



## Analytical Methods

## Phenolic-based non-ionic deep eutectic solvent for rapid determination of water soluble neonicotinoid insecticides in tea infusion



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## ABSTRACT

Challenges were raised to established analytical method for monitoring water soluble neonicotinoid insecticide (NEOs) residues in tea infusion. Phenolic-based non-ionic deep eutectic solvent (NIDES) composed by a mixture of DL-menthol and thymol (molar ratio of 1:3) was applied to achieve the determination of selected NEOs. Factors influenced extraction efficiency have been evaluated and molecular dynamics approach was conducted aiming to provide a new insight to explain its extraction mechanism. It is found that Boltzmann averaged solvation energy of NEOs was negatively correlated with extraction efficiency. The method validation results indicated good linearities ( $R^2 \geq 0.99$ ), sensitive LOQs ( $0.05 \mu\text{g L}^{-1}$ ), high precisions ( $\text{RSD} < 11\%$ ) and satisfactory recoveries (57.7%–98%) at  $0.05 \mu\text{g L}^{-1} \sim 100 \mu\text{g L}^{-1}$ . The intake risk of NEOs in tea infusion samples were acceptable which residues in range of  $0.1 \mu\text{g L}^{-1} \sim 3.5 \mu\text{g L}^{-1}$  for thiamethoxam imidacloprid and thiacloprid. This method showed advantages of rapid, green, and easy operation.

## 1. Introduction

As a healthy and popular beverage, tea was consumed by two-thirds of the population (Karak & Bhagat, 2010). During risk monitoring of tea safety, many efforts were put on the water-soluble pesticide residues due to their high transfer potential from tea to its infusion (Wang, Zhou, Zhang, Luo, & Chen, 2019). It has been reported neonicotinoid insecticides (NEOs) showed a high transfer rate in range of 62.2% to 97% (Hou, Hu et al., 2013; Chen, Pan, Liu, & Lu, 2017) due to their highly water-soluble properties (IUPAC Pesticides Properties Database, 2022). NEOs were regularly used in tea cultivation due to their excellent activity against aphids, leaf hoppers, whiteflies et al (Hou, Hu et al., 2013; Gupta & Shanker, 2007; Shanker, Sood, Kumar, & Ravindranath, 2002) and easily residue in tea infusion (Chen et al., 2017; Wang, Zhou et al., 2019). At present, the extraction technologies of NEOs not only involved some traditional methods, such as liquid–liquid extraction base on organic solvents, QuEChERS method (Maryam et al.) and solid phase extraction (SPE) method applying with hydrophilic–lipophilic balance

sorbents (Hou, Jiang et al., 2013), but also some novel extraction methods, for example stir bar sorptive extraction (SBSE), magnetic solid phase extraction (MSPE), solid phase microextraction (SPME) (Maryam et al.), and dispersive liquid–liquid microextraction (DLLME) applying with extraction materials innovation (covalent organic frameworks, metal organic frameworks, ionic liquids) (Kokosa, 2019; Maryam, Hossein, & Amirhassan, 2020). However, those methods applying with above materials had the disadvantages of 1) tedious and time–cost on materials preparation; 2) high cost of purchasing raw materials for synthesis of those materials; 3) usage of hazards solvent for materials synthesis. Therefore, to overcome above drawbacks, it was necessary to explore a rapid, green, simple determination method for NEOs in tea infusion.

In the last decade, many studies have been published on deep eutectic solvent (DES) fundamental and their applications research, which was first raised by Abbott, Capper, Davies, Rasheed, and Tambyrajah (2003). DESs are systems formed from a eutectic mixture of Lewis or Brønsted acids and bases which can contain variety of anionic

