

Analytical Methods

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5 **Rapid determination of trace phenols migrating into drinking water from**
6 **plastic-based pipe materials and household water treatment equipments using**
7 **vortex-assisted emulsification microextraction**
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Abstract

A simple and rapid vortex-assisted emulsification microextraction (VAEME) combined with spectrophotometry was developed for the determination of trace phenols migrating into potable water from plastic-based pipe materials and household water treatment equipments. The oxidative coupling reaction of phenolic compounds with 4-aminoantipyrine was carried out employing potassium peroxodisulfate as oxidant in alkaline medium. The cloudy mixture was formed facilitating mass transfer of reaction products into the fine droplets of toluene. The extraction equilibrium could rapidly achieve within 3 min by the combination effects of vibration and heating. The extract was concentrated in narrow neck of the vessel, which could be easily withdrawn with syringe. The VAEME could effectually avoid the analytical error resulting from the leak of fluid, which often occurred in conventional liquid-liquid extraction with separation funnel during extraction process. Under optimal conditions, linearity ranges of 0.2–180 $\mu\text{g L}^{-1}$ and detection limit of 0.08 $\mu\text{g L}^{-1}$ (expressed as $\text{C}_6\text{H}_5\text{OH}$ concentration) were achieved. This approach was successfully applied to the determination of trace amounts of phenols in 36 soaked solutions covering different matrices. The recoveries were in the range of 86.0–99.8% and the relative standard deviations (RSDs) ranged from 0.53% to 6.5%. Compared with the official method, the proposed method exhibited higher sensitivity and lower consumption of operation time and reagent.

Key words: Vortex-assisted emulsification microextraction; total phenols; plastic-based pipe materials and household water treatment equipments; 24 h immersion test

1 Introduction

The pervasive problem afflicting people is probably inadequate access to clean drinking water and sanitation. Point-of-use household water treatment (POUHWT) has emerged as an attractive approach that empowers people without access to safe water to improve water quality by treating it in the home. Although a variety of POUHWT technologies have been suggested, tested, and disseminated, not all have a sufficient evidence base of effectiveness and sustainable use [1]. Plastic pipe materials and water treatment equipments are frequently used in municipal water supply systems and household water treatment. Some plastic materials contain phenolic antioxidants that are added to enhance the durability of products in manufacturing process. These phenolic antioxidants such as alkylphenols, butylated hydroxytoluene (BHT) in plastic materials may be gradually decomposed or degraded to release phenolic compounds, leading to potential contamination of drinking water [2]. Phenols are generally considered as one of the major organic pollutants that cause an unpleasant taste and odor in drinking water. Approximately 165 kinds of phenolic compounds are known to have toxic effects on aquatic life and human health, and several types of phenols (e.g., nonylphenols, nitrophenols and chlorophenols) are included in the list of priority pollutants by both the US Environmental Protection Agency (US EPA) and the European Union (EU) [3, 4]. Many countries have formulated strict limits about phenols in potable water. The EU legislation requires that the maximum contaminant level (MCL) of phenols in drinking water should be $0.5 \mu\text{g L}^{-1}$ for the total content [5]. This rather low MCL value makes the analysis of total phenols particularly challenging. Thus, the development of simple, sensitive and reliable analytical methods to detect trace phenolic compounds is extremely necessary to support the implementation and enforcement of the restrictive legislation and ensure the safety of drinking water.

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Several instrumental procedures, such as gas chromatography-flame ionization detection (GC-FID) [6, 7], gas chromatography-mass spectrometry (GC-MS) [8], and liquid chromatography tandem mass spectrometry (LCTMS) [9] have been developed for the determination of certain phenolic compounds in water samples. All these methods are focused on the speciation analysis of phenols, but the detailed determination of the whole range of phenols presenting in a complex sample is still a knotty problem due to excess phenol species and relatively low concentration. In some sense, their monitoring can suitably be performed by detecting total phenols with spectrophotometry instead of the quantification of individual species to save time and reduce cost [10, 11]. However, the concentrations of phenols in drinking water are so low that sample separation and preconcentration are commonly required for the reliable result.

