Microchemical Journal 196 (2024) 109675

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Natural deep eutectic solvents as sustainable alternative for the Ultrasound-Assisted extraction of triazines from agricultural soils

Esther Turiel *, Myriam Díaz-Álvarez, Antonio Martín-Esteban

Departamento de Medio Ambiente y Agronomía, INIA-CSIC, Carretera de A Coruña km 7.5, 28040 Madrid, Spain

ARTICLE INFO

Keywords:
Natural deep eutectic solvents
Ultrasound-assisted extraction
Sustainable solvents
Triazines
Soil samples

ABSTRACT

Natural deep eutectic solvents (NADES) have gained much attention as a viable and sustainable alternative to traditional organic solvents in multiple areas of analytical chemistry, including extraction of contaminants from samples of environmental concern. In this work, a total of 68 potential NADES have been assayed and further evaluated as sustainable solvents in the development of an ultrasound (US)-assisted extraction method for triazinic herbicides from agricultural soil samples and final determination by HPLC-UV. Choline chloride (ChCl) was used as hydrogen bond acceptor (HBA), and different carboxylic acids, alcohols and amines were tested as hydrogen bond donors (HBDs) in different molar ratios in order to find the optimum combination able to form appropriated NADES for the extraction of triazines. Among the different ChCl:carboxylic acids mixtures tested, those consisting of ChCl:formic acid and ChCl:acetic acid, both in a molar ratio 1:2, presented the better physicochemical properties (pH, stability at room temperature, water miscibility, etc.). Concerning amines, NADES could not be obtained at any of the combination assayed whereas, among the alcohols tested, 2,3-butanediol was found to be the most appropriated for NADES formation. A three-level factorial design was then used to further evaluate the effect of time and temperature on the ability of these selected optimum NADES for the US-assisted extraction of triazines from agricultural soil samples. Under optimal conditions, the developed US-assisted extraction method provided quantitative recoveries (from 87 to 104 %) with good reproducibility (RSDs lower than 12 %) and limits of detection (LODs) lower than 0.05 μg g^{-1} for all target triazines.

1. Introduction

Increased environmental awareness is driving the scientific community to consider environmental protection in the design of methods and procedures. In 1998, Anastas and Warner introduced the concept of "Green Chemistry" to prevent threats to human health and the environment in all types of chemical processes [1]. Later, Green Analytical Chemistry (GAC) emerged as one of the most active areas of green chemistry, focused on the design and development of new analytical methods that correlate analytical needs with environmental problems [2]. Since then, several approaches were used to meet the objectives of GAC such as miniaturization, use of alternative solvents or solvent-free extraction techniques, among others [3]. However, it was not until 2013 that Gałuszka *et al.* [4] proposed the "12 Principles of Green Analytical Chemistry" as an essential set of guidelines for greening analytical laboratories. The first principle recommended avoiding sample preparation and using direct analytical techniques. Although analytical instrumentation has drastically improved sensitivity and selectivity, the direct sample analysis is not always possible. In this regard, sample preparation remains one of the most important step with goals including the use of smaller initial sample sizes, improved extraction selectivity, increased automation, waste reduction, and minimization or, if possible, elimination of organic solvents [5]. To assist in the systematic development of greener sample preparation methods, López-Lorente *et al.* [6] introduced "The Ten Principles of Green Sample Preparation (GSP)". These include using safer solvents/reagents and materials that are renewable, recycled, and reusable; minimizing waste generation and energy requirements; and enabling high sample throughput, miniaturization,

Abbreviations: A, Atrazine; ChCl, Choline chloride; CPP, Cloud point preconcentration; DEA, Desethylatrazine; DES, Deep eutectic solvent; DIA, Desisopropylatrazine; DMAME, Dynamic microwave-assisted micelle extraction; GAC, Green analytical chemistry; GSP, Green sample preparation; HBA, Hydrogen bond acceptor; HBD, Hydrogen bond donor; HCOOH, Formic acid; IL, Ionic liquid; MAE, Microwave-assisted extraction; NADES, Natural deep eutectic solvents; PLE, Pressurized liquid extraction; PPZ, Propazine; SIM, Simazine; TER, Terbuthylazine; UAE, Ultrasound-assisted extraction; US, Ultrasound.

* Corresponding author.
E-mail addresses: turiel@inia.csic.es (E. Turiel), mdalvarez@inia.csic.es (M. Díaz-Álvarez), amartin@inia.csic.es (A. Martín-Esteban).

https://doi.org/10.1016/j.microc.2023.109675
Received 5 September 2023; Received in revised form 13 November 2023; Accepted 16 November 2023
Available online 19 November 2023

procedural simplification/automation, and operator safety. Accordingly, the development and use of new solvents to replace the traditional organic solvents is of particular importance for the design of new sustainable analytical methods [7,8].

Over the past two decades, new environmentally friendly solvents - the so-called "green" solvents - have been developed and introduced. Ionic liquids (ILs), organic salts in the liquid state at ambient conditions (consisting of an organic cation and an organic or inorganic anion were initially considered as "green" solvents. However, despite their promising technical performance, recent studies have shown that several ILs families are eco(cyto)toxic, rather resistant to biodegradation and capable of producing harmful secondary metabolites [9].

Alternatively, deep eutectic solvents (DESs) are considered as a new class of environmentally friendly solvents and have attracted much attention due to their favorable physical and thermodynamic properties [10]. DESs were first introduced by Abbott *et al.*[11] and can be described as mixtures of two or more components, a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), linked by hydrogen bond interactions to form a mixture with a melting point much lower than the individual components. Depending upon the components of the mixtures, DES are classified in four different groups [12]. In this regard, mixtures classified as Type III eutectic solvent, usually employ choline chloride (ChCl) as hydrogen bond acceptor and urea, glycerol, ethylene glycol or malonic acid are typically used as HBDs among others [13]. Because of their biodegradability, relatively low cost and availability, ChCl-based DES have been used for a variety of applications, including solubilizing, electrochemistry and purification procedures [14]. Besides, when DES are prepared with compounds of natural origin such as carboxylic acids, amino acids and sugars, they are called Natural Deep Eutectic Solvents (NADES). NADES have interesting properties for use in extraction processes, such as a very high solubility of both non-polar and polar compounds, an adjustable viscosity, and their inner sustainability among others. NADES are compliant with green chemistry principles and are becoming increasingly popular for the extraction of active natural compounds from plants, foods and other natural matrices [15,16].

In recent years, they have also been successfully applied for the extraction of contaminants such as residual organic solvents [17], benzophenone-type UV filters [18], anti-inflammatory drugs [19], phthalic acid esters [20,21], sulfonamides [22–24], and parabens [25] from environmental water samples, beverages, foods and pharmaceuticals of personal care products. Besides, NADES have been used for the analysis of pesticides in environmental waters [26–28], but the application of NADES for the extraction of triazines in environmental samples is a recent area of research [29–31].

Triazines are a class of pesticides that belong to the family of herbicides. They are the most widely used as pre- and post-emergent herbicides for weed control in food crops. Despite their important role in weed control, triazines have been banned from production and use in the European Union and several developed countries. However, they are still used in most parts of the world [32]. As a result, their residues can be found in the soil, they can also get into the water through runoff, and they can accumulate in sediments. Triazines are considered hazardous compounds with high environmental persistence, stability and toxicity. Thus, they have been widely analyzed in the aquatic environment. However, there is a need to monitor them in topsoil, where less attention has been paid to the presence of parent compounds and their transformation products [33].

In view of this comments, the aim of this work was to prepare a ChCl-based NADES to be used as extractant solvent in an ultrasound US-assisted extraction method for triazinic herbicides in soil samples. A total of 68 NADES using ChCl as HBA and various natural compounds (carboxylic acids, alcohols and amines) as HBDs were prepared in different molar ratios. Three NADES were selected considering their stability, easy and reliable handling of micropipettes, and compatibility with HPLC. Then, the extraction time and temperature of the US-assisted extraction method was optimized for the three selected NADES and applied for the extraction of agricultural soil samples. Finally, the greenness of the sample preparation method was assessed with the metric tool AGREEprep [34] and compared with other published methods.

