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Simultaneous determination of five nitroaniline and dinitroaniline isomers in wastewaters by solid-phase extraction and high-performance liquid chromatography with ultraviolet detection

Changlun Tong *, Yun Guo, Weiping Liu

MOE Key Laboratory of Environmental Remediation and Ecological Health, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310029, China

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ABSTRACT

A high-performance liquid chromatography (HPLC)-ultraviolet detection method, combined with solid-phase extraction (SPE), was developed for the determination of five nitroaniline and dinitroaniline isomers including 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 2,4-dinitroaniline and 2,6-dinitroaniline in wastewater samples. Extraction of the five isomers was carried out with a hydrophile–lipophile balance cartridge, the Oasis HLB. The cartridge was washed by a mixed aqueous solution containing 10% (v/v) acetonitrile and 10% (v/v) ethyl acetate before the five isomers were eluted by a mixture of methanol and acetic acid. Separation of the five isomers was achieved by using an Agilent TC-C_{18} column at 30 °C, and using a mixture of acetonitrile/water 30/70 (v/v) as mobile phase under an isocratic condition at a flow rate of 1.0 mL min^{-1}. The analytes were detected by a UV detector at a wavelength of 225 nm. Recoveries of the five isomers in the spiked sewage sample were between 84.6% and 94.0% with a relative standard deviation of less than 4.7%. The limits of quantification (LOQ) determined in a spiked sewage sample of 500 mL were 2.0×10^{-9} M for 2-nitroaniline, 3-nitroaniline and 2,6-dinitroaniline, and 4.5×10^{-9} M for 4-nitroaniline and 2,4-dinitroaniline. The proposed method was applied to determine the five isomers in real samples of acidic wastewater and printing and dyeing wastewater.

1. Introduction

Nitroaniline and dinitroaniline isomers such as 2-nitroaniline (2-NA), 3-nitroaniline (3-NA), 4-nitroaniline (4-NA), 2,4-dinitroaniline (2,4-diNA) and 2,6-dinitroaniline (2,6-diNA) (see Fig. 1), as nitro-substituted derivatives of aromatic amines, have become more and more significant in environmental science due to their highly toxic nature and their suspected carcinogenic properties (Dimou et al., 2004; Xiang et al., 2007). These nitroaniline and dinitroaniline isomers are mainly used as intermediates in the synthesis of dyestuff, pharmaceuticals, pesticides, and herbicides (Voyksner et al., 1993; Kataoka, 1996), and they are released into the environment directly as industrial waste or indirectly as degradation products of herbicides and pesticides. After they enter into the environment, these compounds can experience complex environmental transformations at trace level, and they can thus be harmful to the environment potentially. Acute or chronic exposure to nitroanilines and dinitroanilines can produce symptoms of headache, dizziness and nausea. With the growing use of these compounds in different industries, some of these compounds such as 4-NA, 2,4-NA and 2,6-NA have been included in the list of priority pollutants in many countries. In view of the environmental importance of these compounds, it is necessary to develop a simple, rapid and sensitive analytical method for the determination of them in the environmental water samples.

Nowadays various analytical techniques have been developed for the determination of aromatic amines and their derivatives by gas chromatography (GC) (Longo and Cavallaro, 1996; Chiang and Huang, 2008), high-performance liquid chromatography (HPLC) (Patsias and Papadopoulou-Mourkidou, 2000; Wang and Chen, 2002; Yazdi and Es'haghi, 2005; Yazdi et al., 2009), ion chromatography (Zhu et al., 2002) and capillary electrophoresis (CE) (Guo et al., 2006). Since these compounds are thermolabile and polar, a derivatization step is often required to obtain a good GC performance (Haas et al., 1997). Yet most of the derivatization processes are not straightforward and sometimes require handling of hazardous chemicals (Patsias and Papadopoulou-Mourkidou, 2000). Unlike that of GC, there is no derivatization requirement in HPLC analysis, HPLC thus appears to be a good alternative in comparison with GC analysis (Puig and Barceló, 1996a). However, the separation of their isomers has become one of the most challenging areas in separation science because their isomers usually possess similar physical and chemical properties. Up to now, very limited literatures on the determination of nitroaniline (Yao et al.,

* Corresponding author. Tel./fax: +86 571 86968415.
E-mail addresses: cltong@zju.edu.cn (C. Tong), guoy@zju.edu.cn (Y. Guo), wliu@zju.edu.cn (W. Liu).

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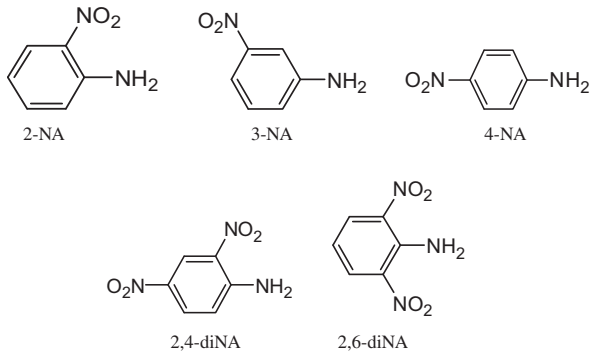

Fig. 1. Molecular structure of nitroaniline and dinitroaniline isomers.

