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Molecular complex-based dispersive liquid–liquid microextraction: Analysis of polar compounds in aqueous solution

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ABSTRACT

A novel molecular complex-based dispersive liquid–liquid microextraction (DLLME) method was established *via* hydrogen bond interaction between the extractant and the analytes. In this approach, tri-*n*-butylphosphate (TBP), a Lewis base, was directly used, instead of the traditional water-immiscible organic solvents, as the extractant for DLLME. The phenols (*p*-benzenediol, *m*-benzenediol, *o*-benzenediol and phenol), which are typical Lewis acids, were successfully extracted from environmental aqueous samples. In addition, phase separation was achieved in a disposable polyethylene pipet with the open and narrow tip upside, for a collection of the above extractant layer, i.e. TBP. To achieve satisfactory extraction performance, several extraction parameters, such as type of extractant solvents, extractant volume, pH of sample solution, ionic strength of sample solution and extraction time, were optimized. Additionally, the proposed method was applied to environmental water samples. Under the optimized conditions, the limits of detection and limits of quantification for the phenols were 7–29 and 25–98 μg/L, respectively. The calibration curves showed good linearity ($r^2 \geq 0.9961$) over the investigated concentration range. The repeatability of the method was investigated by evaluating the intra- and inter-day precisions. The relative standard deviations (RSDs) obtained were lower than 11.2% and 13.9% at different concentration levels. The recoveries ranged from 83.2% to 117.8%, with RSDs less than 13.1%. The developed approach provides a new way to facilitate DLLME of organic polar compounds from aqueous solutions. Moreover, it enables a convenient collection of solvent less dense making use of a cheap and disposable polyethylene pipet.

1. Introduction

Sample preparation, which aims at concentrating analytes of interest and/or eliminating/decreasing matrix interference, is of great importance for complex sample analysis. An ideal sample preparation method should have favorable features, e.g. low consumption of samples and reagents, high capability of preconcentration, high throughput and operational convenience [1,2]. Miniaturization and automation are the approaches towards these goals. In the past two decades, a diversity of miniaturized extraction methods, especially microextractions, such as solid-phase microextraction (SPME) [3,4] and liquid-phase microextraction (LPME) [5,6], have been developed. Wide applications of these technologies have manifested their advantages of high sensitivity, simplicity, environmental friendship as well as ease of automation. However, because of the limited interface between the samples and the extractants, for most of these techniques, a considerable extraction time is required to obtain satisfactory extraction efficiency. To enhance extraction efficiency further, timesaving sample preparation methods are necessary [6].

Recently, a new microextraction technique, dispersive liquid–liquid microextraction (DLLME), has drawn much attention [6–13]. In addition to the merits of other microextraction techniques, a notable advantage of it is timesaving. In DLLME, the extraction solvent (water immiscible) is dispersed in aqueous sample solutions with the assistance of a disperser solvent (water miscible). In such a dispersive mode, the contact between the extractant and the analytes is dramatically increased. As a result, the extraction is almost time-independent, which is admirable in high throughput sample preparations.

Nevertheless, the recovery of the extractants dispersed in aqueous solutions is somewhat inconvenient. Currently, high-density organic solvents such as chlorobenzene, chloroform and carbon disulfide, are recovered after extraction using centrifugation. For extractants with density lower than water, special apparatuses, materials or techniques were proposed for their retrieval [2,6,11–14]. In such cases, any kind of solvents immiscible with aqueous solutions can be utilized in DLLME, which expands the applicability of this technique.

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In traditional DLLME, the partition of analytes in the extraction solvents and aqueous phases is determined by their solubility in these two phases. For analytes with high oil–water partition coefficients, such as hydrophobic polycyclic aromatic hydrocarbons (PAHs), high enrichment factor is easily achieved. However, for hydrophilic analytes, including metal ions and polar organic chemicals, the extraction by traditional DLLME may be problematic.

Recently, several reports of DLLME based on chemical or electric interaction have been documented [15–19]. In these reports, appropriate chemicals were added into the extractants to form ion pair or ion association with the target analytes (metal ions), which promoted the extraction. Though this approach has opened a new route in DLLME, for most organic analytes, the method is not applicable. To discover new DLLME methods suitable for organic polar analytes remains a challenge.

