample analysis in combination with gas chromatography–flame ionization detection (GC–FID).

2. Experimental

2.1. Reagents and real samples

The studied MNTs including *o*-mononitrotoluene, *m*-mononitrotoluene, and *p*-mononitrotoluene were purchased from Merck (Darmstadt, Germany). The stock standard solutions (500 mg L⁻¹) were prepared in methanol. All of the standard solutions were kept in the fridge at 4 °C. HPLC grade acetonitrile, ethanol, and methanol were supplied by Merck. Reagent grade chlorobenzene, carbon tetrachloride, tetrachloroethylene as well as sodium chloride were also purchased from Merck. Double distilled water used for preparing the working solutions was purified with a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Tap water sample was collected freshly from our laboratory (Tehran Payamenoor University, Tehran, Iran). Also, the river and well water samples were taken from the south and north of Tehran (Tehran, Iran) respectively. Amber glass bottles (250 mL) with PTFE screw caps were used for the collection of the mentioned samples. The bottles were fully filled to avoid the volatile organic compounds evaporation. All water samples, except for tap water, were filtered by using a 0.45 μm nylon membrane filter (Whatman, Maidstone, UK).

2.2. Instrumentation

The analysis was performed on a Hewlett-Packard (Agilent Technologies, Palo Alto, CA, USA) HP 7890 series GC, equipped with FID and split/splitless injector. The chromatographic data were recorded using HP Chemstation software, which was controlled by Microsoft Windows NT. The analytes were separated on a 30 m × 0.32 mm i.d. × 0.25 μm film thickness DB-5 gas chromatographic column (J&W Scientific, Folsom, CA, USA) with the following oven temperature program: the initial temperature was 50 °C, was increased from 50 to 140 °C at a rate of 10 °C min⁻¹ in 2 min, and then raised to 250 °C at a rate of 40 °C min⁻¹ and finally held for 15 min. The injector and detector temperatures were 250 and 280 °C, respectively. The injection port was operated at a split ratio of 1:2. The gas flow rates were as follows: carrier (helium, 99.999%) 2.0 mL min⁻¹, make-up (nitrogen, 99.999%) 30 mL min⁻¹, and hydrogen and air (for FID) 30 and 300 mL min⁻¹, respectively.

2.3. Extraction procedure

A proper amount of double distilled water (5 mL) was placed in a 10 mL screw-capped glass test tube with conic bottom and then spiked at the level of 100 μg L⁻¹ of the MNTs. Acetonitrile (0.50 mL)

as the disperser solvent, containing 10.0 μL chlorobenzene (as the extracting solvent) was injected rapidly into the sample solution using a 2.0 mL syringe (gastight, Hamilton, USA). At this step, a cloudy solution (water/acetonitrile/chlorobenzene) was formed in the test tube and the MNTs in the water sample were extracted into fine chlorobenzene droplets. The mixture was then centrifuged for 5 min at 4000 rpm. The volume of the sedimented phase, measured by a 10 μL microsyringe, was about 5.0 μL, of which 1.0 μL was withdrawn by a 5.0 μL microsyringe (SGE, Australia) and immediately injected into the GC system. All experiments were performed three times and pre-concentration factor (PF), as the index of extraction efficiency, was calculated for each experiment and the mean value of PFs was used as the analytical signal.

3. Results and discussion

There are various parameters affecting the DLLME performance and efficiency, including the nature and volume of the extracting and the disperser solvents and also the ionic strength. These parameters were investigated and the optimal conditions were then established. One at a time strategy was employed to optimize the influential factors in this method. To screen the mentioned parameters, PF was calculated using the following expression:

$$PF = \frac{C_{\text{sed}}}{C_0} \quad (1)$$

where C_{sed} and C_0 are the concentration of analyte in sedimented phase and initial concentration of analyte in aqueous sample solution, respectively. These parameters were known, except for C_{sed} . The C_{sed} calculation was conducted by the direct injection of the MNT standard solutions in chlorobenzene with the concentrations in the range of 0.5–5.0 mg L⁻¹.