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Liquid-liquid extraction (LLE) is the most widespread technique for the extraction of a wide range of organic compounds from various matrices. Nevertheless, the conventional LLE is a rather laborious and high-cost procedure, which often needs large amounts of toxic solvents and multi-step operations. These disadvantages have led to the development of miniaturized sample preparation techniques. The solvent microextraction is also known as liquid-phase microextraction (LPME) representing a miniaturization of the traditional LLE whereby the organic solvent to aqueous phase ratio is substantially reduced. There are various operational paradigms of LPME, such as single-drop microextraction (SDME) and dispersive liquid-liquid microextraction (DLLME) [12]. These modified solvent extraction procedures have been successfully applied to the isolation of target analytes from different matrices [13, 14]. However, several analytical problems, such as instability of microdrop, poor repeatability or relative low precision are sometimes encountered.

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DLLME is a simplified and miniaturized method of LLE that only requires microliter volumes of extraction solvents [15]. Since the initial introduction of the DLLME, various modified

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2 approaches have provided satisfactory results. Low-density solvents, such as *n*-hexane, cyclohexane
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4 and some long-chain alcohols are used as extractants instead of the highly toxic halogenated
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6 hydrocarbons that are usually used in the classical DLLME. Additionally, certain surfactants [16-18]
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8 and ionic liquids (IL) [19] are being employed for DLLME techniques to reduce or even avoid the
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10 use of toxic solvents. In some cases, organic solvent dispersion can be performed by means of the
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12 mechanical effects, such as ultrasound action [20], multiple bubbling air [21] and vortex agitation
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14 [22]. Among these assistant techniques, the application of ultrasonic radiation facilitates the
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16 emulsification phenomenon leading to an improvement of extraction efficiency [23]. Ultrasound
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18 assisted liquid-liquid microextraction (USALLME) has been developed as a promising technique to
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20 conventional LLE for analyzing organic compounds in diverse samples. But the extraction time
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22 needed for USALLME is much longer than that required by DLLME. In addition, an ultrasonication
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24 is propitious to any oxidation taking place in an aqueous medium through the well-known radical
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26 formation process [24]. The analyte degradation may occur during ultrasonication extraction [25].
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35 To overcome the disadvantages of DLLME (need for dispersive solvent) and USALLME
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37 (potential analyte degradation), a vortex-assisted emulsification microextraction (VAEME) was
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39 introduced by Yiantzi and co-workers [26]. A mild emulsification process can be achieved by
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41 dispersing extraction solvent into aqueous solution with vortex agitation. The dispersed fine
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43 droplets of extractant phase can extract analytes toward equilibrium in a short time. Centrifugation
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45 is typically performed for the purpose of rapid phase separation after extraction equilibrium. The
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47 selection of suitable extractant is vitally important to attain high extraction efficiency due to no use
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49 of disperser solvent. VAEME has been used to determine bisphenol-A, 2, 4-dichlorophenol,
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51 bisphenol-AF and tetrabromobisphenol-A in liquid food [27].
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58 This study was aimed at developing simple, fast and sensitive approach to tackle the difficult
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3 problem of the determination of trace phenolic compounds in complex samples. In alkaline medium,
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5 phenolic compounds including phenol, orto- and meta- substituted phenols, para- substituted by
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7 groups of halogen, carboxyl, sulphonic acid, hydroxyl and methoxyl were oxidatively coupled with
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9 4-AAP to form antipyrine dyes, which were extracted with toluene. The dispersion of toluene in
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11 sample solution was performed by the combination effects of vibration and heating which
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13 accelerated extraction and enhanced extraction efficiency. After extraction toward equilibrium, the
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15 dispersed fine droplets of the extractant phase were rapidly accumulated on the surface of aqueous
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17 solution at the narrow neck of the vessel by gravity, which could be easily recovered using syringe.
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19 Several experimental parameters affecting derivatization reaction and extraction of analytes were
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21 optimized to obtain maximum extraction efficiency. Finally, the vortex-assisted emulsification
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23 microextraction coupled with ultraviolet/visible (UV/vis) spectrophotometry was applied to the
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25 determination of total phenols in soaked solutions of the plastic-based pipe materials and household
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27 water treatment equipments.
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38 **2 Experimental**

39 **2.1 Instrumentation**

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43 Absorbance measurements were carried out on an UV/vis spectrophotometer (Shimadzu
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45 UV-2500) with two pairs of 0.5-cm optical path length matched quartz cells. A Metrohm 744 pH
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47 meter (Metrohm Technology Ltd, Herisa, Switzerland) was used to adjust the pH value of solution.
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51 A Vortex-genie 2 vibrator (Scientific Industries INC, New York, USA) and a constant temperature
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53 water bath (Chang An Scientific Instrument Co. Ltd., Beijing, China) were utilized throughout this
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60 study.

