



# New Potentials in the Extraction of Trace Metal Using Natural Deep Eutectic Solvents (NADES)

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## Abstract

The aim of the study was to concentrate on developing new solvents for extraction of selected metal complexes from young barley. Estimation of the amount of elements in compound, not only their total concentration, is very important because only a part from total content of metal is absorbed by human organism. At the beginning, the total amount of elements in young barley was established as  $16.69 \pm 0.22 \mu\text{g g}^{-1}$  (RSD 1.36%) for copper,  $156.29 \pm 0.82 \mu\text{g g}^{-1}$  (RSD 0.52%) for manganese,  $155.35 \pm 1.29 \mu\text{g g}^{-1}$  (RSD 0.83%) for zinc,  $9.10 \pm 0.21 \mu\text{g g}^{-1}$  (RSD 2.36%) for molybdenum, and  $0.35 \pm 0.01 \mu\text{g g}^{-1}$  (RSD 1.63%) for cobalt. The LOD of analyzed elements were as follows ( $\mu\text{g L}^{-1}$ ): Mn 0.59, Co 0.05, Cu 0.33, Zn 1.2, and Mo 0.12. The LOQ of studied metals were as follows ( $\mu\text{g L}^{-1}$ ): Mn 1.9, Co 0.18, Cu 1.1, Zn 4.0, and Mo 1.4. After that, the most suitable solvents were identified. The determination of total and extractable amount of metals in young barley was carried out by standalone inductively coupled plasma mass spectrometry (ICP-MS). In addition, a complementary analysis of extracted metal complexes was performed using size exclusion chromatography coupled with inductively coupled plasma mass spectrometry (SEC-ICP-MS) method. It was confirmed that the natural deep eutectic solvents (NADES) are able to extract different metal and metal species in comparison with commonly used solvents. The study indicated that extraction by using the NADES has been successfully applied for determination of metals and metal complexes in young barley.

**Keywords** Ionic liquids · NADES · Young barley · ICP-MS

## Introduction

Deep eutectic solvents (DES) are new class of solvents obtained by mixing solid compounds that are not necessarily salts, such as choline chloride and sugars. Mixing these compounds helps obtaining a eutectic mixture with a melting point much lower than the individual components (Dai et al. 2013b). Over the past two decades, the scientific community has paid much more attention to ionic liquids (ILs) to find a replacement for organic solvents. Ionic liquids are molten salts, liquid at room temperature, whose enormous potential arises from particular characteristics of these liquids, namely, their physicochemical properties (viscosity, density, hydrophilicity, and solubility), which can be tuned by the combination of different cations and anions (Paiva et al. 2014). However, in recent years,

research studies in solvents have provided an alternative to ILs—the deep eutectic solvents (DES). They may also have an ionic character and consist a mixture of organic compounds with a melting point significantly lower than the individual component (Paiva et al. 2014; Smith et al. 2014). Recently, researcher Yuntao Dai and her co-workers from Leiden University have reported a large number of stable natural deep eutectic solvents (NADES) based on natural compounds, particularly primary metabolites, such as organic acids, amino acids, and sugars (Dai et al. 2013a; Zainal-Abidin et al. 2017).

DES or NADES are obtained by the complexation between a hydrogen acceptor compounds and a hydrogen bond donor compounds. The occurrence of the charge delocalization is responsible for the decrease in melting point of the mixture in relation to the melting points of the raw materials. A major advantage of NADES over ILs is the simplicity of these solvent preparations.

The scientific literature mostly presents the extraction of biological active organic compounds using NADES, DES, and ILs (García et al. 2016; Huang et al. 2017; Ruesgas-Ramón et al. 2017). High percentage of those works involves

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the determination of phenols and flavonoids and the evaluation of their antioxidant activity (Bosiljkov et al. 2017; González et al. 2018). Only few publications have described the extraction of metals by DES, for example desulfurization of fuel (Xu et al. 2018), mercury in the blood sample (Akramipour et al. 2018), chromium species in environmental samples (Panhwar et al. 2018), selenium species from food sample (Panhwar et al. 2017), and ionic liquid extraction of copper complexes from chia seeds (Wojcieszek et al. 2016).

Unfortunately, still little is known about metal complexes with bioligands present in plants and fruits rich in biologically active compounds so exhaustive research of new extraction medium in this area is still necessary.