Phenols are toxic compounds widely existed in environment, which have been included in the US Environmental Protection Agency (EPA) (Methods 604) list of priority pollutants [20]. EPA regulations call for lowering phenol content in the wastewater to be less than 1 mg/L [21]. The National Standard of Integrated Wastewater Discharge of China (GB 8978-1996) also sets a maximum concentration of 300 μg/L. To determine phenols or phenol derivatives, several pretreatment methods, such as DLLME [22–26], SPE [27–29], SPME [30] and liquid–liquid –liquid microextraction [31], have been reported for their extraction, followed by liquid chromatography (LC) or capillary zone electrophoresis (CZE) separation coupled with ultraviolet (UV) [27,28,30,31], mass spectrometric (MS) [29] or electrochemical (EC) detection [32–36].

In this work, for the first time, a new DLLME method based on extracting the analytes by molecular complex was proposed. Tri-*n*-butylphosphate (TBP) was used as the extractant as well as the complex reagent to extract some phenols from environmental aqueous samples. The Lewis acid–base interaction between TBP and the phenols led to a satisfactory extraction result. Another notable feature of the present work is that the extraction is achieved in a cheap, disposable polyethylene pipet. Compared with previous DLLME using extractants less dense, in which special devices or tedious procedures were necessary, the proposed method is obviously easy, simple and economical.

2. Experimental

2.1. Chemicals and reagents

Sodium hydroxide (NaOH), hydrochloric acid (HCl), acetic acid, *n*-octanol, methyl *iso*-butyl ketone (MIBK), and tri-*n*-butylphosphate (TBP) were purchased from Shanghai General Chemical Reagent Factory (Shanghai, China) and were of analytical reagent grade. Acetonitrile, *n*-hexane, and methanol (HPLC grade) were purchased from Fisher Scientific (Massachusetts, USA). Purified water was obtained with an Aike water purification apparatus (Chengdu, China). *p*-Benzenediol, *m*-benzenediol, *o*-benzenediol and phenol were purchased from Acros (New Jersey, USA). The disposable polyethylene pipets were purchased from Weierkang Medical Plastic Factory (Jiangsu, China). The sketch of it was plotted in Fig. 1.

2.2. Sample preparation

A stock solution (containing 1000 mg/L of each analyte) was prepared by dissolving the standards with water and was stored in the refrigerator at 4 °C. Water samples were prepared by spiking deionized water with the analytes at a known concentration (1.0 mg/L) to study the extraction performance under different conditions. The pH value of the samples was adjusted to 2.0 with 0.1 mol/L HCl or NaOH before extraction, which value was determined by a Delta 320 pH-meter (Mettler Toledo, Switzerland). The samples were processed directly or after being spiked with the phenols at a concentration level of 1.0 mg/L.

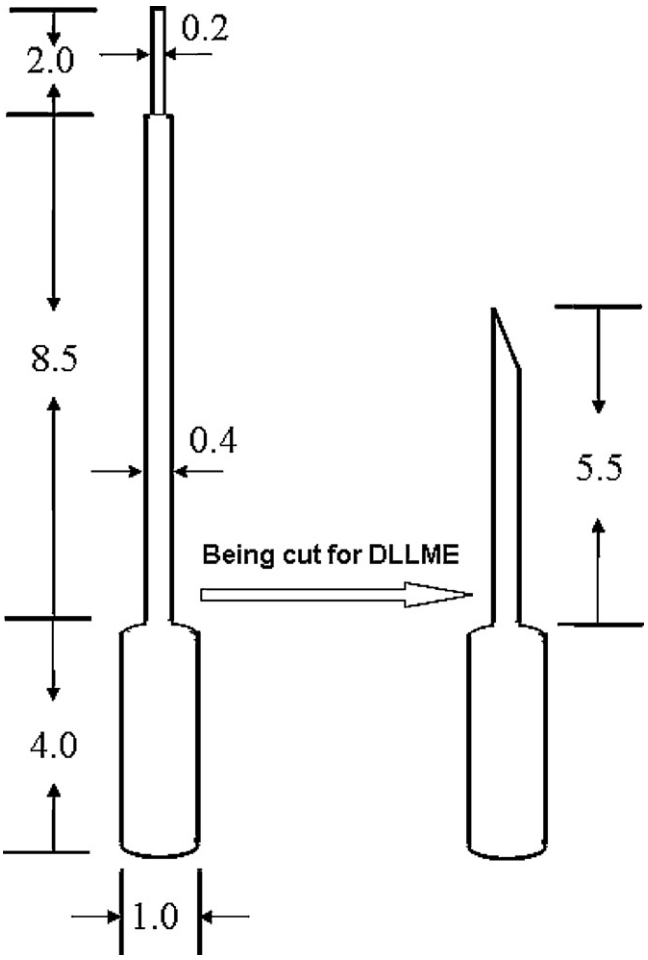

Fig. 1. The sketch of the disposable polyethylene pipet (the unit of length: cm).