2.2 Reagents and standard solutions

All reagents used were of analytical grade or HPLC grade and the deionized water (specific resistivity $18.1 \text{ M}\Omega \text{ cm}^{-1}$) was produced by a Millipore Milli-Q water purification system (Bedford, MA, USA). Reagents employed for derivatization reaction included 4-aminoantipyrine (4-AAP), potassium hexacyanoferrate, potassium peroxodisulfate, ammonium hydroxide and potassium hydrogen phosphate, all of which were purchased from Guangzhou Chemical Reagent Factory (Guangdong, China). Cyclohexane, toluene, trichloromethane and ether were attempted as potential extraction solvents, which were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and required further purification with a rotary evaporator at reduced pressure prior to use.

A 1000 mg L^{-1} stock standard solution of phenol was prepared by dissolving phenol (Merck, Darmstadt, Germany) in methanol (Merck) and stored in a freezer at $4 \text{ }^{\circ}\text{C}$. A series of working solutions were prepared daily by appropriate dilution of the concentrated stock solution with deionized water. The soak solution contained 1.0 mmol L^{-1} of sodium bicarbonate and calcium chloride (Guangzhou Chemical Reagent Factory, China) and 2.0 mg L^{-1} of residual chlorine, whose pH was adjusted to 8.

2.3 Sample preparation

Thirty-six commercially available plastic water pipe, pipe fitting, filter cartridge and household water purifier were obtained from suppliers in Guangdong, China. These samples were thoroughly rinsed for 20 min in tap water and washed again thrice with deionized water, followed by being filled with soak solution. After 24 h immersion at room temperature, these used soak solutions were collected for the determination of total phenols.

Three water samples were daily prepared by adding the stock standard solution to the soaked solution of plastic water pipe (without phenols) with the final phenol concentrations at 0.20, 10.0

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2 and 15.0 $\mu\text{g L}^{-1}$, respectively. These spiked solutions are sufficiently blended to reduce the
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4 uncertainty of measurement arising from unevenness of sample. After homogenization, each spiked
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6 aqueous solution was split into ten independent samples for the optimization of extraction
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8 performance and the validation of method.
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11 12 **2.4 VAEME procedure**

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14 An aliquot of 100 mL soaked solution or spiked sample was placed in a flat-bottomed spherical
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16 flask with a long narrow neck. A 1.0 mL of 0.5 mol L^{-1} hydrogen phosphate and ammonia buffer
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18 solution was added to adjust the solution to pH 9.8. The sample solution was mixed with 1.0 mL of
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20 1% (w/v) 4-AAP and 0.5 mL of 2.0% (w/v) potassium peroxodisulfate, and left for 10 min in a
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22 water bath at 40 °C. After adding 300 μL of toluene, the mixture solution was vigorously shaken for
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24 2 min on a vortex agitator with periodic venting to release excess pressure. The resulting emulsion
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26 was colloiddally unstable and the phase separation automatically occurred after a short time (1 min),
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28 then, about 2 mL of deionized water was injected to make the extractant phase elevate to the narrow
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30 part of vessel. The upper layer (approximately 250 μL) could be retrieved with a disposable syringe
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32 and about 250 μL of toluene was added to a final extract volume of 500 μL in a 1-mL graduated
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34 glass vial for absorbance measurement with UV/vis spectrophotometer at 530 nm. Owing to the
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36 method could not discriminate among different phenols, the result obtained by oxidative coupling of
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38 phenolic compounds with 4-AAP was commonly referred as total phenol content, and expressed as
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40 $\text{C}_6\text{H}_5\text{OH}$ concentration [28].
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53 **3 Results and discussion**

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58 In VAEME system, an extraction vessel, which was composed of a flat-bottomed spherical flask
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2 with a long narrow neck, was introduced to VAEME procedure. Its volume could be altered by
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4 selection flasks with approximate sizes. The role of vortex agitation was to swirl liquid and create a
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6 vortex where organic phase could be broken up into very fine emulsion droplets facilitating mass
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8 transfer of the analytes due to short diffusion distance and large contact surface areas between the
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10 extraction solvent and the aqueous sample. Since no disperser solvent was used, the formed
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12 emulsion solution was extremely unstable and could be rapidly separated into two distinct phases by
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14 gravity. Derivatization reaction was affected by some parameters including pH, reaction
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16 temperature and reagent concentration, while the extraction of the reaction products was influenced
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18 by others such as the type of extraction solvent and its volume, vortex time and ionic strength, all of
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20 these factors were individually optimized as follows.
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28 **3.1 Optimization of the VAEME**