2. Experimental

2.1. Chemicals and materials

Desethylatrazine (DEA), desisopropylatrazine (DIA), simazine (SIM), atrazine (ATR), propazine (PPZ), terbutylazine (TER), choline chloride (ChCl), 1,2-butanediol, 2,3-butanediol trimethylamine and 2-butylamine were purchased from Sigma-Aldrich (Madrid, Spain). Panreac (Barcelona, Spain) supplied formic acid and acetic acid. Acetonitrile (ACN) and methanol (MeOH) were obtained from Scharlab (Barcelona, Spain). Purified water was obtained from a Millipore (Madrid, Spain) purification system. All other chemicals were of analytical grade and used as received. Stock standard solutions for each triazine (1 g/L) were prepared in acetonitrile and stored in the dark at −20 °C. Stock solutions were diluted in the appropriate solvents to the required concentrations.

2.2. Preparation of NADES

NADES were prepared by mixing appropriate amounts of ChCl (acting as HBA) and different natural carboxylic acids, amines and alcohols acting as HBDs in screw cap 8 mL glass tubes. For each HBD group, four HBA:HBD molar ratios were assayed (2:1, 1:1, 1:2 and 1:4). Subsequently, tubes were tightly closed and then introduced into an oven at a temperature of 60 °C, equipped with a low-profile roller (Barloworld Scientific, Staffordshire, UK) that provided a rotation of 24 rpm, for a minimum time of 30 min. Once formed, NADES were stored at room temperature until use.

Optimum NADES were characterized by Fourier-transform infrared (FT-IR) spectroscopy on a Jasco FTIR-460 Plus spectrophotometer. All spectra were recorded by attenuated total reflectance between 4000 and 400 cm^{-1}, with the sample in the solid state without other treatment.

2.3. Ultrasound-assisted extraction of triazines from soil samples

Soil samples were collected from an experimental plot located in the Madrid region (La Canaleja, Alcalá de Henares). Soil samples were sieved (2 mm) and stored at room temperature until analysis. Soil characterization data are presented in Table S1. Spiked samples were prepared by adding 0.2 mL of a mixture of triazines in acetonitrile to 1 g of soil placed in 6 mL empty solid-phase extraction glass cartridges dotted with PTFE filters (Supelco) and were closed using one-way stopcocks. Spiked samples were stored in dark conditions overnight at room temperature to allow solvent evaporation and sample equilibration.

For the extraction of triazines, 1 mL of NADES was added to soils and the cartridges were closed using glass caps. Subsequently, they were placed upright in a tube rack and immersed in the ultrasonic water bath (Bransonic 3800, Emmerson I.A., Alcobendas Madrid), keeping water level above the extraction solvent level inside the cartridges. After performing extraction at the corresponding times and temperatures, the cartridges were placed in the vacuum manifold and extracts were conveniently collected. A volume of 1 mL of purified water was then added and collected in the same vials. Finally, the aqueous NADES extracts were diluted up to 4 mL with purified water before chromatographic analysis. The experimental setup allowed the simultaneous extraction of 3 samples.

2.4. HPLC-DAD analysis

All chromatographic measurements were performed on an Agilent Technologies 1200 series HPLC instrument equipped with a quaternary

high-pressure pump, vacuum degasser, autosampler and diode array detector. Prior to analysis, NADES-based sample extracts were diluted up to 4 mL with purified water. Target analytes were separated by gradient elution from 80 % water (A) and 20 % acetonitrile (B) to 40 % A and 60 % B in 25 min using a sample volume of 100 μL injected into a Kromasil 100 C18 5.0 μm (150 x 4.6 mm i.d.) analytical column. Triazines were simultaneously monitored at 220 and 230 nm. Quantification was performed by external calibration using peak area measurements.

3. Results and discussion

3.1. Preparation of ChCl based-NADES

As mentioned in the Introduction, the use of ChCl as HBA allows the obtainment of mainly polar NADES depending on the type of HBD, which theoretically would be appropriated for the extraction of selected medium to high polar triazines. In the present work, three groups of natural chemical compounds were evaluated as HBD, namely carboxylic acids, alcohols and amines. For the three groups studied, different ChCl: HBD molar ratios were assayed from 2:1 to 1:4. Those mixtures able to lead NADES formation in less than 240 min at 60 °C were selected and some physical and chemical characteristics as well as the feasibility for micropipette retrieval were studied.

3.1.1. Choline chloride:carboxylic acids NADES

Table 1 shows the different combinations tested and summarizes the physico-chemical properties obtained using the selected carboxylic acids as HBD in the preparation of ChCl based-NADES, arranged according to the length of the alkyl chain (number of carbons) of the carboxylic acids and the different molar ratios tested. As mentioned in Experimental, the different ChCl:HBD mixtures were transferred to centrifuge tubes and introduced in an oven at 60 °C equipped with a roller that allows rotation at 24 rpm. All tubes were maintained a minimum of 30 min incubation time, and up to 240 min for those mixtures showing no NADES formation at shorter incubation times.

As it can be observed, only using formic acid as HBD, NADES were obtained at 60 °C after 30 min regardless of the ChCl:HCOOH molar ratio assayed. Besides, it was observed that the longer the alkyl chain of the carboxylic acids tested, the larger amount of carboxylic acid was required for NADES formation. These results correlates with the diminishment of the acidic strength of the carboxylic acid used as HBD and thus with the ability of forming strong hydrogen bonds with ChCl. Such ability decreases as the pKa of the carboxylic acid increases and accordingly, mixtures using hexanoic acid did lead to NADES formation only at 1:4 M ratio. Also, it has to be mentioned that in some cases, and also related with the length of the alkyl chain of the carboxylic acid used, obtained NADES at 60 °C did precipitate after reaching room temperature, thus preventing its subsequent use.

Another important aspect that has to be taken into account is the possibility of the obtained NADES to be accurately handled by micropipettes. Accordingly, only NADES for which micropipette use is labelled as "easy" or "medium/easy" in Table 1 allowed taking NADES microvolumes in an accurate manner.

Finally, the miscibility of NADES with water is also an important parameter to be taken into account from a practical point of view. It is clear that the usually high viscosity of NADES prevents the direct injection of NADES extracts in the chromatographic system making necessary their previous dilution with water. In our study, all NADES successfully obtained and stable at room temperature (NADES 1,3,4,7, 8, 12 and 16) showed good miscibility with water up to 10 fold.

Taking all this comments into account, it was concluded that formic and acetic acids were the most appropriated carboxylic acids to form ChCl based-NADES. Among the different tested mixtures, the molar ratio 1:2 was selected for both acids as optimum for further experiments.

3.1.2. Choline chloride:Alcohols NADES

Table 2 summarizes the physico-chemical properties of the different mixtures tested for the preparation of ChCl-based NADES using several natural alcohols (mono- and diols) as HBD. As it can be seen, and similarly as the characteristic observed using natural carboxylic acids, the increase in the length of the alkyl chain of the alcohols tested negatively affects their ability to act as HBD in NADES. Among the mono-alcohols tested, only NADES 28 (ChCl:ethanol, molar ratio 1:4) was successfully obtained, however it precipitated after 8 h at room temperature, thus preventing its further use.

Comparing the results obtained for 2-propanol and 1,3-propanol, it is evident that the presence of an additional hydroxyl group in the alkyl

Table 1
Physico-chemical properties of mixtures of ChCl and selected carboxylic acids as HBD after 30 min at 60 °C.