2.3. Extraction procedures

The extraction procedures are illustrated in Fig. 2. An aliquot of the sample (3.7 mL, pH 2.0) containing the analytes was placed in a disposable polyethylene pipet. Subsequently, a mixture of 50 μL of TBP (as the extractant) and 0.5 mL of methanol (as the disperser solvent) were injected into the sample solution with a 1.0-mL syringe rapidly. Once the organic mixture was injected, a cloudy solution consisting of many dispersed fine droplets was formed (Fig. 2b). Subsequently the pipet was placed into a 10-mL Eppendorf tube and was agitated with a vortex mixer for 0.5 min. Then it was centrifugated at 5000 rpm for 5.0 min. As a result, the organic phase (32 μL) floated on the aqueous solution was concentrated in the narrow neck of the pipet (Fig. 2d), which can be easily withdrawn by a 10.0-μL microsyringe (Shanghai Gaoge, Shanghai, China).

2.4. HPLC separation

An Agilent 1100 liquid chromatography system (Agilent Technologies, California, USA) equipped with a diode array detector and a quaternary pump was used. The analytes were separated on a homemade ODS column (250 mm × 4.6 mm i.d., 5 μm) with methanol–water (3/7, v/v, containing 1% acetic acid) as the mobile

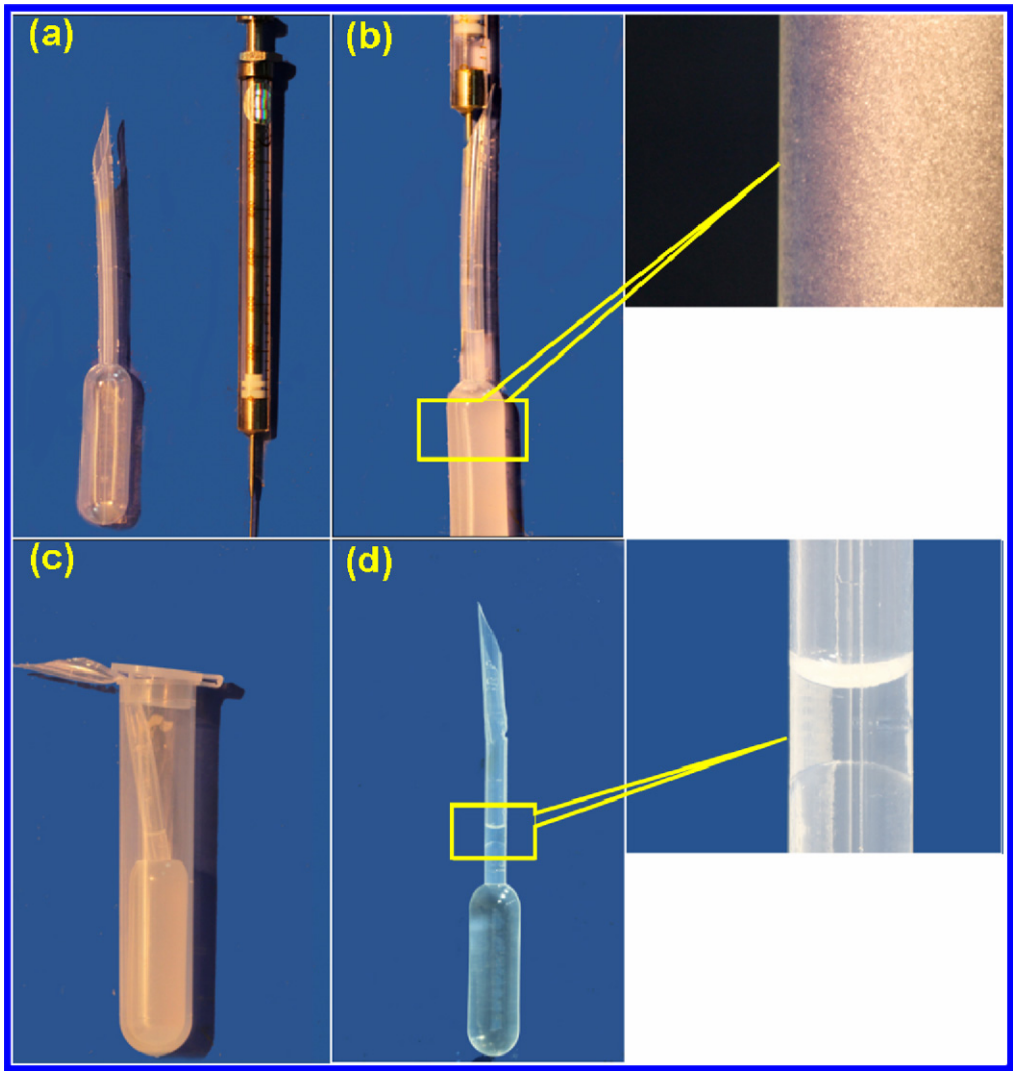

Fig. 2. Schematic diagrams of different steps of DLLME: (a) before injection of disperser solvent and extractant into sample solution; (b) injection and enlarged view of the fine particles in cloudy state; (c) the pipet was placed into a 10-mL Eppendorf tube; (d) optical photography after centrifugation and enlarged view of the floating organic phase.

phase. The flow rate was 1.0 mL/min and the detection wavelength was 274 nm. The column temperature was set at 40 °C and the injection volume was 5 μL. The data were collected and processed by Agilent ChemStation software.

3. Results and discussion

3.1. Extraction mechanism