29 **3.1.1 Type and volume of the extraction solvent**

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33 The type of extraction solvent is of great importance, affecting the extraction performance of the
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35 VAEME. It should meet some criteria, such as good extractability for target analytes, low aqueous
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37 solubility and weak background absorbance. Various organic solvents have been typically used as
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39 extractants for the extraction of target analytes. Four non-chlorinated organic solvents with low
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41 density and different water solubility including toluene, cyclohexane, ether and 1-octanol were
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43 preferred for this study. The compatibility of these solvents with the VAEME technique was
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45 investigated by adding 300 μL of each mentioned solvent into 100 mL of soaked solution of plastic
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47 water pipe containing 10.0 $\mu\text{g L}^{-1}$ of phenol. After derivatization reaction and extraction toward
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49 equilibrium, the extractant phase was retrieved with a disposable syringe and detected using UV/vis
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51 spectrophotometer. Results demonstrated that no phase separation was observed in the use of ether
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60 owing to the formation of steady-state solution. Toluene could provide better phase separation and

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2 higher absorbance value than those of cyclohexane and 1-octanol (data not shown). Thus, it was
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4 finally selected as an extraction solvent.
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7 The volume of extraction solvent was another crucial factor. Effect of toluene volume on
8 extraction efficiency was tested by performing triplicate experiments in which seven different
9 volumes (50, 100, 200, 250, 300, 400 and 500 μL) were used. Other experimental conditions were
10 kept constant during extraction. The extract was collected and diluted with toluene to a final volume
11 of 500 μL in 1-mL graduated glass vial that was calibrated prior to use. As shown in Fig. 1, there
12 was a gradual increase in absorbance value with the increase in volume of toluene employed, and
13 then reached a relative equilibrium value larger than 300 μL . Thus, 300 μL of toluene was used for
14 all further experiments.
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27 **3.1.2 Vortex time**

28 Optimization of the vortex time was a further step in the development of the VAEME
29 procedure. The effect of vortex time on extraction efficiency was studied by lasting agitation from
30 1.5 to 20 min after derivatization reaction at temperature of 20°C, 40°C and 60°C, respectively. The
31 vortex agitator was set to the maximum rotational speed (3000 rpm), and all the extraction
32 experiments were repeated three times in triplicate. The results were presented in Fig. 2, which
33 indicated that by increasing the vortex time, the absorption value increased as expected result, and
34 reaching a plateau after 15 min at lower reaction temperature (20°C). While the absorption intensity
35 of extract could rapidly attain maximum value within 2 min at higher reaction temperature (40°C),
36 but it would be slightly decreased after 2 min with further rise in reaction temperature to reach 60°C.
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38 The most probable reason was that the extraction solvent dispersions and mass transfer of phenols
39 from aqueous solution to extractants were mainly endothermic process. The higher temperature
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2 time. However extraction efficiency would be decreased at high temperature due to the high
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4 volatility of phenolic compounds. Hence, the optimum conditions including 2 min vortex extraction
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6 time and the vortex agitator set at maximum rotation speed were adopted for the subsequent
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8 experiments.
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11 12 **3.1.3 Ionic strength**

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14 The addition of salt to aqueous solution could generally decrease the water solubility of
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16 hydrophilic compounds, which would improve extraction efficiency of highly polar analyte due to
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18 salting-out effect. The influence of ionic strength on absorbance value of extract was investigated
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20 by adding different amounts of sodium chloride (0-10%, w/v) into the above spiked samples as
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22 model electrolyte while other experiment variables were set according to the results of former
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24 optimization steps. A slightly increase in the absorbance value of extract (less than 0.01) was
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26 observed as the sodium chloride concentration varied from 0 to 10% (w/v). The effect of salt
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28 addition could be considered as the result of two major competitive effects between salting-out
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30 effect and viscous resistance effect in the extraction process. The latter would counteract the
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32 favourable effects of the former at least to some extent [29, 23]. The salt addition had little
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34 influence on the extraction of phenolic compounds. The similar result had been previously reported
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36 by Zgoła-Grześkowiak [15]. Therefore, the further experiments were performed in the absence of
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48 **3.2 Optimization reaction conditions**

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50 The derivatization reaction conditions were studied to improve the sensitivity and precision of
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52 the method. The oxidative coupling reaction of phenolic compounds with 4-AAP was carried out
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54 employing appropriate oxidant in an alkaline condition. The effect of pH in sample solution was
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56 investigated within the range of 6-13 at eight levels (Fig. 3 a). The maximum absorbance of extract
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2 was found to occur in the narrow pH range 9.6-10, and pH 9.8 was the most favorable for the
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5 reaction.