Designation	ChCl:Acid	C number	Molar ratio	NADES formation	Aspect at room temperature	pH[a]	Use of micropipettes
NADES-1	Choline chloride:Formic acid:	1	1:1	YES	Homogeneous liquid	0.5–1	Medium
NADES-2	Choline chloride:Formic acid	1	2:1	YES	Precipitated	0.5–1	——
NADES-3	Choline chloride:Formic acid	1	1:2	YES	Homogeneous liquid	0.5–1	Easy
NADES-4	Choline chloride:Formic acid	1	1:4	YES	Homogeneous liquid	0.5–1	Easy
NADES-5	Choline chloride:Acetic acid:	2	1:1	NO	———	———	———
NADES-6	Choline chloride:Acetic acid	2	2:1	NO	———	——	———
NADES-7	Choline chloride:Acetic acid	2	1:2	YES	Homogeneous liquid	1–1.5	Medium/easy
NADES-8	Choline chloride:Acetic acid	2	1:4	YES	Homogeneous liquid	1–1.5	Medium/easy
NADES-9	Choline chloride:Propanoic acid	3	1:1	NO	———	———	———
NADES-10	Choline chloride:Propanoic acid	3	2:1	NO	———	——	———
NADES-11	Choline chloride:Propanoic acid	3	1:2	YES	Precipitated	Not measurable	———
NADES-12	Choline chloride:Propanoic acid	3	1:4	YES	Homogeneous liquid	2.0–2.5	Medium
NADES-13	Choline chloride:Butyiric acid	4	1:1	NO	———	———	———
NADES-14	Choline chloride.Butyric acid	4	2:1	NO	———	——	———
NADES-15	Choline chloride:Butyric acid	4	1:2	YES	Precipitated	Not measurable	———
NADES-16	Choline chloride:Butyric acid	4	1:4	YES	Homogeneous liquid	2.5–3.0	Difficult
NADES-17	Choline chloride:Valeric acid	5	1:1	NO	———	———	———
NADES-18	Choline chloride.Valeric acid	5	2:1	NO	———	——	———
NADES-19	Choline chloride:Valeric acid	5	1:2	YES	Precipitated	Not measurable	———
NADES-20	Choline chloride:Valeric acid	5	1:4	YES	Precipitated	Not measurable	———
NADES-21	Choline chloride:Hexanoic acid	6	1:1	NO	———	———	———
NADES-22	Choline chloride.Hexanoic acid	6	2:1	NO	———	——	———
NADES-23	Choline chloride:Hexanoic acid	6	1:2	NO	Precipitated	Not measurable	————
NADES-24	Choline chloride:Hexanoic acid	6	1:4	YES	Precipitated	Not measurable	————

MISCIBILITY WITH WATER: NADES 1, 3, 4, 7, 8, 12 and 16 are miscible up to a ratio 1/10 NADES/Water.
[a] , Measured with pH test strips; room temperature.

Table 2
Physico-chemical properties of mixtures of ChCl and selected alcohols as HBD after 30 min at 60 °C.

Designation	CHCL:Alcohol	C number	Molar ratio	NADES formation	Aspect at room temperature	pH[a]	Use of micropipettes
NADES-25	Choline chloride:Ethanol	2	1:1	NO	Precipitated	———	———
NADES-26	Choline chloride:Ethanol	2	2:1	NO	Precipitated	———	——
NADES-27	Choline chloride:Ethanol	2	1:2	NO	Precipitated	———	———
NADES-28	Choline chloride:Ethanol	2	1:4	YES	Precipitated	———	———
NADES-29	Choline chloride:2-propanol	3	1:1	NO	Precipitated	———	———
NADES-30	Choline chloride:2-propanol	3	2:1	NO	Precipitated	———	———
NADES-31	Choline chloride:2-propanol	3	1:2	NO	Precipitated	———	———
NADES-32	Choline chloride:2-propanol	3	1:4	NO	Precipitated	———	———
NADES-33	Choline chloride:1-Butanol	4	1:1	NO	Precipitated	———	———
NADES-34	Choline chloride:1-Butanol	4	2:1	NO	Precipitated	———	———
NADES-35	Choline chloride:1-Butanol	4	1:2	NO	Precipitated	———	———
NADES-36	Choline chloride:1-Butanol	4	1:4	NO	Precipitated	———	———
NADES-37	Choline chloride:1-Pentanol	5	1:1	NO	Precipitated	———	———
NADES-38	Choline chloride:1-Pentanol	5	2:1	NO	Precipitated	———	———
NADES-39	Choline chloride:1-Pentanol	5	1:2	NO	Precipitated	———	———
NADES-40	Choline chloride:1-Pentanol	5	1:4	NO	Precipitated	———	———
NADES-41	Choline chloride:1-Hexanol	6	1:1	NO	Precipitated	———	———
NADES-42	Choline chloride:1-Hexanol	6	2:1	NO	Precipitated	———	———
NADES-43	Choline chloride:1-Hexanol	6	1:2	NO	Precipitated	———	———
NADES-44	Choline chloride:1-Hexanol	6	1:4	NO	Precipitated	———	———
NADES-45	Choline chloride:1,3-Propanediol	3	1:1	NO	Precipitated	———	———
NADES-46	Choline chloride:1,3-Propanediol	3	2:1	NO	Precipitated	———	———
NADES-47	Choline chloride:1,3-Propanediol	3	1:2	YES	Homogeneous liquid	5.0	Easy
NADES-48	Choline chloride:1,3-Propanediol	3	1:4	YES	Homogeneous liquid	5.0–5.5	Easy
NADES-49	Choline chloride:1,3-Butanediol	4	1:1	NO	Precipitated	———	———
NADES-50	Choline chloride:1,3-Butanediol	4	2:1	NO	Precipitated	———	———
NADES-51	Choline chloride:1,3-Butanediol	4	1:2	YES	Homogeneous liquid	5.5	Medium
NADES-52	Choline chloride:1,3-Butanediol	4	1:4	YES	Homogeneous liquid	4.5	Easy/Medium
NADES-53	Choline chloride:2,3-Butanediol	4	2:1	NO	Precipitated	———	———
NADES-54	Choline chloride:2,3-Butanediol	4	1:1	NO	Precipitated	———	———
NADES-55	Choline chloride:2,3-Butanediol	4	1:2	YES	Homogeneous liquid	4.5	Medium
NADES-56	Choline chloride:2,3-Butanediol	4	1:4	YES	Homogeneous liquid	4.5	Easy/Medium

MISCIBILITY WITH WATER: NADES 47, 48, 51, 52, 55 and 56 are miscible up to a ratio 1/10 NADES/Water.
[a] , Measured with pH test strips; room temperature.

chain, has a very positive effect in terms of NADES formation. As it can be seen in Table 2, using 1,3-propanediol as HBD allows NADES formation at 1:2 ChCl:1,3-propanediol molar ratio, whereas NADES formation did not occur when 2-propanol was used even at 1:4 M ratios. The same effect can be observed by comparing the results obtained for butanol and butanediol isomers (1,3- and 2,3-butanediol). The use of both butanediol isomers allows the obtainment of the corresponding NADES both at 1:2 and 1:4 M ratios, whereas it does not occur when butanol was used even increasing reactions time up to 240 min.

Concerning handling with micropipettes, NADES obtained using 1,3-propanediol (NADES 47 and 48) and those prepared using 1,3- and 2,3-butanediol at 1:4 M ratio (NADES 52 and 56) were accurately handled. Besides, all of them resulted miscible with pure water up to a 1:10 v/v ratio. However, blank injections of diluted 1,3-propanediol and 1,3-butanediol NADES led to the obtainment of dirty chromatograms (high background noise and large amount of unknown interference peaks) and thus they were discarded for further studies. On the contrary, the injection of NADES 52, based on 2,3-butanodiol, led to clean enough chromatograms and thus it was selected for further experiments.

3.1.3. Choline chloride:Amines NADES

Triethylamine and 2-butylamine were also evaluated as HBDs to form ChCl based NADES. However, none of them succeeded in forming NADES in any of the ratios tested (from 2:1 to 1:4), probably due to the weaker hydrogen bonds of ChCl-amines compared to those formed when alcohols or carboxylic acids are used as HBDs. Finally, glycine, which presents both hydroxyl and amine groups in its structure, was tested but NADES formation was not achieved either.