Classical DLLME is based on the better dissolution of analytes in organic extractants than in aqueous samples. Nonpolar or hydrophobic analytes can be extracted by classical DLLME very well. However, for most polar or hydrophilic analytes, they cannot be easily partitioned to organic solvents as hydrophobic ones do. As a result, classical DLLME may not work for them. Therefore, chemical reaction was used to assist DLLME of polar compounds, e.g. chlorophenols, from aqueous solution [37,38]. However, introduction of chemical reaction to extraction is confined to the reactivity of analytes as well as the chemicals added. Development of new DLLME methods suitable for polar analytes remains necessary.

It is known that many analytes can form molecule complex via hydrogen bonding. Compared with strong covalent bond and weak molecule interaction such as van der Waals force, hydrogen bond could provide stable as well as reversible interaction between molecules [39–42]. The complex would exhibit different characteristics from the analyte itself, including solubility, hydrophobicity or hydrophilicity, etc. As a result, their extraction behavior would be different.

Herein, a new DLLME method, based on hydrogen bond interaction, was proposed. TBP, a Lewis base, was used as the complex reagent for several phenols, which are typical Lewis acids. As shown in Fig. 3, via hydrogen bonding, a molecule complex is formed between TBP and the phenols. Additionally, since TBP is hardly soluble in water, it also directly acted as the extractant in this study.

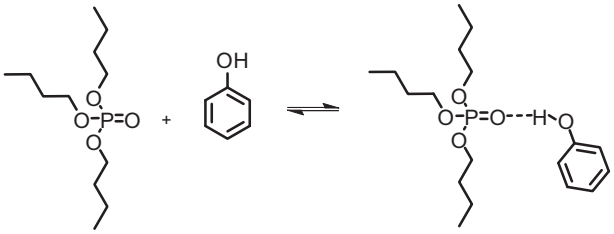

Fig. 3. Representative equilibrium equation of hydrogen bond interaction.

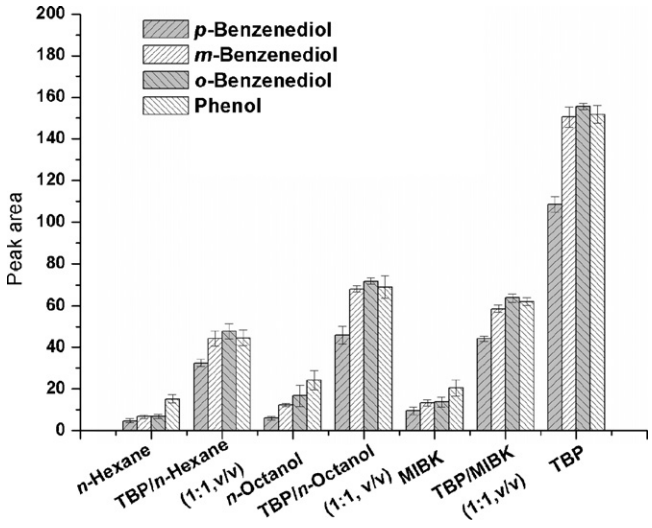

Fig. 4. Comparison of different extractants in extraction efficiency. The samples were spiked with 1 mg/L of each analyte. DLLME conditions: 3.7 mL of sample (pH 2.0), 50 μL of extractant, 2.0 min for extraction, centrifugation at 5000 rpm for 5.0 min.