3.1. Selection of extracting solvent

The selection of an appropriate extracting solvent is very important to achieve good recovery and high PF for the target compounds. The extracting solvent has to meet four requirements; it should demonstrate (a) a higher density than water, (b) a good chromatographic behavior, (c) extraction capability for the interested compounds, and (d) low solubility in water [18]. Chlorobenzene, carbon tetrachloride, and tetrachloroethylene were examined in order to find the most suitable extracting solvent for DLLME. For this purpose, a series of sample solutions were studied by using 0.5 mL acetonitrile containing different volumes of the extraction solvent to achieve 5.0 μL volume of the sedimented phase. Therefore, 7.9, 10.0, and 9.7 μL of tetrachloroethylene, chlorobenzene, and carbon tetrachloride were used, respectively. Based on Fig. 1, chlorobenzene presented the highest PF in comparison with the other two solvents. For this reason, it was selected as the optimal extracting solvent.

3.2. Selection of disperser solvent

The miscibility of the disperser solvent in the organic phase (extracting solvent) and the aqueous phase (sample solution) is the main point for the selection of a disperser solvent [28]. Acetonitrile, ethanol, and methanol, illustrating the above ability, were selected for this purpose. In order to achieve the sedimented phase with a volume around 5.0 μL, a series of aqueous sample solutions were injected by adding 0.5 mL of acetonitrile, ethanol, and methanol, as the disperser solvent, containing 10.0, 12.2, and 11.7 μL chlorobenzene, respectively. Based on the results demonstrated in Fig. 2, acetonitrile was selected as the optimal disperser solvent for further studies.

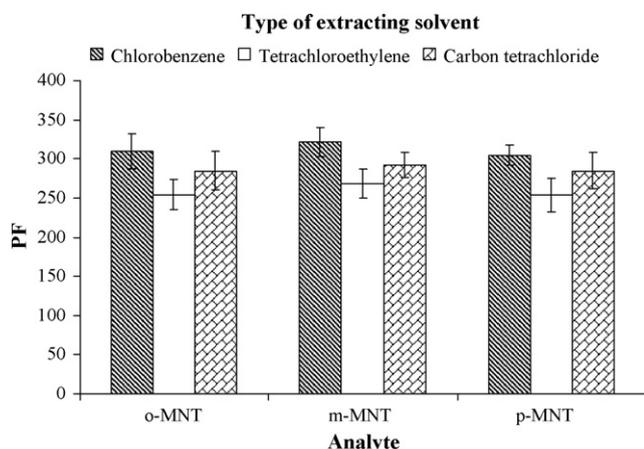


Fig. 1. The effect of type of extracting solvent on the PF. Extraction conditions: aqueous sample volume, 5.0 mL; the solutions of 0.5 mL acetonitril containing 10.0, 9.7 and 7.9 μL of chlorobenzene, carbon tetrachloride and tetrachloroethylene were used, respectively.

3.3. Effect of the extracting solvent volume

In order to evaluate the effect of the extracting solvent volume on the extraction efficiency, additional experiments were performed using 0.5 mL acetonitrile containing different chlorobenzene volumes (10.0, 14.0, 22.0 and 32.0 μL). It is clear that by increasing the volume of extracting solvent, the volume of the sedimented phase increases (5.0–27.2 μL) and, as a result, the PF decreases (Fig. 3). Taking all the above mentioned points into account, the volume of 10.0 μL of chlorobenzene was selected in the following studies.