2004; Guo et al., 2006) or dinitroaniline isomers have been reported. To our knowledge, no literatures on the simultaneous determination of two types of these isomers have been found (see Table 1). HPLC is one of the most popular techniques for positional isomer separation, especially stationary phases, which can provide various retention mechanisms, are prepared for separation of positional isomers (Xu et al., 1998; Yao et al., 2004). The most widely used detection methods in HPLC analysis of nitroaniline and dinitroaniline isomers should be ultraviolet detection (UVD) and electrochemical detection (Puig and Barceló, 1996a; Patsias and Papadopoulou-Mourkidou, 2000). Since nitro group in these molecules can significantly extinguish the fluorescence of the compounds, direct or indirect fluorescence detection is very difficult. While UV detector can provide very good signal stability, it is short of selectivity. Electrochemical detector is more sensitive than the UV detector. However, their performance is highly dependent on the type of samples analyzed. Components from dirty samples are deposited on the electrochemical cell and the detector's sensitivity is rapidly decreased (Jáuregui and Galceran, 1997; Lacorte et al., 1999).

Nitroaniline and dinitroaniline isomers are present in the wastewaters, surface waters and other environments at trace level or ultra trace level. Thus, a pre-concentration step is generally required for the determination of these pollutants at trace levels in the environment (Zhu et al., 2001). The preparation of samples is traditionally carried out by liquid–liquid extraction (LLE) or solid-phase extraction (SPE) techniques (Puig and Barceló, 1996a; Hennion et al., 1998; Patsias and Papadopoulou-Mourkidou, 2000). In recent years, a number of different modified purification techniques such as solid-phase microextraction (SPME) (Louch et al., 1992; Yan et al., 2004) and liquid phase microextraction (LPME) (Zhao et al., 2002) have been developed. With a number of different sorbents applied in SPE and all kinds of commercial SPE cartridges emerged in the market, especially the applications of the molecularly imprinted and immuno-affinity technologies, SPE can almost meet all the demands of pre-concentrations in the environmental monitoring. Currently, SPE is the popular pre-concentration method in the conventionally environmental monitoring. With further improved technologies, SPE will become more attractive and convenient either in the on-line or in the off-line mode (Puig and Barceló, 1996b; Castillo et al., 1997; Lacorte et al., 1999).

In the present work, a simple, reliable and convenient method for the simultaneous determination of five nitroaniline and dinitroaniline isomers was developed using HPLC with ultraviolet detection without any additives. To accomplish its application in environmental monitoring of wastewaters, Oasis HLB SPE cartridges, which was filled by the reversed-phase sorbents of hydrophilic–lipophilic polymers, was selected for the pre-concentrations. A mixed aqueous solution containing both 10% acetonitrile and 10% ethyl acetate was selected as the purification reagent. This process could help to remove the complicated matrix interferences existed in the wastewaters, and it did not cause the loss of the analytes or reduced the loss to the minimum. This method was successfully used in monitoring the spiked sewage water sample, and satisfactory assay results were obtained. Compared with the literature works (see Table 1), this method was simple, sensitive and convenient, and it could be applied as a conventional environmental analysis method to monitor these compounds in the wastewaters.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents were of analytical reagent grade unless with specific instruction. 2-NA, 3-NA, 4-NA, 2,4-diNA and 2,6-diNA were purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China). Ethyl acetate was purchased from Hangzhou Gaojing Chem. Reagent Co. Ltd. (Hangzhou, China), acetonitrile was purchased from Tedia Company Inc. (Fairfield, USA), and methanol was purchased from Tianjin Shield Company (Tianjin, China). Acetonitrile and methanol were both HPLC grade and were used without any further purification.

Stock solutions of 2-NA, 3-NA, 4-NA, 2,4-diNA and 2,6-diNA (2.0×10^{-3} M) were dissolved in ethanol and stored in a refrigerator at 4 °C. Standard sample solutions were provided daily at different concentrations by diluting the stock standard solution with

Table 1
A comparison with some recently reported methods for determining these five isomers.

Methods	Objective compounds	Sample determination	LOD ($S/N = 3$)	References
CZE–AD[a]	2-NA, 3-NA, 4-NA	Dyestuff wastewater	9.06–39.2 nM	Guo et al. (2006)
MEKC[b]-HPLC	2-NA, 3-NA, 4-NA	Hair dyes	2.2–5.8 μM	Wang and chen (2002)
HPLC	2-NA, 3-NA, 4-NA	HPLC separation	–	Yao et al. (2004)
LLLME[c]-HPLC	2-NA, 4-NA	Sea water, dye plant	0.072–0.22 nM	Yazdi et al. (2005)
SPE–HPLC	2-NA, 4-NA	River water	0.72–1.4 nM[d]	Patsias and Papadopoulou-Mourkidou (2000)
LLLME[c]-HPLC	3-NA	Ground/river water	7.2 nM	Yazdi et al. (2009)
IC-AD[e]	2-NA	Wastewater	1.5 μM	Zhu et al. (2002)
LC-AD[f]	4-NA	River water	0.16 μM	Cao et al. (2004)
This method	2-NA, 3-NA, 4-NA, 2,4-diNA, 2,6-diNA	Wastewaters	2.0–4.5 nM[d]	

[a] Capillary zone electrophoresis with amperometric detection.
[b] Micellar electrokinetic chromatography.
[c] Liquid–liquid–liquid phase microextraction.
[d] Limit of quantification.
[e] Ion chromatography column with amperometric detection.
[f] Liquid chromatography with amperometric detection.