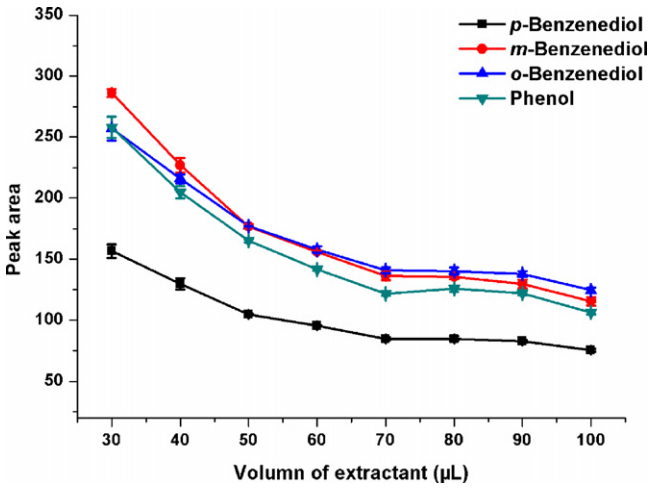

Fig. 5. Effect of the volume of the extractant on extraction efficiency.

3.2. Extraction device

In DLLME, organic extractants with density higher than water were readily recovered by centrifugation. However, for extractants less dense, the recovery step is relatively tedious. Hitherto, several methods have been developed for this purpose, including solidification of the floating organic drops [11,13,14], adsorption by nanoparticles [6], centrifugation in special designed apparatuses [2,12]. In this work, we provided a much simpler method to recover the extractant of TBP, using a disposable polyethylene pipet as the extraction device. After DLLME, the pipet was placed into an Eppendorf tube and was then centrifugated to separate the TBP from the aqueous solution. Since the pipet has a narrow neck, the TBP was readily phase separated for recovery. It is manifest that the new extraction device is simple, facile and economical.

3.3. Comparison of several extractants

For comparison, in addition to TBP, several extractants commonly used in DLLME such as *n*-hexane, *n*-octanol, MIBK and the mixtures of TBP and these solvents, were investigated to study their extraction behavior for the phenols. The results are shown in Fig. 4. It is observed that pure TBP shows the best extraction results, followed by the extractants containing TBP and finally by the extractants without TBP. These results indicate that TBP was vital for a successful extraction of the phenols. The explanation to this observation could be the formation of a molecule complex between TBP and the phenols. These results demonstrate a novel mechanism for constructing DLLME methods, which is anticipated to open a new route for related extraction researches.

3.4. Optimization of the DLLME

Several parameters, including TBP volume, type and volume of disperser solvents, ion strength and extraction time, were investigated to achieve the optimal extraction conditions. Every experiment was repeated three times.

3.4.1. Extractant volume

The effect of TBP volume on the extraction efficiency was investigated, with TBP ranging from 30 to 100 μL. As shown in Fig. 5, the peak areas decreased as the TBP volume increased. Although the use of less extractant would lead to higher enrichment, after extraction, the collection of the floating organic solvent was an obstacle if less than 50 μL of TBP was used. Therefore, 50 μL was selected as the compromise extractant volume.

3.4.2. Disperser solvents

In DLLME, disperser solvents are used to facilitate the dispersion of extractants in aqueous solutions to accelerate the extraction. Acetone, methanol, tetrahydrofuran and acetonitrile, which are commonly used disperser solvents, were investigated in this study. The result indicated that, when acetone or methanol were used as the disperser solvents, better extraction performance was achieved. Considering the compatibility with the HPLC mobile phase (methanol–water mixture), methanol was selected.

The volume of the disperser solvent was also investigated. The results indicate that, when methanol was less than 500 μL, TBP could not be dispersed in aqueous solutions very well, while an excess of methanol may decrease the extraction efficiency. Therefore, 500 μL was selected as the suitable volume for the disperser solvent.