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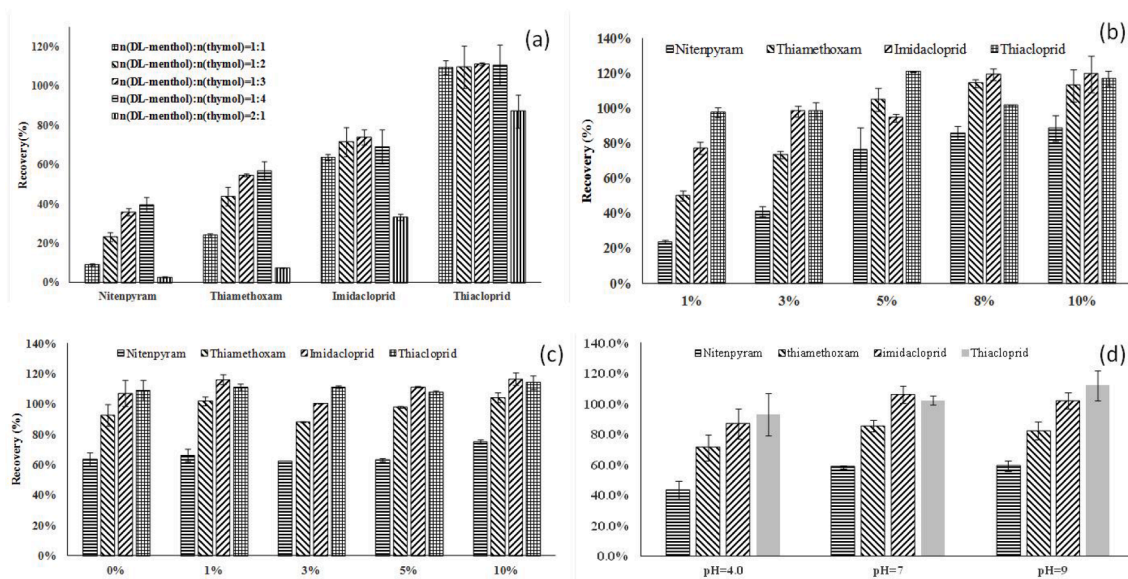


Fig. 1. Impact of phenolic-based NIDES composition (a), weigh ratio (b), ionic strength (c), and pH (d) on the recoveries of NEOs ( $n = 3$ ).

and/or cationic species. As an extraction material, DES showed the advantages of simple preparation procedures, greener nature, easy tunability, and bioavailable characterization (Abbott, Capper, & Gray, 2006; Florindo, Oliveira, Rebelo, Fernandes, & Marrucho, 2014; Zhao et al., 2015). The majority of the DES reported to date is classified into four main types depending on their constituents (Dwamena, 2019). These DES are based on at least one ionic chemical and dominated by strong hydrogen-bond interactions, rendering the resulting mixture hydrophilic. The design of hydrophobic eutectic mixtures solely consist of non-ionic species has received particular recent attention in the literature for aqueous sample analysis.

The concept for non-ionic deep eutectic solvent (NIDES) as a new class (type V) of DES raised by Abranches and coworkers (2019), had benefit from hydrophobic property for easy separation from water sample. There was an abnormal strong interaction identified stemming from the acidity difference of the phenolic and aliphatic hydroxyl groups. This type of interaction is found to be the key to prepare non-ionic DES. Osch, Zubeir, Bruinhorst, Rocha, and Kroon (2015) prepared 507 combinations of non-ionic natural substances and identified 17 liquid mixtures, 8 of which based on thymol. Therefore, phenolic-based NIDES composed by thymol and its applications were significance important to be further investigated. However, few study was performed for dissecting extraction mechanism of NIDES. More studies should be conducted to supervise component selection of NIDES base on extraction principle instead of blindly testing.

In this study, phenolic NIDES were prepared using thymol as Lewis acid and DL-menthol as Lewis base in this work. Main factors influenced extraction efficiency as well as extraction mechanism were studied and explained using molecular dynamics approach. The method will not only provide an easy, green, simple analytical method for NEOs residue analysis in tea infusion, but also give suggestions on experiment design of NIDES component selection in the future.

## 2. Experimental procedures

### 2.1. Chemicals, reagents and materials

Four NEOs standards (thiacloprid, imidacloprid, nitenpyram, and thiamethoxam) of  $100 \text{ mg L}^{-1}$  were purchased from ANPEL (ANPEL Laboratory Technologies Inc, Shanghai, China). Methanol (HPLC grade) was obtained from Merck (Merck, Massachusetts, USA). DL-menthol and thymol were obtained from Macklin (Macklin Biochemical Co., Ltd,

Shanghai, China). Sodium chloride (NaCl) was purchased from Sino-pharm (Sinopharm Chemical Reagent Co. Ltd, Beijing, China). Purified water was obtained with a Millipore Milli-Q system (Merck, Massachusetts, USA).

### 2.2. Tea infusion preparation method

Six tea samples were collected from local markets. The typical brewing method referred to the methodology of organoleptic evaluation in China (Chinese Ministry of Agriculture. (2009), 2009). 150 mL boiling water poured into 3 g of the grinded tea sample and keep for 5 min, then the infusion was filtered and cooled down to yield the infusion sample for further analysis.