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7 The oxidizing agent plays a critical role in derivatization process since it affects the extent and
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9 rate of reaction. A large excess of oxidant was undesirable because 4-AAP could also be oxidized to
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11 cause high blank value and the formed dyes would be decolourized; on the contrary, an insufficient
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13 amount of oxidant would result in incomplete oxidation of phenols. Several chemical agents could
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15 be used as oxidant for the oxidative coupling reaction. Among them, hexacyanoferrate was the most
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17 common oxidant that had high blank value and low sensitivity of method. To overcome these
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19 disadvantages, potassium peroxodisulfate was introduced in this experiment. Its effect on
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21 absorbance value was evaluated by adding various volumes of 2.0% (w/v) $K_2S_2O_8$ solution to above
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23 spiked sample. As can be seen in Fig. 3 (b), a 0.5 mL of potassium peroxodisulfate solution was
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25 most suitable for the oxidation reaction. The effect of 4-AAP on the reaction and extraction
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27 efficiency of phenols was studied in the concentration range from 0.006% to 0.024% (w/v). The
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29 absorbance values for both spiked and blank samples were increased with increasing 4-AAP
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31 concentration. Taking these effects into account, a 0.010% (w/v) 4-AAP was selected as the
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33 optimum concentration to minimize blank value.
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43 Temperature affected the rate of derivatization reaction of phenols with 4-AAP and the
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45 extraction of products, and its effect on reaction was investigated by varying water bath
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47 temperatures from 20 °C to 60°C. Results displayed in Fig. 3 (c) showed that the equilibrium time
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49 at 40°C and 60°C was substantially shorter than that at 20 °C. Additionally, the high blank
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51 absorbance value indicated that the 4-AAP might be partially oxidized at 60°C. To enhance the
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53 reaction ratio and reduce the blank value, the derivatization reaction was carried out in a water
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55 bath at 40°C.
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3.3 Interference trial

The effect of potential interferences was evaluated by adding chemical substances to the soaked solutions of blank sample spiked with phenol. The tolerance level was defined as the maximum concentration of the foreign species causing an absorbance value change less than 10%. Results demonstrated that the common anions (F^- , Cl^- , NO_3^- , SO_4^{2-} , HPO_4^{2-}) and cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} , Co^{2+} , Al^{3+}) did not interfere with the quantification of $10 \mu g L^{-1}$ phenol in aqueous sample under $100 mg L^{-1}$ tolerance concentration. But several metal ions including Pb^{2+} , Fe^{3+} , Sn^{2+} and Zn^{2+} could be readily hydrolyzed to form hydroxyl precipitations of these metal ions in alkaline medium, leading to serious interference with phenols detection. Fortunately, the interferences could be neglected due to the rare presence of these metal ions in real samples.

3.4 Analytical figures of merit

The optimized VAEME procedure was characterized in terms of linearity, limit of detection (LOD), limit of quantification (LOQ), precision (expressed as RSD) and extraction efficiency (extraction recovery). The linear regression equation, calculated using seven phenol standards in the concentration range $0.2-180 \mu g L^{-1}$ was the following: $A=0.0053 \times c+0.0152$, where A is absorbance and c is the concentration of phenol ($\mu g L^{-1}$). The correlation coefficient (r) was 0.9995. The LOD and LOQ were calculated following the 3 SD (standard deviation) and 10 SD criteria, respectively. The SD value was acquired from analyzing seven soaked solutions of blank samples fortified with $0.2 \mu g L^{-1}$ of phenol. The LOD and LOQ values were 0.08 and $0.25 \mu g L^{-1}$, both of which were less than the MCL of $0.5 \mu g L^{-1}$ for total phenols in potable water.