3.4.3. The pH of sample solutions

In this study, the phenols were extracted by hydrogen bond interaction with TBP. As the molecular status of the phenols is severely affected by the pH of the solutions, this parameter is expected to significantly influence the extraction performance of the proposed method. The pH of the sample solutions was investigated in the range of 2–11. As shown in Fig. 6, the peak areas of the phenols decreased a little as the pH increased from 2.0 to 9.0; as the pH was further increased, the peak areas decreased dramatically. This behaviour should be ascribed to the change in the molecular status of the phenols. The pK_a values of *p*-benzenediol, *m*-benzenediol, *o*-benzenediol and phenol are 9.91, 9.44, 9.36 and 9.99, respectively. When the pH is less than the pK_a values, the phenols exist in their neutral forms, which is beneficial for the formation of the molecule complex with TBP. However, when the pH is higher than the pK_a values of the analytes, they were ionized, which was detrimental to the formation of the complex. Therefore, at high pH values, the extraction performance decreased sharply. The results demonstrate that a pH value of 2.0 is the most optimal for the extraction.

3.4.4. Ion strength

Sodium chloride in the range of 0–12.7 mmol was added to the sample solution in order to investigate the influence of ionic

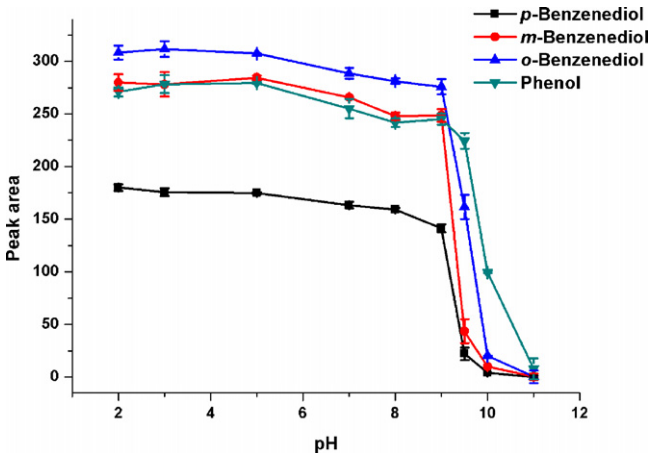

Fig. 6. Effects of different pH on extraction efficiency.

strength on the extraction. The results (no shown) demonstrate that the salt addition had no significant effect on the extraction of the phenols. Therefore, no salt was added to the sample solution in subsequent experiments.

3.4.5. Extraction time

DLLME is notable for fast extraction. In this study, the extraction time (that is the agitation time on the vortex mixer) was investigated over the range of 0–5 min (0, 0.5, 1, 2, 3, 4, 5 min). The results indicate that the extraction efficiency was increased by vortex agitation within 0.5 min, and the prolonged vortex time did not provide any increase in extraction efficiency. Hence, 0.5 min was selected as the extraction time.

Table 1
Linear range, regression data, limits of detection (LODs), limits of quantification (LOQs) of the phenols of the DLLME method.

Analytes	Linear range (mg/L)	r^2	LOD (μg/L)	LOQ (μg/L)
p-Benzenediol	0.05–100	0.9982	16	53
m-Benzenediol	0.05–100	0.9961	15	49
o-Benzenediol	0.05–100	0.9992	7	25
Phenol	0.1–100	0.9966	29	98

3.5. Method evaluation

A series of experiments with regard to the linearity, limit of detection (LOD) and reproducibility were performed to validate the proposed method at the optimized working conditions. The results obtained are listed in Table 1. It can be observed that good linearities were obtained for the phenols ranging from 0.05 to 100 mg/L, with regression coefficients (r^2) higher than 0.9961. The LODs for the phenols, calculated at a signal-to-noise of 3, ranged from 7 to 29 μg/L. The limits of quantitation (LOQs), calculated at a signal-to-noise of 10, were in the range of 25–98 μg/L. The enrichment factors of the phenols were calculated to be 51.6, 48.4, 35.4 and 55.3 times for *p*-benzenediol, *m*-benzenediol, *o*-benzenediol and phenol, respectively. Comparing with previous procedures for the analysis of phenols, as shown in Table 2, the proposed method is

Table 2
Comparison of sample preparation procedures and LODs among different methods.