3.4. Effect of the disperser solvent volume

The variation of acetonitrile volume (as the disperser solvent) causes changes in the volume of the sedimented phase. To avoid this problem and in order to achieve a constant volume of the sedimented phase, the volume of acetonitrile and chlorobenzene were changed simultaneously. The experimental conditions were fixed and included the use of different acetonitrile volumes (0.25, 0.50, 0.75, 1.00, and 1.25 mL), each of which contains 9.2, 10.0, 11.5, 13.1, 14.9 μL chlorobenzene respectively. At this step, the volume of sedimented phase was constant (5.0 \pm 0.3 μL). It seems that at low volumes of acetonitrile the cloudy state is not fully formed, and

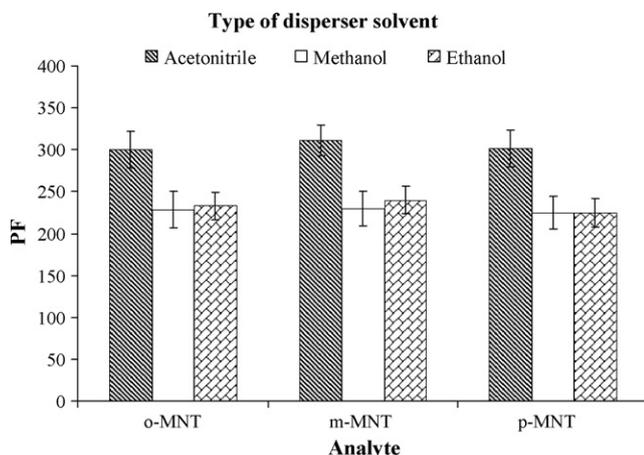


Fig. 2. The effect of type of disperser solvent on the PF. Extraction conditions: aqueous sample volume, 5.0 mL; disperser solvent volume, 0.5 mL.

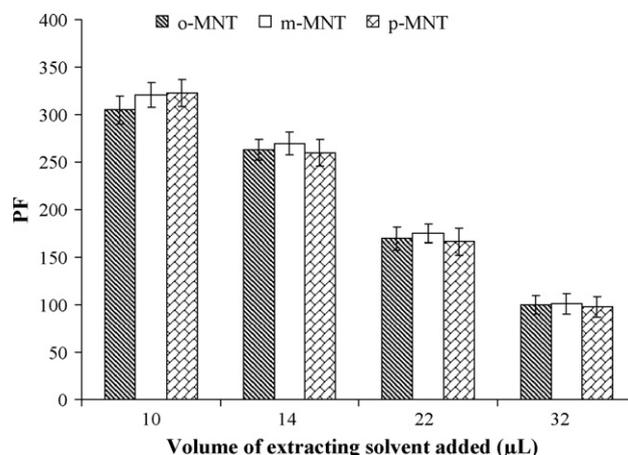


Fig. 3. The effect of extracting solvent (chlorobenzene) volume on the PF obtained from DLLME. Extraction conditions: as in Fig. 2.

thus the PF is low; while at higher volumes of acetonitrile the solubility of the analytes in aqueous samples increases. The PF decreases because of a decrease in the distribution coefficient of the analytes. Taking all the mentioned points into consideration, a constant volume of acetonitrile (0.5 mL) has been selected as the optimal value (Fig. 4).

3.5. Effect of the ionic strength

The salt addition to the sample may have several effects on the extraction efficiency. To investigate the influence of the ionic strength on the performance of DLLME, various experiments were performed by adding different amounts of NaCl (0–8, w/v%). However, the rest of experimental conditions were kept constant. Based on the experimental results, the addition of salt produced almost no sedimented phase within the above range. This can be ascribed to the interaction between the saline solution and the organic solvents (acetonitrile and chlorobenzene). Therefore, the strategy of no salt addition was performed as a consequence.