The precisions of repeatability (intra-day) and reproducibility (inter-day) were determined by carrying out seven independent extraction experiments of the soaked solutions of plastic water pipe spiked at $10.0 \mu g L^{-1}$ phenol within a day and during three consecutive days. Their RSDs values

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2 were 5.9% and 18.7%, respectively, indicating that the method had acceptable repeatability and
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5 problematical reproducibility. The reason was probably due to unstable nature of trace phenol in
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8 water sample. Hence, sample was usually stored in alkaline condition and detected as quickly as
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10 possible.

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12 The accuracy of the proposed method was estimated by performing triplicate analysis of a
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14 certified reference material of GSBZ50003-88 environmental water ($36.9 \mu\text{g L}^{-1}$ of phenol) supplied
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17 by National Institute for Environmental Reference Materials (Beijing, China). The obtained value
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20 (presented as mean \pm SD, $\mu\text{g L}^{-1}$) was 35.5 ± 1.9 with recovery of 96.2%, which was in good
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22 agreement with the certified value.
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24 25 **3.5 Analysis of real samples**

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28 To validate the applicability of the current method for the determination of total phenols in
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30 various sample matrices, thirty-six commercially available products including plastic water pipe,
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32 pipe fitting, filter cartridge and household water purifier were used for 24 h immersion test at room
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34 temperature, and their soaked solutions were analyzed under the optimum conditions. External
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36 calibration was used to quantify accurately the total phenols in samples. The concentration of total
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38 phenols in the majority of samples was larger than the quantification limit, and even was above the
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40 MCL sometime. Twelve types of samples covering different matrices were used for 24 h immersion
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42 test, each soaked solution was spiked with phenol at two concentration levels of 0.50 and $15.0 \mu\text{g}$
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44 L^{-1} , and then was analyzed by the proposed procedure with three independent extraction
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46 experiments to study the potential matrix effect on extraction recovery. The results displayed in
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49 Table 1 suggested that acceptable mean recoveries were obtained in the range of 86.0-99.8%, and
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52 the repeatability given as RSD ranged from 0.53% to 6.5% in all cases.
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58 **3.6 Comparison of analytical characteristics of the VAEME with other methods**

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3 The VAEME was compared with the 5530 APHA standard method (4-AAP method) [30] to
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5 check the accuracy and reliability of the proposed procedure. Two groups soaked solution samples
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7 (ten independent samples for each group) spiked with phenol at $15.0 \mu\text{g L}^{-1}$ were assayed in order to
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9 evaluate if both procedures yield similar results according to the Student's *t*-test. These two
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11 analytical values (mean \pm SD, $\mu\text{g L}^{-1}$) were 14.7 ± 0.57 and 14.9 ± 0.55 , and the experimental *t*-value
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13 of 0.835 was below the critical *t*-value of 2.101 (at the 95% confidence level), which revealed that
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15 there were no statistically significant differences between the results. But the proposed method
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17 consumed much less extraction time (3 min) and organic solvent (0.5 mL of toluene) than that the
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19 official method did (65min and 10 mL of chloroform). In addition, the analytical characteristics of
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21 this procedure were compared with other LLE-based methods for the determination of phenol in
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23 water and wastewater samples reported in the literature (Table 2). Its remarkable advantages were
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25 rapidity and sensitivity, and the extraction and detection devices were inexpensive, convenient and
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27 easy to handle. This was an efficient sample preparation procedure that could be used for the
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29 preconcentration of trace phenols in samples.
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40 **4 Conclusions**

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45 A rapid and efficient VAEME was developed for the determination of trace phenols migrating
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47 into drinking water from plastic-based pipe materials and household water treatment equipments. It
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49 incorporated derivatization reaction, extraction and concentration into one single step. The extract
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51 was rapidly detected by spectrophotometric method with sufficient sensitivity. Low density solvent
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53 was preferably used as extractant to avoid the use of centrifugation. Extraction equilibrium time
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55 was shortened and extraction efficiency was markedly improved under synergistic effects of
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2 vibration and heating. Compared with chromatographic methods for the detailed determination of
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4 the whole phenolic compounds, the procedure could greatly simplify operation and reduce run time.
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6 Additionally, it could considerably decrease solvent consumption and the detection limit was much
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8 lower than the MCL set by the EU. The present method was well suitable for the determination of
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10 trace organic compounds in complex samples.
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Figure Captions

Fig. 1. Effect of the extraction solvent volume on the absorbance value of soaked solution spiked with $10.0 \mu\text{g L}^{-1}$ of phenol keeping all other experimental conditions constant. The volumes were varied from $50 \mu\text{L}$ to $500 \mu\text{L}$.