The selection process of metals chosen for this study was based on their essential micronutrient element to most life forms. The determination of total amount of metals was carried out by standalone ICP-MS. In order to confirm the presence of different metal complexes, the extracted fractions from young barley were also analyzed by SEC-ICP-MS technique. To the best of our knowledge, there is no report about using NADES in extraction of metal complexes from young barley (*Hordeum vulgare* L.).

The proposed research gives new possibilities for speciation analysis and plays an important role in the biological and medical fields. As the presented results reflect, NADES allow to prepare sample efficiently for speciation analysis of selected metals that play an important role in food and medical analysis.

Additionally, NADES as functional liquid media can dissolve natural or synthetic chemicals of low water solubility. NADES were applied to the solubilization of wide range of biomolecules for example non-water soluble bioactive natural products (BIONPs), such as: gluten, starch and DNA. It has allowed to find answer to some of the fundamental biological questions, for instance, how organisms deal with their non-water soluble BIONPs or lipid soluble metabolites?

## Materials and Methods

### Chemicals and Materials

The dried grounded young barley was purchased from the firm Intenson (Poland). Choline chloride, glycerol, betaine, ethylene glycol, malic acid, citric acid, fructose, glucose,  $\beta$ -alanine, methanol, ammonium acetate ( $\geq 99.995\%$ ), acetonitrile, hydrochloric acid, 1-methylimidazole, and 1-bromobutane of analytical reagent grade were purchased from Sigma-Aldrich (USA). Nitric acid of purity for trace element analysis was obtained from Fluka (Switzerland). High purity water (18 M $\Omega$  cm) was obtained with Milli-Q Elix 3 Water Purification system Millipore (France). The SEC column was calibrated using size exclusion standard (BIO-RAD, Poland). The calibration curves were prepared using solution of

Environmental Spike Mix (1000 mg L<sup>-1</sup> of Fe, K, Ca, Na, Mg and 100 mg L<sup>-1</sup> of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, U; matrix 5% HNO<sub>3</sub>) purchased from Agilent Technologies (USA).

### Preparation of DESs and Ionic Liquids

The ionic liquid used in this study was 1-*n*-butyl-3-methylimidazolium bromide ([C<sub>4</sub>mim]Br), synthesized based on references (Kim et al. 2004). For the synthesis, a 500-mL flask, equipped with a magnetic stirrer and condenser, was used. To a solution of 151.5 g (1.85 mol) of freshly distilled 1-methylimidazole, 100 mL of acetonitrile and 220 g (2.4 mol) of 1-bromobutane were added. The mixture was stirred at  $T = 373.15$  K for 96 h, and afterward, the solution was allowed to cool down when the 1-*n*-butyl-3-methylimidazolium bromide crystallized. Crystals were filtered and washed with ethyl acetate. The product was recrystallized from acetonitrile/ethyl acetate mixture (6/1). Crystals were dried in vacuum at  $T = 353.15$  K for 24 h. The solution of ionic liquid used during extraction was prepared by dilution in MQ water.

The following procedure of NADES synthesis is based on heating method (Dai et al. 2013a) to obtain natural deep eutectic solvents (NADES) with volume  $\sim 10$  mL. Presented method was employed to obtain NADES with a known amount of water. The two-component mixture with calculated amount of water was placed in a bottle with a stirring bar and cap and heated in a water bath below 50 °C, with agitation till a clear liquid was formed (about 30–90 min).

### Instrumentation

Chromatographic separations were performed using Agilent 1100 gradient HPLC pump (Agilent Technologies, Waldbronn, Germany). All connections were made of PEEK tubing (0.17 mm i.d.). As an element-specific detector for quantification of metal content in chia seeds and as online HPLC detector, Agilent 7500a ICP Mass Spectrometer (Agilent Technologies, Tokyo, Japan) was used. Ni skimmer was installed in the interface; the position of the torch and the gas flow nebulizer were adjusted daily with special emphasis to decrease the level of CeO<sup>+</sup> below 0.2% with the aim to minimize the risk of polyatomic interferences caused by oxides. The working conditions were optimized daily using a 10- $\mu$ g L<sup>-1</sup> solution of <sup>7</sup>Li<sup>+</sup>, <sup>89</sup>Y<sup>+</sup>, and <sup>209</sup>Bi<sup>+</sup> in 2% (v/v) HNO<sub>3</sub>.