### 2.3. Phenolic-based NIDES preparation method

DL-menthol and thymol were added in a round-bottomed flask mixed with molar ratio of 1:3, followed by magnetic stirring and heated in a water bath at  $60 \text{ }^\circ\text{C}$  for 2 h at a rotational speed of 800 rpm, until the homogeneous clear transparent solution was formed for later use.

### 2.4. Sample preparation method of phenolic-based NIDES extraction

A weigh of 0.8 g NIDES was placed into a 15 mL centrifuge tube, then 10 mL water sample was added, followed by vortex for 5 min. After NIDES evenly dispersed in the sample solution and reach the extraction equilibrium, the tube was centrifuged with Thermo centrifuge (Thermo, USA) for 10 min at 4654g. After removing water layer below using a syringe, the upper hydrophobic NIDES phase was transferred to a metered graduated test tube. Then NIDES was dissolved with methanol keeping volume to 2 mL. After that, the solution was filtered through a  $0.22 \text{ }\mu\text{m}$  filtered before instrumental analysis.

### 2.5. LC-MS/MS analytical conditions

The analytes were performed on a Shimadzu Nexera X2 LC-30AD LC (Kyoto, Japan) with a Shimadzu 8050 tandem quadrupole mass spectrometer (Kyoto, Japan). The LC-MS/MS instrument, chromatographic column, and MS condition referring to our previous study (Wang, Qi et al, 2019). The mobile phase consisted of a gradient of  $5 \text{ mmol L}^{-1}$  methanamide (phase A) and methanol (phase B) at a flow rate of  $0.3 \text{ mL min}^{-1}$ . The volume ratio of phase B was held at 40% for the first 1 min,

**Table 1**  
Analytical performance of the proposed method.

NEOs			Mean recovery (%)			Intra-day RSD <sup>***</sup> (%)		Inter-day RSD <sup>***</sup> (%)	
	LOD	LOQ				(n = 3)		(n = 3)	
	( $\mu\text{g L}^{-1}$ )	( $\mu\text{g L}^{-1}$ )	0.05( $\mu\text{g L}^{-1}$ )	10( $\mu\text{g L}^{-1}$ )	100( $\mu\text{g L}^{-1}$ )	MIN*	MAX**	MIN*	MAX**
Nitenpyram	0.03	0.05	57.7	59.5	58.1	4.1	8.3	4.3	7.8
Thiamethoxam	0.03	0.05	83.2	77.2	76.8	2.6	5.5	2.7	5.2
Imidacloprid	0.03	0.05	95.0	93.2	87.6	3.6	10.4	3.5	10.5
Thiacloprid	0.03	0.05	84.6	98.0	90.5	0.6	6.1	0.6	5.9

Note: \*MIN: minimum value; \*\*MAX: maximum value; \*\*\*RSD: relative standard deviation.

then increased to 80% from 1 min to 3 min, then increased to 95% from 3 min to 5 min and held at 95% for 2 min, and then reduced back to 5% within 0.1 min and held at 5% for 1.9 min. The injection volume was 2  $\mu\text{L}$ . Electrospray ionization (ESI) was used with a capillary voltage of 4000 V for positive-ion mode. The detailed ion pairs and corresponding collision energies for each pesticide are provided in Table S1.

### 2.6. Molecular dynamics analysis method

DREDDING force field has been applied for the molecular dynamic simulation with Lammmps package. 60 solvents and 1 solute molecular were equilibrated in a cubic box (30  $\text{\AA}$   $\times$  30  $\text{\AA}$   $\times$  30  $\text{\AA}$ ) under constant NVP conditions. Time step was set as 1 fs and a 100 ps trajectory was carried out to equilibrate solute–solvent system.

For the solvation energy simulation, all the equilibrate solute–solvent geometry obtained by dynamics simulation were optimized B3LYP-D3/6-31G (d, p) method with PCM model by using G09D package. Eps of solvent mixture (thymol: menthol = 3:1) is 4.2. The stationary points have been testified by frequency analysis. The different conformers of solute were located and optimized, moreover, the corresponding averaged solvation energies were weighted by free energy.

## 3. Results and discussion

### 3.1. Impact of phenolic-based NIDES composition on the extraction efficiency

It has been reported that phenolic-based NIDES could boost the solubility of phenolic compounds or any other aromatic compounds through the formation of  $\pi$ -interactions between solvent and solute. For NEOs, their structures contain benzene ring and amide group. The lone pair electrons on the nitrogen atom will obviously conjugated with the carbonyl group. Besides the benzene ring contains  $\pi$  bond, which were predicted to easily interact with NIDES.