3.6. Evaluation of the method performance

Under the selected optimum experimental conditions, the proposed methodology was applied to a series of standard solutions containing various concentrations of the analytes, in order to develop the respective calibration curves. For each level, three similar extractions were performed. The limits of detection (LODs),

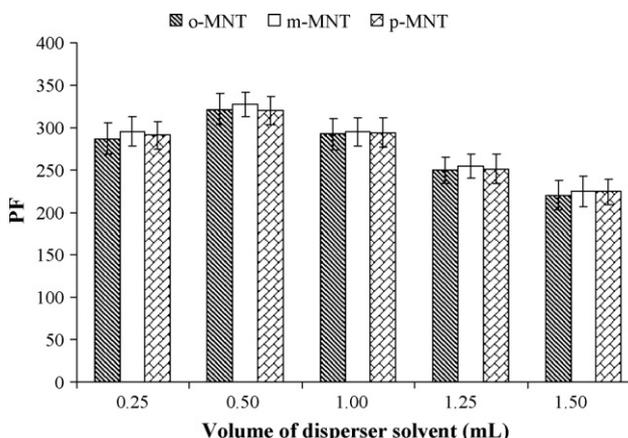


Fig. 4. The Effect of disperser solvent (acetonitrile) volume on the PF obtained from DLLME. Extraction conditions: as in Fig. 2.

Table 1
Some quantitative data obtained after DLLME and GC–FID determination of MNTs.

| Analyte | LR ($\mu\text{g L}^{-1}$) | Regression equation | r^2 | LOD ($\mu\text{g L}^{-1}$) | PF |
|---------------|-----------------------------|-------------------------|--------|------------------------------|-----|
| <i>o</i> -MNT | 1–1000 | $A^a = 2.58C^b + 20.89$ | 0.9964 | 0.5 | 355 |
| <i>m</i> -MNT | 1–1000 | $A = 2.67C + 24.03$ | 0.9962 | 0.5 | 357 |
| <i>p</i> -MNT | 1–1000 | $A = 2.52C + 22.87$ | 0.9961 | 0.5 | 351 |

^a Peak area.

^b Concentration, $\mu\text{g L}^{-1}$.

Table 2
Results obtained for analysis of the MNTs in three different spiked aquatic real samples.

| Sample | | <i>o</i> -MNT | <i>m</i> -MNT | <i>p</i> -MNT |
|--|--|-----------------|---------------|---------------|
| Tap water ($5.0 \mu\text{g L}^{-1}$ added) | Concentration ($\mu\text{g L}^{-1}$) | ND ^a | ND | ND |
| | Found ($\mu\text{g L}^{-1}$) | 4.5 | 5.1 | 4.7 |
| | Relative recovery (%) | 90 | 102 | 94 |
| | RSD% ($n = 6$) | 8.7 | 9.3 | 9.0 |
| River water ($10.0 \mu\text{g L}^{-1}$ added) | Concentration ($\mu\text{g L}^{-1}$) | ND | ND | ND |
| | Found ($\mu\text{g L}^{-1}$) | 11.3 | 11.1 | 11.2 |
| | Relative recovery (%) | 113 | 111 | 112 |
| | RSD% ($n = 6$) | 8.4 | 8.7 | 8.6 |
| Well water ($10.0 \mu\text{g L}^{-1}$ added) | Concentration ($\mu\text{g L}^{-1}$) | ND | ND | ND |
| | Found ($\mu\text{g L}^{-1}$) | 9.3 | 9.2 | 9.3 |
| | Relative recovery (%) | 93 | 92 | 93 |
| | RSD% ($n = 6$) | 8.0 | 9.3 | 9.4 |

^a Not detected.

Table 3
Comparison of different analytical methods applied for the determination of MNTs in water samples.

| Analytical technique | LOD ($\mu\text{g L}^{-1}$) | LR ($\mu\text{g L}^{-1}$) | RSD% | Extraction time (min) | Reference |
|----------------------------------|------------------------------|-----------------------------|-------|-----------------------|--------------------|
| DLLME–GC–FID | 0.5 | 1–1000 | <9.4 | ≤ 3 | Represented method |
| SPME–GC–MS | 0.03 | 20–1000 | <3.6 | 15 | [22] |
| SDME ^a –GC–MS | 0.08–0.11 | 20–1000 | <11.3 | 15 | [23] |
| HSSME ^b –GC–FID | 0.02–0.06 | 1–600 | <12.9 | 15 | [24] |
| HLLME ^c –GC–FID | 0.09–0.10 | 0.5–500 | <13.2 | ≤ 3 | [25] |
| DLLME (CCD ^d)–GC–FID | 0.09–0.5 | 0.5–300 | <10.1 | ≤ 3 | [26] |

^a Single drop microextraction.