Matrix	Extraction technique	Characteristics	LOD	Instrumental analysis	Ref.
River water	On-line SPE	Polymeric sorbent materials (Hysphere-GP and Hysphere-SH)	Phenol: 1 μg/L	HPLC-UV	[27]
Tap, river water	On-line SPE	polypyrrole	Phenol: 0.07 μg/L	LC-UV–vis	[28]
River water, wastewater and treatment plant influents	On-line SPE	Polymer based SPE adsorbents (Hysphere GP, Oasis HLB)	Phenol: 14–197 ng/L	LC–APCI-MS	[29]
River water	SPME	Carbowax–templated resin (CW–TPR) and polydimethylsiloxane–divinylbenzene (PDMS–DVB)	Phenol: 10 μg/L	HPLC-UV	[30]
Lake water, landfill leachate	LLLME	a new LLLME apparatus	*p*-Benzenediol: 0.6 μg/mL *o*-Benzenediol: 0.6 μg/mL *m*-Benzenediol: 0.6 μg/mL Phenol: 0.5 μg/mL	HPLC-UV	[31]
Distilled water	–	CZE	*p*-Benzenediol: 0.19×10^{-6} mol/L *o*-Benzenediol: 0.28×10^{-6} mol/L *m*-Benzenediol: 0.22×10^{-6} mol/L	EC	[32]
Hair dyes	–	CZE	As low as 10^{-7} mol/L	EC	[33]
Artificial wastewater	–	Nanogold/glassy carbon modified electrode (nano-Au/GCE)	*p*-Benzenediol: 5.0×10^{-7} mol/L *o*-Benzenediol: 6.5×10^{-7} mol/L *m*-Benzenediol: 9.0×10^{-7} mol/L	EC	[34]
Tap water, local river	–	Disposable electrode modified with multiwalled carbon nanotubes (MWCNTs) and gold nanoparticles (AuNPs)	*p*-Benzenediol: 3.9×10^{-7} mol/L *o*-Benzenediol: 2.6×10^{-7} mol/L *m*-Benzenediol: 7.2×10^{-7} mol/L	EC	[35]
Artificial sewage sample	–	The single-wall carbon nanotube (SWNT) electrode	*p*-Benzenediol: 1.2×10^{-7} mol/L *o*-Benzenediol: 2.6×10^{-7} mol/L *m*-Benzenediol: 3.0×10^{-7} mol/L	EC	[36]
Tap water, East Lake water, sewage outfall of a hospital, a fishpond, waste outlet of a hoggery and a fermentation factory	DLLME	Molecular complex	*p*-Benzenediol: 16 μg/L o-Benzenediol: 7 μg/L *m*-Benzenediol: 15 μg/L phenol: 29 μg/L	LC-UV	This work

Table 3
Repeatability of the DLLME method.

Analyte	Intra-day precision (RSD %, $n = 6$)			Inter-day precision (RSD %, $n = 3$)		
	Low[a]	Medium	High	Low	Medium	High
p-Benzenediol	3.9	5.8	5.6	10.8	2.1	3.0
m-Benzenediol	5.4	6.6	6.8	4.2	4.2	5.7
o-Benzenediol	11.2	5.2	5.0	13.9	4.5	2.9
Phenol	5.7	6.7	6.8	7.8	5.1	6.7

[a] The low, medium and high concentrations of the phenols were 0.1, 1.0 and 10 mg/L respectively.

much more sensitive than most of them. Moreover, the extraction process is simpler and more economical.

The repeatability of the proposed method was evaluated by investigating the intra- and inter-day precisions. The results, shown in Table 3, demonstrate that the relative standard deviations (RSDs) were less than 11.2% and 13.9%, respectively.

3.6. Analysis of real water samples

The proposed method was applied to the analysis of environmental water samples from a tap in our laboratory, East Lake, sewage outfall of a hospital, a fishpond, waste outlet of a hoggery and a fermentation factory. All the samples were collected in Wuhan, China. The results are listed in Table 4. It can be observed that 360 μg/L phenol in the East Lake water, and 370 μg/L *p*-benzenediol, 980 μg/L phenol in sewage outfall of a hospital were detected, which are higher than the criterion of National Standard of Integrated Wastewater Discharge of China (phenol: 300 μg/L, GB 8978-1996). No analyte was found in the other water samples. The chromatograms of spiked and not spiked samples were shown in Fig. 7. Recovery was studied by the spiked water samples. Satisfied recoveries in the range of 83.2–117.8% were obtained, with RSDs ranging from 2.1% to 13.1% (as shown in Table 4). These results demonstrated that the proposed method was reliable for the analysis of the phenols in environmental water samples.