Previous study has shown that, in the thymol–menthol system, an abnormal strong interaction was identified stemming from the acidity difference of the phenolic and aliphatic hydroxyl groups. This type of interaction is found to be the key to prepare NIDES (Abranches et al., 2019). Therefore, phenolic NIDES were prepared using thymol as Lewis acid and DL-menthol as Lewis base in this work. A series of mole ratio (1:1, 1:2, 1:3, 1:4, 2:1) between DL-menthol and thymol were optimized. As shown in Fig. 1a., mole ratio 1:3 between DL-menthol and thymol was the optimum ratio.

### 3.2. Influence of phenol-based DES weigh ratio on extraction efficiency

Different mass of phenolic NIDES added into samples were studied by comparing the recoveries of NEOs extracted by five different weigh percentages (1%, 3%, 5%, 8%, 10%) of NIDES respectively. With increment of NIDES amount from 1% to 8%, the recoveries of NEOs increased (Fig. 1b.). However, 10% of NIDES showed the same extraction efficiency compared with 8%. Therefore, 8% of NIDES was applied for future study.

### 3.3. Influence of ionic strength and extraction time on extraction efficiency

In most applications, the ionic strength of sample solution can be adjusted by adding salt which will change analytes partition between extraction phase and aqueous phase and affecting their recoveries. Besides, with the increment of the ionic strength, the density and viscosity of the aqueous solution are also enhanced, which will reduce the mass transfer efficiency process of target analytes (Naing & Lee, 2018). In this study, five different weigh percentages of NaCl (0%, 1%, 3%, 5%, 10%) were compared by testing their extraction efficiency. Results indicated recoveries increased along with the increment of ionic strength. Therefore, 10% of NaCl was the most sufficient ionic strength for all target analytes (Fig. 1c.).

During extraction process, there were boundary layers between extraction phase and targets analytes and will affect their extraction efficiency. In order to minimize the mass transfer distance between analytes and extraction phase, and to make all targets reached their extraction equilibrium, vortex operation was conducted by comparing 30 s, 60 s, 90 s, 120 s, 300 s extraction time under 2500  $\text{r min}^{-1}$  vortex frequency. The results showed the 90 s extraction was sufficient for all analytes with good extraction efficiency.

### 3.4. Influence of pH on extraction efficiency

Generally, sample pH values are adjusted to a proper range to keep analytes in non-dissociated/neutral forms (Pawliszyn, 2009). Low pH can improve extraction efficiency of acidic compounds, or vis versa. The stability of NEOs were also needed to be considered during method development. Previous study showed that most of NEOs were easily hydrolysis in alkaline solution and stable in neutral solution. In this study, different pH values were compared by testing their extraction efficiency. Buffers was prepared with proper molar ratios of  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  in water for pH 4 and 9. The original sample pH value was 7. Compared with pH 4, neutral and alkaline solution obtained better recoveries for nitenpyram, thiamethoxam and imidacloprid. It also indicated that recoveries were not significantly different between pH 7 and pH 9 (Fig. 1d.). Therefore, there was no need to adjust sample pH for easy operation.

### 3.5. Method validation

The performance of method was validated by evaluating its linearity, accuracy, precision, limit of quantification (LOQ), and limit of detection (LOD). Linearities were determined by analyzing 0.1, 1.0, 10, 20, 50, 100, 200  $\mu\text{g L}^{-1}$  matrix matched standards. Good linearities were obtained for all target NEOs with coefficients of determination ( $R^2$ ) equal or greater than 0.996.

The recoveries and precisions were evaluated at concentrations of 0.05  $\mu\text{g L}^{-1}$ , 10  $\mu\text{g L}^{-1}$ , and 100  $\mu\text{g L}^{-1}$  (n = 3) in tea infusion. Most of analytes obtained satisfactory recoveries (ranged from 76% to 98%) at 0.05  $\mu\text{g L}^{-1}$  ~ 100  $\mu\text{g L}^{-1}$ . Only nitenpyram showed lower recoveries ranged from 57.7%~59.5% for all spiking levels (Table 1). Comparing water solubility between these four NEOs, the order for NEOs is

**Table 2**

The concentrations of NEOs residues detected in white tea infusion using this method.