3.2. Characterisation of optimum NADES by FT-IR spectroscopy

FT-IR spectroscopy was used for the characterization of optimum NADES, namely NADES 3, 7 and 56, and their individual components (choline chloride, formic acid, acetic acid and 2,3-butanediol), and their corresponding spectra are shown in Figs. S1-S3. Regarding the infrared spectra of NADES 3 (Fig. S1), an intense peak is observed at 1708 cm^{-1} corresponding to C = O stretching, which is shifted from the corresponding band at 1684 cm^{-1} observed in the infrared spectra of formic acid, indicating that hydrogen bonds are present in that area during NADES formation. Besides, the wide band from ~3400 to ~2500 cm^{-1} corresponds to the stretching of the O–H bond, which is characteristic of carboxylic acid dimers or the existence of hydrogen bonding to carboxylic acid molecules, suggesting again the interaction by hydrogen bonding between formic acid and ChCl. In addition, the band at 3214 cm^{-1}, corresponding to O-H vibration in the ChCl spectra, becomes imperceptible in the spectrum of NADES 3, thus indicating the formation of new hydrogen bonds. Similar conclusions about the formation of NADES 7 can be derived according to the spectra shown in Fig. S2. As can be seen, the C = O stretching band present in acetic acid spectra at 1690 cm^{-1} is shifted to 1711 cm^{-1}, and the O-H vibration band at 3214 cm^{-1}, which was present in the ChCl spectra, disappears upon NADES formation.

Finally, Fig. S3 shows the spectra of NADES 56 compared with those of ChCl and 2,3-butanediol. In this case, apart from the disappearance of the O-H vibration band at 3214 cm^{-1} present in the ChCl spectra, only a slight shift of the O-H vibration typical of diols from 3358 cm^{-1} to 3308 cm^{-1} was observed, indicating the formation of new hydrogen bonds after NADES 56 formation. It is important to point out that previous works have also shown similar variations in the spectra obtained during NADES formation compared to the spectra of the independent components [35,36].

3.3. Ultrasound-assisted extraction of triazines from soil using NADES

According to the results obtained in the above section, the NADES selected as optimum were NADES 3, NADES 7, and NADES 56. Selected NADES were further evaluated as alternative sustainable solvents for the extraction of triazines in soil samples using an ultrasound-assisted extraction method in small columns as shown in Fig. 1 and following the experimental setup presented in Table S2.

Soil amounts were fixed in 1 g, NADES volume in 1 mL, and a three-level factorial design was then used to further evaluate and optimize the time and temperature for the ultrasound-assisted extraction of triazines by the different selected NADES. Experimental design and data analysis were performed using the statistical package Statgraphics Centurion XVII, release 17.2.00 (The Plains, Virginia, USA), and Table S2 shows the 9 randomised experiments performed, which were run in triplicate for each selected NADES. Figs. S4–S6 show the response surface charts generated from the experimental design on the effect of extraction time (min) and temperature (°C) on the recovery (%) of spiked samples with triazines at 0.5 μg g^{-1} concentration level. For an easy visualization and interpretation of the obtained results, Figs. 2–4 shows the recoveries obtained under the different experimental conditions (extraction time and temperature) of each target analyte using the three optimum selected NADES.

According to the results depicted in Fig. 2 using NADES 3 (ChCl: formic acid, molar ratio 1:2) as extracting solvent, it seems evident that increasing temperature resulted unfavourable for the extraction of the selected triazines, with a significant reduction of the obtained recoveries at 43 °C and more so at 60 °C compared to those obtained at 25 °C. It is well-known that viscosity decreases when temperature increases and thus theoretically solvent would easily reach pores of samples favouring the extraction of target analytes. However, it has been reported that an increase of temperature leads to a reduction of the polarity of deep eutectic solvents [37]. In this regard and in spite of the reduction of the viscosity, the lower polarity of NADES 3 at high temperatures results unfavourable to the extraction of the selected triazines. Regarding extraction time, at 25 °C there is an initial increase in recoveries at 17.5 min followed by a decrease in the recoveries at 30 min. This result suggests that although the temperature of the ultrasonic bath can be easily controlled, local increments of temperature inside the extraction cartridges may occur at long extraction times, resulting in the aforementioned change in polarity of NADES, which negatively affects the extraction of target analytes. The effect of extraction time is not so significant at higher temperatures although, in general, it can be observed that long extraction times did not favour the extraction of triazines using NADES 3.

The results obtained using NADES 7 (ChCl:acetic acid, molar ratio 1:2) are depicted in Fig. 3. The viscosity values that can be found in the literature for NADES 3 and NADES 7 are 18.00 and 39.00 mPa.s, respectively [35]. According to these values, recoveries obtained after 5 min extraction at 25 °C using NADES 7 were lower than those achieved with NADES 3, although they can easily be improved by increasing extraction time up to 30 min. Concerning the extraction temperature, working at 43 °C generally provides better recoveries than working at 25 °C, likely due to the effect of the reduction in viscosity with the increase in temperature explained above. However, it seems that at 60 °C, the polarity of NADES 7 would also be reduced, negatively affecting the recoveries at 5 min, which were even lower than those obtained at 25 °C.

Finally, the results obtained for the extraction of triazines using NADES 56 (ChCl: 2,3-butanediol, 1:4) are shown in Fig. 4. As can be observed, increasing temperature produced a positive effect on the extraction of selected triazines in this case, in such a way that quantitative recoveries for all of them were achieved in just 5 min at 60 °C. To the best of our knowledge, viscosity of NADES 56 has not been reported. However, the viscosity of a NADES formed by ChCl and 1,3-butanediol in a 1:3 molar ratio was reported to be 88 mPa.s by Abbott et al. [38]. Accordingly, it can be assumed that viscosity of NADES 56 would be similar to this value and thus higher than that of NADES 3 and 7. However, it seems that despite this higher viscosity, NADES 56 presents a much more suitable polarity for the extraction of triazines than NADES 3 and 7, which compensates for the negative effect of the higher viscosity. As a result, higher recoveries were obtained for all analytes regardless of the extraction temperature. In fact, the increase in temperature with NADES 56 was not detrimental, but slightly improved the recoveries obtained for all the triazines. Regarding the extraction time, the influence of this parameter was most appreciated at 25 °C, allowing quantitative recoveries to be obtained for all the triazines in 30 min.

Apart from these theoretical discussions, and according to all the results obtained, the following conditions for the simultaneous extraction of the seven triazines for each NADES were selected as optimum for further experiments: 17.5 min at 25 °C for NADES 3, 30 min at 25 °C for NADES 7 and 5 min 60 °C for NADES 56.

3.4. Compatibility of selected NADES used for the extraction of triazines with final HPLC-DAD analysis

Fig. 5 shows a comparison of the UV-chromatograms at 220 nm obtained after injection of standard solutions of triazines (0.5 μg g^{-1}) in 1 mL of NADES 3 (Fig. 5a), NADES 7 (Fig. 5b), and NADES 56 (Fig. 5c) diluted up to 4 mL with purified water. As can be seen, several interferences are observed in the obtained chromatograms regardless of the NADES tested, that could complicate or even prevent the final determination of the selected triazines. When diluted NADES 3 and 7 were injected, a big hump appeared at the beginning of the chromatogram as a consequence of their strong absorbance at 220 nm. Although monitoring at 230 nm improved in a certain extent the chromatogram cleanliness (chromatograms not shown), DIA and DEA still remained strongly interfered. In fact, the match factors obtained (provided by the Spectra comparison tool associated with the HPLC-DAD equipment used

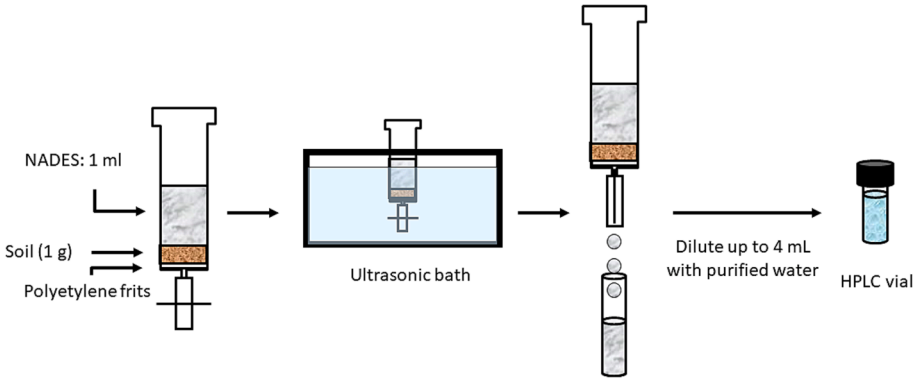

Fig. 1. Ultrasound-assisted extraction scheme.