^b Headspace solvent microextraction.

^c Homogenous liquid–liquid microextraction.

^d Central composite design.

based on the signal to noise ratio (S/N) of 3, correlation coefficients (r^2), linear ranges (LRs) and PFs were calculated and the results were summarized in Table 1. As shown in this table, LODs for all tested MNTs was $0.5 \mu\text{g L}^{-1}$. Linearity values varied in the range of $11000 \mu\text{g L}^{-1}$ with correlation coefficient of 0.9961–0.9964. Furthermore, the PFs varied from 351 to 357.

3.7. Analysis of real samples

Applicability of the extraction method was investigated in three different spiked aquatic samples. The initial results proved that the samples were free of the analytes contamination. Also, all the real water samples were spiked into with the MNTs standards at different concentration levels to assess the matrix effects. The results of relative standard deviations (RSDs%) based on six similar determinations were within the ranges of 8.0–9.4%, as presented in Table 2. The data demonstrated a good recovery in the range of 90–113%, indicating that the real water matrices had almost little effect on the extraction efficiency. Fig. 5 depicts the DLLME–GC–FID chromatograms of the MNTs at the concentration level of $10.0 \mu\text{g L}^{-1}$ in the well water sample before and after spiking. As shown in Table 3, comparing the proposed method with other analytical techniques employed for the determination of MNTs in water samples, this technique, along with its simplicity, demonstrated wide linearity range, low sensitivity, and an accept-

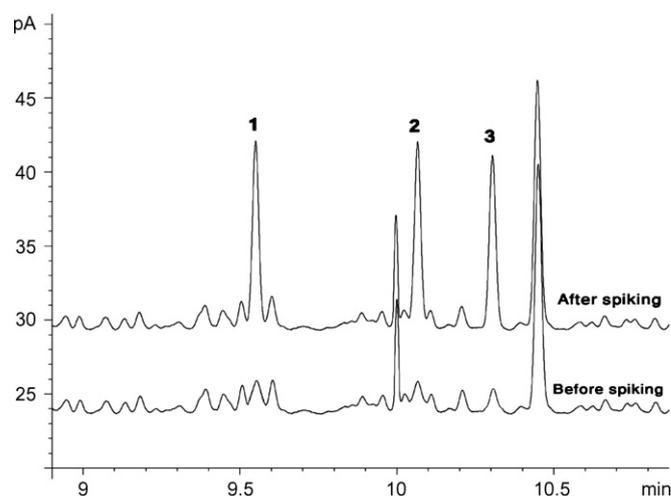


Fig. 5. The DLLME–GC–FID chromatograms of MNTs at the concentration level of $10.0 \mu\text{g L}^{-1}$ in the well water sample before and after spiking. Extraction conditions: aqueous sample volume, 5.0 mL; extracting solvent (chlorobenzene) volume, 10.0 μL ; disperser solvent (acetonitrile) volume, 0.5 mL. The Peak number corresponds to (1) *o*-MNT (2) *m*-MNT (3) *p*-MNT.

able reproducibility with an important emphasis on the extraction time which seems to be quite short.

4. Conclusion

The present work shows that DLLME technique in combination with GC–FID is a valid means of pre-concentration and quantification of MNTs at trace levels in water samples. The method designed was concluded to be precise, reproducible, time-independent, and linear over a wide concentration range. Moreover, the entire analytical process presents a simple, economical and rapid way for screening purposes. Excellent extraction efficiencies are achieved almost independent of the matrices, in the actual applications. Finally, putting all the benefits together, this method possesses great potentials to be employed in routine analyses.

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