Sample information	Residues( $\mu\text{g L}^{-1}$ )		
	thiamethoxam	imidacloprid	thiacloprid
White tea infusion 1#	0.1	2.9	
White tea infusion 2#	1.1	2.6	0.2
White tea infusion 3#	1.3	3.5	
White tea infusion 4#	2.0	1.1	
White tea infusion 5#	2.3	1.7	0.6
White tea infusion 6#	0.2	0.2	0.1

thiacloprid ( $184 \text{ mg L}^{-1}$ ) < imidacloprid ( $610 \text{ mg L}^{-1}$ ) < thiamethoxam ( $4100 \text{ mg L}^{-1}$ ) < nitenpyram ( $590000 \text{ mg L}^{-1}$ ) at  $20^\circ\text{C}$ . And the order of logP for NEOs is thiacloprid (1.26) > imidacloprid (0.57) > thiamethoxam (0.13) > nitenpyram (0.66) (IUPAC Pesticides Properties Database, 2022). NIDES showed worse performance on extracting nitenpyram with high water soluble property and low logP.

Overall, excellent accuracies and precisions results were obtained according to intra- and inter-day data. The intraday and inter-day RSDs were all below 11%. LODs was  $0.03 \mu\text{g L}^{-1}$  for all analytes which calculated by signal-to-noise (S/N) ratios of 3, indicating of high instrument sensitivity. The LOQs were  $0.05 \mu\text{g L}^{-1}$  which calculated using minimum spiking level.

### 3.6. Extraction mechanism explanation using molecular dynamics method

The reason for the low recovery of nitenpyram was further explained using molecular dynamics methods. Compared the solvation energy of NEOs in different solvents, solvation energies of NEOs in mixture solvation are bigger than that in water. The Boltzmann averaged solvation energy of NEOs were summarized in supplementary data Table S2-S5.

The biggest solvation energy of NEO is given by thiacloprid as  $-4.69 \text{ kcal mol}^{-1}$ , which indicates thiacloprid can be easily extracted from the solvent. The order of solvation energy for NEOs is thiacloprid ( $-4.69 \text{ kcal mol}^{-1}$ ) > imidacloprid ( $-4.26 \text{ kcal mol}^{-1}$ ) > thiamethoxam ( $-4.11 \text{ kcal mol}^{-1}$ ) > nitenpyram ( $-3.68 \text{ kcal mol}^{-1}$ ) and the calculation results are consistent with experiment results, which indicated extraction efficiency is negatively correlated with the Boltzmann solvation energy. It might be an ideal index for the selection and design of NIDES extraction materials in the future.

**Table 3**

Comparison of this work to reported studies for the determination of NEOs in tea infusion.

Reference	Instrument	Method	Recovery (%)	LOQ ( $\mu\text{g L}^{-1}$ )	RSD (%)	Organic solvent amount (mL/sample)	Sample preparation time (min/sample)
This study	LC-MS/MS	10mL water sample + 10% NaCl (w/w) + 0.8 g DES, vortex for 90 s, centrifuge for 5 min. Then NIDES was dissolved with methanol keeping volume to 2 mL	1. Nitenpyram:57.7% ~58.1% 2. Thiamethoxam:76.8% ~83.2% 3. Imidacloprid:87.6% ~95.0% 4. Thiacloprid:84.6% ~98.0%	0.05	$\leq 15\%$	2 mL	About 9 min
Wang et al., 2019	LC-MS/MS	10 mL tea infusion extracted by 20 mL acetonitrile, then 12 mL supernatant added with NaOAc was further clean up by 100 mg PSA, followed by centrifuge. 10 mL supernatant was evaporated drying. Then it was dissolve in 1 mL solvent.	1. Imidacloprid:79.6% ~113.4% 2. Thiacloprid:90% ~108.1%	1. 2.5 2. 2.0	$1. \leq 17.5$ $2. \leq 18.2$	21 mL	> 30 min
Chen et al., 2017	LC-MS/MS	100 mL tea infusion extracted by 100 mL $\text{CH}_2\text{Cl}_2$ twice, evaporation drying, dissolved with methanol/water keeping volume to 2 mL	1. Imidacloprid:99% ~101% 2. Thiacloprid:89%~93%	1. 0.047 2. 0.088	$1. \leq 4$ $2. \leq 6$	> 200 mL	> 60 min