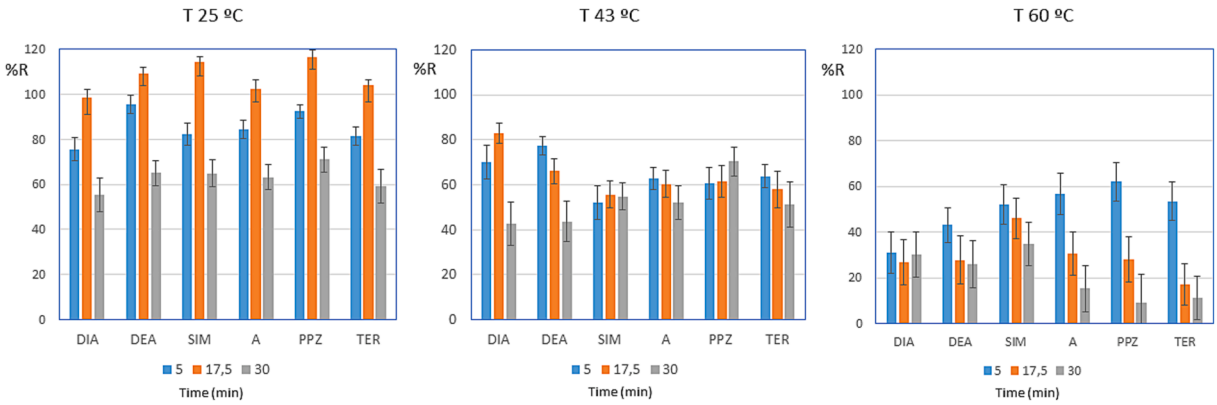

Fig. 2. Effect of extraction time and temperature on the obtained recoveries (R%) of selected triazines by ultrasound-assisted extraction using NADES 3.

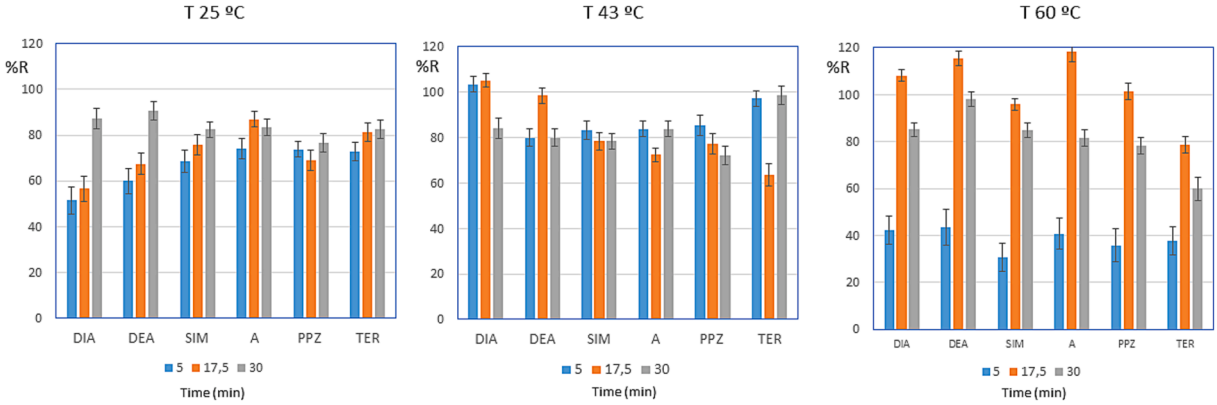

Fig. 3. Effect of extraction time and temperature on the obtained recoveries (R%) of selected triazines by ultrasound-assisted extraction using NADES 7.

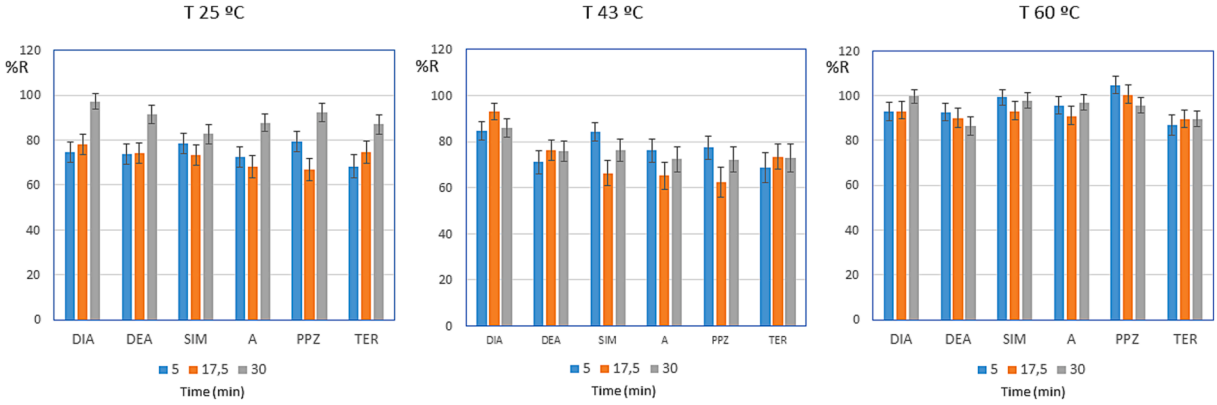

Fig. 4. Effect of extraction time and temperature on the obtained recoveries (R%) of selected triazines by ultrasound-assisted extraction using NADES 56.

in the present work) by comparing the spectra obtained for these analytes with those spectra recorded in purified water were very low, thus preventing the assignment of the corresponding peaks to DIA and DEA. In the case of NADES 56, although chromatograms obtained both at 220 and 230 were not free of interferences, the chromatogram baseline was clearly improved, allowing to achieve match factors over 950 for all the triazines studied. Consequently, NADES 56 was finally selected as optimum sustainable solvent for the US-assisted extraction of triazines from soil samples.

3.5. Analytical performance of the US assisted extraction method using NADES 56

Table 3 summarizes all the analytical parameters for the developed US assisted extraction method for triazines in soil using NADES 56. The linearity of the method was tested by using soil samples spiked with the selected triazines in the range 0.025 to 2.5 μg g^{-1}. The corresponding calibration curves for each analyte were linear in all cases in the concentration range studied and the correlation coefficients obtained by regression analysis ranged from 0.992 to 0.998 depending upon the analyte tested. The limits of detection were calculated as three times the signal over the background noise obtained in the analysis of a blank soil sample at the retention times of the corresponding analytes and the

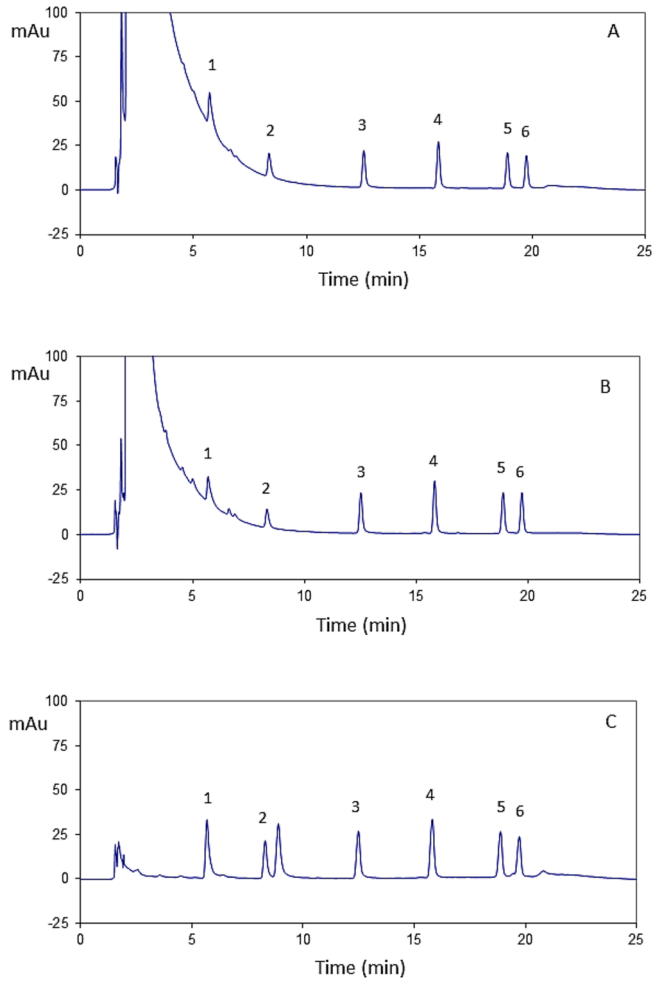

Fig. 5. UV–V is chromatograms at 220 nm of a 0.5 μg g^{-1} standard solution of triazines in NADES diluted up to 4 mL with purified water. (A) NADES 3 (B) NADES 7 (C) NADES 56. Peak numbers: (1) DIA; (2) DEA; (3) SIM; (4) ATZ; (5) PPZ; (6) TER.