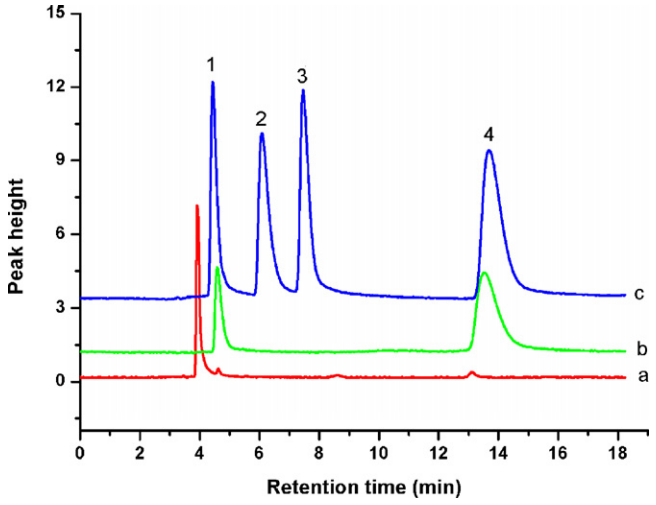

Fig. 7. Chromatograms of spiked and not spiked samples. Mobile phase: methanol/water (3:7, v/v, containing 1% acetic acid), flow rate: 1.0 mL/min and detection wavelength: 274 nm. (a) Sewage outfall of a hospital before DLLME; (b) sewage outfall of a hospital after DLLME; (c) sewage outfall of a hospital spiked with 1.0 mg/L analytes extracted by the DLLME. Peak identification: (1) *p*-benzenediol; (2) *m*-benzenediol; (3) *o*-benzenediol; (4) phenol.

Table 4
Determination of the phenols in environmental samples by DLLME.

Sample	Analyte	Detected-I[a] (μg/L)	Added (μg/L)	Detected-II[b] (μg/L)	Recovery (%)	RSD (%)
Tap water	*p*-Benzenediol	N.D.[c]	1000	860	85.8	9.9
	m-Benzenediol	N.D.	1000	960	96.4	2.7
	o-Benzenediol	N.D.	1000	950	94.8	2.1
	Phenol	N.D.	1000	1060	105.9	12.3
The East Lake water	*p*-Benzenediol	N.D.	1000	830	83.2	9.1
	m-Benzenediol	N.D.	1000	1000	100.2	9.3
	o-Benzenediol	N.D.	1000	960	95.6	8.2
	Phenol	360	1000	1370	100.5	13.1
Sewage outfall of a hospital	*p*-Benzenediol	370	1000	1260	89.8	8.1
	m-Benzenediol	N.D.	1000	940	93.9	3.8
	o-Benzenediol	N.D.	1000	920	92.0	5.4
	Phenol	980	1000	1840	85.9	6.6
Water of a fishpond	*p*-Benzenediol	N.D.	1000	910	90.6	4.4
	m-Benzenediol	N.D.	1000	1030	103.4	3.7
	o-Benzenediol	N.D.	1000	1040	104.2	3.0
	Phenol	N.D.	1000	1120	112.1	4.5
Waste water of a hoggery	*p*-Benzenediol	N.D.	1000	950	94.5	6.7
	m-Benzenediol	N.D.	1000	1090	109.1	6.3
	o-Benzenediol	N.D.	1000	1030	103.0	5.8
	Phenol	N.D.	1000	1040	104.1	6.5
Waste water of a fermentation factory	*p*-Benzenediol	N.D.	1000	900	90.3	2.1
	m-Benzenediol	N.D.	1000	1030	102.7	4.2
	o-Benzenediol	N.D.	1000	990	99.5	4.5
	Phenol	N.D.	1000	1180	117.8	5.1

[a] The samples were analyzed directly.
[b] The samples were analyzed after spiking.
[c] N.D. not detected.

4. Conclusion

In the present study, a novel molecular complex-based dispersive liquid–liquid microextraction (DLLME) method was developed. Tri-*n*-butylphosphate (TBP) was used as the extractant as well as the complex reagent to extract some phenols from environmental aqueous samples. The molecule complex was formed between the extractant and the analytes via hydrogen bond interaction. This new technique expanded the application of classical DLLME for various organic analytes. Another notable feature of the proposed method is that the extraction is achieved in a cheap, disposable polyethylene pipet. Compared with previous DLLME using extractants less dense, in which special devices or tedious procedures were necessary, the proposed method is obviously easy, simple and economical. Under the optimal extraction condition, good linearity and repeatability were also achieved.

Acknowledgements

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