### 3.7. Analysis of tea infusion sample and method comparison

Whitefly is one the main pests happen on white tea in China. It pupates in March and feathering in April. It was recommended to control them during early age. White tea usually harvests starts from early April, and lasting about 20–30 days. Therefore, it was necessary to monitoring NEO residue on white tea. The developed method was employed to analysis six white tea infusion. The concentrations of analytes were listed in Table 2. All samples were detected thiamethoxam and imidacloprid residue in range of  $0.1 \mu\text{g L}^{-1} \sim 2.3 \mu\text{g L}^{-1}$  and  $0.2 \mu\text{g L}^{-1} \sim 3.5 \mu\text{g L}^{-1}$ , respectively. The P50 (50th Percentile) residues were  $1.2 \mu\text{g L}^{-1}$  (thiamethoxam) and  $2.0 \mu\text{g L}^{-1}$  (imidacloprid), respectively. Besides, 50% tea infusion samples were detected thiacloprid with concentration in range of  $0.1 \mu\text{g L}^{-1} \sim 0.6 \mu\text{g L}^{-1}$ . The average residues was  $0.3 \mu\text{g L}^{-1}$ . The EU MRLs in tea were  $20 \text{ mg kg}^{-1}$  (thiamethoxam),  $0.05 \text{ mg kg}^{-1}$  (imidacloprid) and  $10 \text{ mg kg}^{-1}$  (thiacloprid), respectively (EU Pesticides Database, 2022). According to the transfer rates reported by Wang et al (Wang et al, 2009a), the maximum allowable residue in tea infusion will be  $400 \mu\text{g L}^{-1}$  (thiamethoxam),  $0.94 \mu\text{g L}^{-1}$  (imidacloprid) and  $170 \mu\text{g L}^{-1}$  (thiacloprid), respectively. Therefore the imidacloprid residues in five samples facing the chance for exceeding EU MRL from trade respect. However, the Chinese MRLs in tea were  $10 \text{ mg kg}^{-1}$  (thiamethoxam) and  $0.5 \text{ mg kg}^{-1}$  (imidacloprid), respectively. There was no Chinese MRL for thiacloprid in tea. The maximum allowable residue in tea infusion will be  $200 \mu\text{g L}^{-1}$  (thiamethoxam) and  $9.4 \mu\text{g L}^{-1}$  (imidacloprid). The NEOs residues in all samples will not exceed China MRL. Therefore, the intake risk for NEOs residue in white tea samples were acceptable for consumers.

Table 3 displays a comparison between this method and reported methods for NEOs analyzing. The solvent usage of the single sample was reduced by more than 90%, and the analysis time was shortened by 9 min per sample. In addition, LOQs for NEOs was  $0.05 \mu\text{g L}^{-1}$ , which indicated sensitivity was demonstrated to be comparable with previous study. There were several studies reported hydrophobic DES application on analyzing pesticides in aqueous sample using solid-liquid extraction (Nemati, Tuzen, Farazajdeh, Kaya, & Afshar, 2022), and evaporation-assisted dispersive LLME (Nemati, Tuzen et al., 2022). However, the compositions of DES were toxic to environment and health (for example tetrabutylammonium chloride or tetrabutylammonium bromide). The outstanding features of this method was the usage of green, being easily synthesized, low-cost, phenolic-based non-ionic deep eutectic solvent applying with thymol and DL-menthol, which were widely applied as raw material of toothpaste, perfume, drinks, sweets and medicine.

#### 4. Conclusions

In this work, phenolic-based non-ionic deep eutectic solvent (NIDES) consist of thymol and DL-menthol was raised to achieve the determination of selected NEOs in tea infusion samples. The extraction mechanism was studied in details using molecular dynamics approach, indicating Boltzmann averaged solvation energy of the four different species were negatively correlated with extraction efficiency which might be an ideal index for the selection of NIDES in the future. The proposed method was fully validated as evidenced by the satisfactory linearity, LODs, LOQs, precision and accuracy. This work not only provides an analytical method for NEOs with advantages of simple, rapid, green, hydrophobic for easy separation from water sample, but also from theoretical aspect, it provides suggestion on future NIDES experiment design.

#### CRedit authorship contribution statement

**Huiyu Zhao:** Writing – original draft, Investigation, Methodology, Validation. **Ze Wang:** Investigation, Validation. **Cong Zhang:** Investigation, Methodology. **Shanshan Di:** Visualization, Software. **Peipei Qi:** Investigation, Writing – review & editing. **Zhiwei Wang:** Investigation, Writing – review & editing. **Zhenzhen Liu:** Investigation. **Hao Xu:** Writing – review & editing. **Jiao Wang:** Investigation. **Xinquan Wang:** Writing – review & editing, Investigation, Methodology, Funding acquisition.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

The data that has been used is confidential.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2023.135737>.

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