Table 3
Summary of analytical parameters for the developed US assisted extraction method for triazines in soil using NADES 56 (5 min, 60 °C).

	R^2	Recovery (%) (0.1 μg g^{-1})	RSD (%)	Recovery (%) (2 μg g^{-1})	RSD (%)	LOD (μg/g)	LOQ (μg/g)
DIA	0.992	93.0	12.0	99.7	10.5	0.045	0.15
DEA	0.994	94.5	11.2	88.4	9.6	0.032	0.11
SIM	0.993	99.2	9.9	97.9	8.9	0.043	0.14
A	0.998	96.5	7.3	95.1	5.2	0.025	0.08
PPZ	0.996	104.7	6.8	95.2	4.3	0.042	0.14
TER	0.996	87	10.2	89.5	10.1	0.050	0.17

quantification limits, both shown in Table 3, were determined using a value of 10 times the background noise. The values obtained were in all cases low enough to allow the determination and quantification of all the selected triazines at realistic concentration levels in soil samples [39].

Finally, a recovery study using soil samples, previously analysed to confirm the absence of the selected triazines, was used to evaluate the accuracy and precision of the developed method. The study was carried out at two different spiking levels (0.1 and 2.0 μg g^{-1}), close to the extremes of the previously established operating range (from LOQ to 2.5 μg g^{-1}). Five replicates were analysed for each concentration level. Fig. 6 shows an example of the chromatograms obtained for each

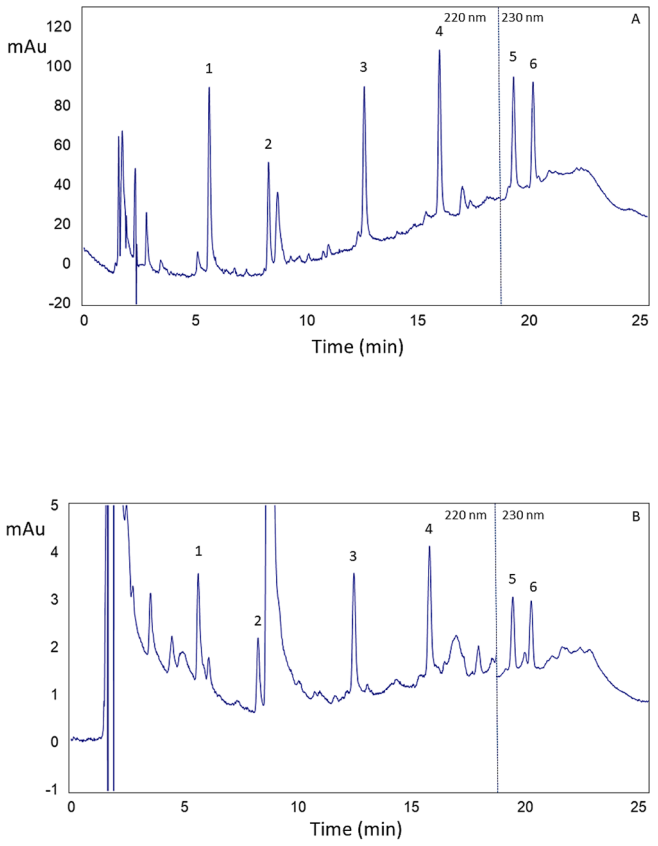

Fig. 6. UV–Vis chromatograms at 220 nm/230 nm obtained after extraction of triazines using NADES 56 from spiked soil samples at (A) 2.0 μg. g^{-1} and (B) 0.1 μg. g^{-1} concentration level. Peak numbers: (1) DIA; (2) DEA; (3) SIM; (4) ATZ; (5) PPZ; (6) TER.

concentration and the mean values of the obtained recoveries (R%) with their corresponding relative standard deviations (RSDs) for each analysis are summarised in Table 3. As can be seen, the recoveries were quantitative in all cases and the RSDs obtained were lower than 12 %, confirming the accuracy and precision of the developed method.

3.6. *Greenness assessment of the proposed method*

The analytical performance of the proposed method was compared with other previously reported methods for triazines determination in soils [40–43], and the results are summarized in Table S3. The analytical performance of the proposed method was slightly inferior to previous methods in terms of sensitivity and recoveries, although good enough to allow the quantification of all the selected triazines in soil samples. In addition, in our work the volume of extraction solvent has been significantly reduced and the organic solvents have been completely replaced by a green solvent. Besides, an evaluation of the method in terms of environmental impact and safety was performed using AGREEprep software [30], a metric tool that assesses the sample preparation step. The rating is based on ten criteria related to various environmental aspects, including the selection and use of solvents, materials and reagents, as well as waste generation, energy consumption, sample size and throughput. The result of that evaluation is a pictogram with a summary of the total greenness of the method. Fig. 7 shows the pictograms obtained after the evaluation of the proposed method and the other methods for triazine analysis in soils compared above. This work received the highest score of those compared (0.69) and stands out in 4 impact categories (criterion 2: use safer solvents and reagents; criterion 3: target sustainable, reusable and renewable materials; criterion 4: minimize waste; and criterion 10: ensure safe procedures for the

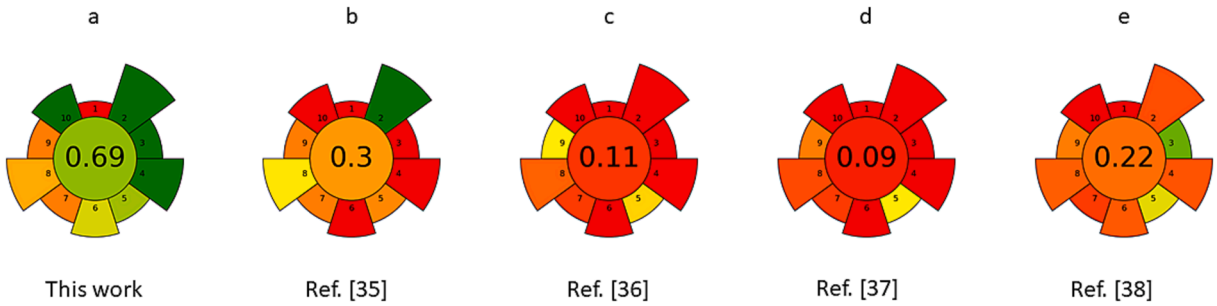

Fig. 7. Pictograms obtained using AGREEprep assessment of procedures for triazines determination in agricultural soils: (a) the proposed method; (b) PLE method [35]; (c) UAE method [36]; (d) MAE method [37]; (e) DMAME-CPP method [38].

operator). In addition, the small sample size and good sample throughput resulted in good scores in criteria 5 and 6. For criterion 8 (minimize energy consumption) the authors decided to consider the heating time of the ultrasonic bath, although it is performed outside the sample preparation step. This energy consumption should not be forgotten as it is relatively high (the final score without this consideration would have been 0.79). Alternatively, the main disadvantage of the proposed method is that the sample preparation is performed "ex situ" (the sample is collected and transported to the laboratory for subsequent preparation). In conclusion, according to the AGREEprep score, the proposed method can be considered significantly greener than the other methods compared.