Fig. 2. Effect of extraction time on the absorbance value of soaked solution spiked with $10.0 \mu\text{g L}^{-1}$ of phenol keeping all other experimental conditions constant.

Fig. 3(a). Optimization of derivatization reaction conditions: effect of the pH.

Fig. 3(b). Effect of the volume of 2.0% (w/v) potassium peroxodisulfate solution.

Fig. 3(c). Effect of the reaction time under constant temperature water bath at 20°C , 40°C and 60°C , respectively.

Table 1

Recoveries of the phenols in real samples (n=3)

Sample	Original	0.50 (Phenol added, $\mu\text{g L}^{-1}$)			15.0 (Phenol added, $\mu\text{g L}^{-1}$)		
	concentration	Found	Recovery	RSD	Found	Recovery	RSD
	($\mu\text{g L}^{-1}$)	($\mu\text{g L}^{-1}$)	(%)	(%)	($\mu\text{g L}^{-1}$)	(%)	(%)
Active carbon water purifier cartridge	1.50	1.95	90.0	5.3	16.20	98.0	3.2
Hollow fiber ultrafine membrane cartridge	0.80	1.23	86.0	2.5	15.68	99.2	2.8
Kinetic degradation fluxion membrane filter cartridge	0.35	0.82	94.0	4.2	15.31	99.7	2.9
Polypropylene pleated membrane filter cartridge	0.40	0.85	90.0	3.4	15.35	99.7	2.7
Nanofiltration water purifier	0.35	0.84	98.0	4.6	15.31	99.7	3.1
Ultrafiltration water purifier	1.81	2.26	90.0	2.6	16.70	99.3	1.6
Reverse osmosis water purifier	0.30	0.75	90.0	3.6	15.27	99.8	2.8
Polyethylene pipe	1.63	2.08	90.0	4.2	16.20	97.1	0.65
Polypropylene pipe	1.42	1.86	88.0	1.6	16.20	98.5	3.5
Random copolymerization polypropylene pipe	0.45	0.88	86.0	3.7	15.42	99.8	4.3

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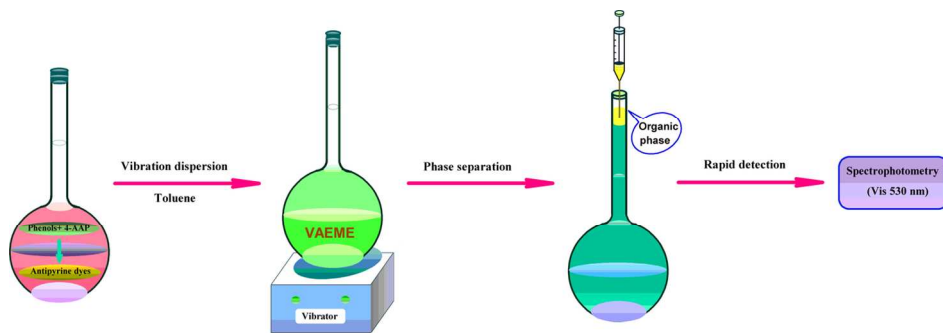
Unplasticized polyvinyl chloride pipe	0.85	1.32	94.0	6.5	15.55	98.0	4.2
Acrylonitrile butadiene styrene pipe fitting	1.71	2.16	90.0	3.2	16.51	98.7	0.53

Table 2

Comparison of the developed VAEME with other methods for the determination of phenols

Method	Sample	Sample volume (mL)	Extraction time (min)	LOD ($\mu\text{g L}^{-1}$)	Recovery (%)	Ref.
LLE-UV/vis	Water, wastewater	500	65	1	- ^b	[30]
LLE-UV/vis	Water, wastewater	24	25	1.27 ^a	95.7-107	[31]
DLLME-MV-UV/vis	Water, wastewater	5	6	0.8	90-99	[10]
MCDLLME-LC-UV	Tap water, lake water, wastewater	3.7	6	29	85.9-117.8	[32]
Two-step	Tap water, lake water	100	25	3.0	93.0-96.4	[33]
LLME-LC-UV	water					
SM-LLLME-LC-UV	Environmental water	20	45	0.082	96-102	[34]
VAEME- UV/vis	Soaked solution of water treatment product	100	3	0.08	86.0-99.8	This method

^a $\mu\text{g kg}^{-1}$, ^b Not reported.



Graphical abstract
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