4. Conclusions

In the present work, 68 different mixtures were tested for the preparation of ChCl-based NADES in combination with natural carboxylic acids, alcohols and amines as HDBs. From this study, valuable insights have been provided related to the influence of the kind and number of functional group present in the HDB as well as their alkyl change length. In this regard, the proper formation of NADES depends of the strength of hydrogen bonding ChCl-HDB and thus the use of carboxylic acid is in general favourable whereas long alkyl chains negatively affects NADES formation. Besides, the use of proper bi-functional HDBs (i.e. diols) results favourable to NADES formation.

Accordingly, three different NADES, using formic acid, acetic acid and 2,3-butanediol were selected as HDB and a three-level factorial design was used to evaluate the effect of time and temperature on the US-assisted extraction of triazines from soil samples. This study not only allowed the optimal experimental conditions to be achieved, but also provided some valuable information on the fate and physicochemical variations of NADES under the common working temperatures used in extraction techniques. In this regard, an increase of the extraction temperature leads to a viscosity reduction, and thus it would favour extraction of target analytes, but in parallel NADES become less polar which might negatively affect the extraction of certain compounds depending upon their physico-chemical properties. Accordingly, the change in both viscosity and polarity of NADES with the temperature has to be taken into account during method development, since both parameters present a significant effect on extraction of target analytes. Nevertheless, the present work allowed the optimisation of extraction conditions for triazines using three different NADES and finally a ChCl-based NADES combined with 2,3-butenodiol was selected due to its compatibility with HPLC-UV analysis.

The final US-assisted extraction developed method using optimum NADES allows the extraction and final determination of triazines from soil samples at realistic concentration levels. Besides, it is important to point out that, under optimum experimental conditions, the extraction was carried out in only 5 min, saving both analysis time and energy consumption, which, together with the use of a sustainable solvent, makes the proposed method a good alternative to other published methods considering the Principles of Green Analytical Chemistry.

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

Data will be made available on request.

Acknowledgements

The Grant PID2021-122327OB-I00 funded by MCIN/AEI/10.13039/501100011033 and by "ERDF A way of making Europe" is gratefully acknowledged. This article is based upon work from the National Thematic Network on Sustainable Sample Treatment (RED2022-134079-T) funded by the Spanish Ministry of Science and Innovation, and the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society. Authors wish thank Mar Albarrán for supplying soil samples.

Author Statement.

Esther Turiel, on behalf of all the authors of the present manuscript, declares that the work described has not been published, that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2023.109675.

References

[1] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998.
[2] P.T. Anastas, Green Chemistry and the role of analytical methodology development, Crit. Rev. Anal. Chem. 29 (1999) 167–175, https://doi.org/10.1080/10408349891199356.
[3] M. Tobiszewski, A. Mechlińska, J. Namieśnik, Green analytical chemistry—theory and practice, Chem. Soc. Rev. 39 (2010) 2869–2878, https://doi.org/10.1039/B926439F.
[4] A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, TrAC -, Trends Anal. Chem. 50 (2013) 78–84, https://doi.org/10.1016/j.trac.2013.04.010.
[5] R.M. Smith, Before the injection - Modern methods of sample preparation for separation techniques, J. Chromatogr. A 1000 (2003) 3–27, https://doi.org/10.1016/S0021-9673(03)00511-9.

[6] Á.I. López-Lorente, F. Pena-Pereira, S. Pedersen-Bjergaard, V.G. Zuin, S.A. Ozkan, E. Psillakis, The Ten Principles of Green Sample Preparation, TrAC Trends Anal. Chem. 148 (2022), 116530, https://doi.org/10.1016/j.trac.2022.116530.
[7] I. Pacheco-Fernández, V. Pino, Green solvents in analytical chemistry, Current Opinion in Green and Sustainable, Chemistry 18 (2019) 42–50, https://doi.org/10.1016/j.cogsc.2018.12.010.
[8] M. Vian, C. Breil, L. Vernes, E. Chaabani, F. Chemat, Green solvents for sample preparation in analytical chemistry, Current Opinion in Green and Sustainable, Chemistry 5 (2017) 44–48, https://doi.org/10.1016/j.cogsc.2017.03.010.
[9] S. Magina, A. Barros-Timmons, S.P.M. Ventura, D.V. Evtuguin, Evaluating the hazardous impact of ionic liquids – Challenges and opportunities, J. Hazard. Mater. 412 (2021), 125215, https://doi.org/10.1016/j.jhazmat.2021.125215.
[10] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep Eutectic Solvents (DESs) and Their Applications, Chem. Rev. 114 (2014) 11060–11082, https://doi.org/10.1021/cr300162p.
[11] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, Chem. Commun. (2003) 70–71, https://doi.org/10.1039/B210714G.
[12] Á. Santana-Mayor, R. Rodríguez-Ramos, A.V. Herrera-Herrera, B. Socas-Rodríguez, M.Á. Rodríguez-Delgado, Deep eutectic solvents, The New Generation of Green Solvents in Analytical Chemistry, TrAC Trends in Analytical Chemistry. 134 (2021), 116108, https://doi.org/10.1016/j.trac.2020.116108.
[13] F. Pradanas-González, G. Álvarez-Rivera, E. Benito-Peña, F. Navarro-Villoslada, A. Cifuentes, M. Herrero, M.C. Moreno-Bondi, Mycotoxin extraction from edible insects with natural deep eutectic solvents: a green alternative to conventional methods, J. Chromatogr. A 1648 (2021), https://doi.org/10.1016/j.chroma.2021.462180.
[14] S.L. Perkins, P. Painter, C.M. Colina, Experimental and Computational Studies of Choline Chloride-Based Deep Eutectic Solvents, J. Chem. Eng. Data. 59 (2014) 3652–3662, https://doi.org/10.1021/je500520h.
[15] K. Owczarek, N. Szczepanska, J. Plotka-Wasylka, M. Rutkowska, O. Shyshchak, M. Bratychak, J. Namiesnik, Natural Deep Eutectic Solvents in Extraction Process, ChChT. 10 (2016) 601–606. https://doi.org/10.23939/chcht10.04si.601.
[16] J. Zuo, S. Geng, Y. Kong, P. Ma, Z. Fan, Y. Zhang, A. Dong, Current Progress in Natural Deep Eutectic Solvents for the Extraction of Active Components from Plants, Crit. Rev. Anal. Chem. 53 (2023) 177–198, https://doi.org/10.1080/10408347.2021.1946659.
[17] M. Wang, S. Fang, X. Liang, Natural deep eutectic solvents as eco-friendly and sustainable dilution medium for the determination of residual organic solvents in pharmaceuticals with static headspace-gas chromatography, J Pharm Biomed Anal. 158 (2018) 262–268, https://doi.org/10.1016/j.jpba.2018.06.002.
[18] D. Ge, Y. Zhang, Y. Dai, S. Yang, Air-assisted dispersive liquid-liquid microextraction based on a new hydrophobic deep eutectic solvent for the preconcentration of benzophenone-type UV filters from aqueous samples, J. Sep. Sci. 41 (2018) 1635–1643, https://doi.org/10.1002/jssc.201701282.
[19] A. Shishov, A. Gerasimov, D. Nechaeva, N. Volodina, E. Bessonova, A. Bulatov, An effervescence-assisted dispersive liquid–liquid microextraction based on deep eutectic solvent decomposition: Determination of ketoprofen and diclofenac in liver, Microchem. J. 156 (2020), 104837, https://doi.org/10.1016/j.microc.2020.104837.
[20] C. Ortega-Zamora, G. Jiménez-Skrzypek, J. González-Sálamo, J. Hernández-Borges, Extraction of phthalic acid esters from soft drinks and infusions by dispersive liquid-liquid microextraction based on the solidification of the floatin g organic drop using a menthol-based natural deep eutectic solvent, J. Chromatogr. A 1646 (2021), 462132, https://doi.org/10.1016/j.chroma.2021.462132.
[21] Á. Santana-Mayor, B. Socas-Rodríguez, R. Rodríguez-Ramos, A.V. Herrera-Herrera, M.Á. Rodríguez-Delgado, Quality assessment of environmental water by a simple and fast non-ionic hydrophobic natural deep eutectic solvent-based extraction procedure combined with liquid chromatography tandem mass spectrometry for the determination of plastic migrants, Anal Bioanal Chem. 413 (2021) 1967–1981, https://doi.org/10.1007/s00216-021-03166-1.
[22] A. Mostafa, H. Shaaban, A.M. Alqarni, M. Alghamdi, S. Alsultan, J. Saleh Al-Saeed, S. Alsaba, A. AlMoslem, Y. Alshehry, R. Ahmad, Vortex-assisted dispersive liquid–liquid microextraction using thymol based natural deep eutectic solvent for trace analysis of sulfonamides in water samples: Assessment of the greenness profile using AGREE metric, GAPI and analytical eco-scale, Microchem. J. 183 (2022), 107976, https://doi.org/10.1016/j.microc.2022.107976.
[23] M. Díaz-Álvarez, A. Martín-Esteban, Preparation and further evaluation of L-menthol-based natural deep eutectic solvents as supported liquid membrane for the hollow fiber liquid-phase microextraction of sulfonamides from environmental waters, Advances in Sample Preparation. 4 (2022), 100047, https://doi.org/10.1016/j.sampre.2022.100047.
[24] H. Shaaban, A. Mostafa, A.M. Alqarni, R. Alsultan, Z.A. shehab, Z. Aljarrash, W. Al-Zawad, S. Al-Kahlah, M. Amir, Dispersive liquid-liquid microextraction utilizing menthol-based deep eutectic solvent for simultaneous determination of sulfonamides residues in powdered milk-based infant formulas, J. Food Compos. Anal. 117 (2023), 105137, https://doi.org/10.1016/j.jfca.2023.105137.
[25] A.M. Alqarni, A. Mostafa, H. Shaaban, M.S. Gomaa, D. Albashrayi, B. Hasheeshi, N. Bakhashwain, A. Aseeri, A. Alqarni, A.A. Alamri, M.A. Alrofaidi, Development and optimization of natural deep eutectic solvent-based dispersive liquid–liquid microextraction coupled with UPLC-UV for simultaneous determination of parabens in personal care products: evaluation of the eco-friendliness level of the developed method, RSC Adv. 13 (2023) 13183–13194, https://doi.org/10.1039/D3RA00769C.
[26] C. Florindo, L.C. Branco, I.M. Marrucho, Development of hydrophobic deep eutectic solvents for extraction of pesticides from aqueous environments, Fluid Phase Equilib. 448 (2017) 135–142, https://doi.org/10.1016/j.fluid.2017.04.002.
[27] H. Sereshti, M. Seraj, S. Soltani, H. Rashidi Nodeh, M. Hossein Shojaee AliAbadi, M. Taghizadeh, Development of a sustainable dispersive liquid–liquid microextraction based on novel hydrophobic and hydrophilic natural deep eutectic solvents for the analysis of multiclass pesticides in water, Microchem. J. 175 (2022), 107226, https://doi.org/10.1016/j.microc.2022.107226.
[28] N. Gissawong, S. Mukdasai, S. Boonchiangma, S. Sansuk, S. Srijaranai, A rapid and simple method for the removal of dyes and organophosphorus pesticides from water and soil samples using deep eutectic solvent embedded sponge, Chemosphere 260 (2020), 127590, https://doi.org/10.1016/j.chemosphere.2020.127590.
[29] T.A. Jouybari, H.A. Jouybari, M. Shamsipur, N. Babajani, A. Kiani, Z. Nematifar, K. Sharafi, M. Moradi, N. Fattahi, Trace determination of triazine herbicides in fruit and vegetables using novel hydrophobic deep eutectic solvent-based dispersive liquid-liquid microextraction followed by high-performance liquid chromatography-ultraviolet, J. Sep. Sci. 45 (2022), https://doi.org/10.1002/jssc.202200665.
[30] C. Wu, S. Yang, Y. Meng, Investigation of pH-switchability of hydrophobic deep eutectic solvents for the extraction and preconcentration of triazine herbicides in water samples, Microchem. J. 194 (2023), 109198, https://doi.org/10.1016/j.microc.2023.109198.
[31] M. Díaz-Álvarez, E. Turiel, A. Martín-Esteban, Hydrophobic natural deep eutectic solvents based on L-menthol as supported liquid membrane for hollow fiber liquid-phase microextraction of triazines from water and urine samples, Microchem. J. 194 (2023), 109347, https://doi.org/10.1016/j.microc.2023.109347.
[32] X. Wang, Q. Liu, Spatial and Temporal Distribution Characteristics of Triazine Herbicides in Typical Agricultural Regions of Liaoning, China, Bull Environ Contam Toxicol. 105 (2020) 899–905, https://doi.org/10.1007/s00128-020-03049-8.
[33] P.N. Kunene, P.N. Mahlambi, Optimization and application of ultrasonic extraction and Soxhlet extraction followed by solid phase extraction for the determination of triazine pesticides in soil and sediment, J. Environ. Chem. Eng. 8 (2020), 103665, https://doi.org/10.1016/j.jece.2020.103665.
[34] F. Pena-Pereira, W. Wojnowski, M. Tobiszewski, AGREE—Analytical GREEnness Metric Approach and Software, Anal. Chem. 92 (2020) 10076–10082, https://doi.org/10.1021/acs.analchem.0c01887.
[35] R. Gautam, N. Kumar, J.G. Lynam, Theoretical and experimental study of choline chloride-carboxylic acid deep eutectic solvents and their hydrogen bonds, J. Mol. Struct. 1222 (2020), 128849, https://doi.org/10.1016/j.molstruc.2020.128849.
[36] P.V. de Almeida Pontes, I. Ayumi Shiwaku, G.J. Maximo, E.A. Caldas Batista, Choline chloride-based deep eutectic solvents as potential solvent for extraction of phenolic compounds from olive leaves: Extraction optimization and solvent characterization, Food Chem. 352 (2021), 129346, https://doi.org/10.1016/j.foodchem.2021.129346.
[37] A. Pandey, S. Pandey, Solvatochromic Probe Behavior within Choline Chloride-Based Deep Eutectic Solvents: Effect of Temperature and Water, J. Phys. Chem. b. 118 (2014) 14652–14661, https://doi.org/10.1021/jp510420h.
[38] A.P. Abbott, R.C. Harris, K.S. Ryder, Application of Hole Theory to Define Ionic Liquids by their Transport Properties, J. Phys. Chem. b. 111 (2007) 4910–4913, https://doi.org/10.1021/jp0671998.
[39] European Commission, Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-Approval Control and Monitoring Purposes. Sante/2020/12830, Rev 2 February.
[40] T. Dagnac, S. Bristeau, R. Jeannot, C. Mouvet, N. Baran, Determination of chloroacetanilides, triazines and phenylureas and some of their metabolites in soils by pressurised liquid extraction, GC-MS/MS, LC-MS and LC-MS/MS, J Chromatogr a. 1067 (2005) 225–233, https://doi.org/10.1016/j.chroma.2004.11.058.
[41] S. Stipičević, S. Fingler, L. Zupančič-Kralj, V. Drevenkar, Comparison of gas and high performance liquid chromatography with selective detection for determination of triazine herbicides and their degradation products extracted ultrasonically from soil, J. Sep. Sci. 26 (2003) 1237–1246, https://doi.org/10.1002/jssc.200301420.
[42] J. Shah, M. Rasul Jan, B. Ara, F.-N. Shehzad, Quantification of triazine herbicides in soil by microwave-assisted extraction and high-performance liquid chromatography, Environ Monit Assess. 178 (2011) 111–119, https://doi.org/10.1007/s10661-010-1676-0.
[43] L. Wu, Z. Li, M. Hu, Dynamic Microwave-Assisted Micelle Extraction Coupled with Cloud Point Preconcentration for the Determination of Triazine Herbicides in Soil, J Chromatogr Sci. 60 (2022) 493–500, https://doi.org/10.1093/chromsci/bmab096.