The fractionation of the metal complexes was performed by means of size exclusion chromatography coupled to ICP-MS. Metal species were eluted from SEC Superdex200 10/300GL (GE Healthcare Life Sciences, Freiburg, Germany) column with 10 mM ammonium acetate buffer (pH 7.4) as a mobile phase. Before the analysis, the column was calibrated with a mixture of thyroglobulin (670 kDa),  $\gamma$ -globulin

**Table 1** Operational parameters for HPLC and ICP-MS

Settings	
ICP-MS	Agilent 7500a
RF power	1350 W
Plasma, auxiliary, and nebulizer gas flow	15.0, 1.0, and 1.05 L min <sup>-1</sup>
Cones	Sampler—Ni, Skimmer—Ni
Monitored isotopes	<sup>55</sup> Mn, <sup>63</sup> Cu, <sup>65</sup> Cu, <sup>66</sup> Zn, <sup>68</sup> Zn, <sup>95</sup> Mo,
Dwell time	0.1 ms
<b>HPLC separation</b>	
Pump	Agilent 1100
Column	Superdex 200 (10 × 300 mm × 10 μm)—GE Healthcare Life Sciences
Mobile phase	10 mM ammonium acetate buffer (pH 7.4)
Elution program	isocratic
Flow	0.7 mL min <sup>-1</sup>
Injection volume	100 μL
Column temperature	24 °C

(158 kDa), ovalbumin (44 kDa), myoglobin (17 kDa), and vitamin B<sub>12</sub> (1.35 kDa).

Operational parameters are summarized in Table 1.

A Bandelin Sonorex Model 1210 ultrasonic bath (Bandelin, Berlin, Germany), MPW Model 350R centrifuge (MPW Warsaw, Poland), water bath with thermostatically controlled temperature (Mammert, Germany), and sonication probe (Bandelin Sonoplus, Berlin, Germany) were used for extraction procedures. Microwave digestion Speedwave®four Berghof (Berghof, Chemnitz, Germany) was used for samples' mineralization and extraction procedure.

## Sample Preparation

### Samples Mineralization Toward Metal Determination in Young Barley

The young barley powder was stored at 4 °C. In order to determine total amount of elements, samples (0.05 g dry mass) were digested by microwave assisted mineralization with a mixture of 5 mL of HNO<sub>3</sub> and 3 mL of H<sub>2</sub>O<sub>2</sub> (both concentrated). The digests were diluted to a final volume of 25 mL with MQ water. Further dilutions toward ICP-MS analysis were prepared using 2% nitric acid solution and 10 ng mL<sup>-1</sup>

**Table 2** Types of NADES applied in the extraction of metal compounds

Components			Molar ratio	References
Hydrogen bond acceptors	Hydrogen bond donors			
Choline chloride	Glycerol	Water	1:2:8	(Jhong et al. 2009)
Choline chloride	Ethylene glycol	Water	1:4:8	(Xia et al. 2015)
Choline chloride	Ethylene glycol	Betaine	1:2:1:8*	(Qi et al. 2015)
Organic acids				
Choline chloride	Malic acid	Water	1:1:6	(Choi et al. 2011)
Choline chloride	Citric acid:	Water	1:1:6	(Zhao et al. 2015)
Sugar				
Choline chloride	Fructose	Water	1:1:10	(Ilgen et al. 2009)
Citric acid	Fructose	Water	1:1:10	(Choi et al. 2011)
Choline chloride	Glucose	Water	1:1:10	(Ilgen et al. 2009)
Amino acids				
Malic acid	β-Alanina	Water	1:1:10	(Espino et al. 2016)

\*Water

**Table 3** Extraction efficiency of selected metals from young barley

Components	Efficiency of extraction (%)			
	Mn	Cu	Zn	Mo
ChCl:glycerol	10	nd	27	43
ChCl:ethylene glycol	11	30	81	41
ChCl:ethylene glycol:betaine	10	nd	65	39
ChCl:malic acid	26	8	24	52
ChCl:citric acid	29	4	28	50
ChCl:fructose	31	1	2	64
ChCl:glucose	15	nd	43	54
Fructose:citric acid	22	24	116	50
$\beta$ -Alanina:malic acid	30	7	27	53
Methanol	10	nd	42	40
Ammonium acetate	10	nd	52	42
Ionic liquid	18	nd	44	109

nd < LOD

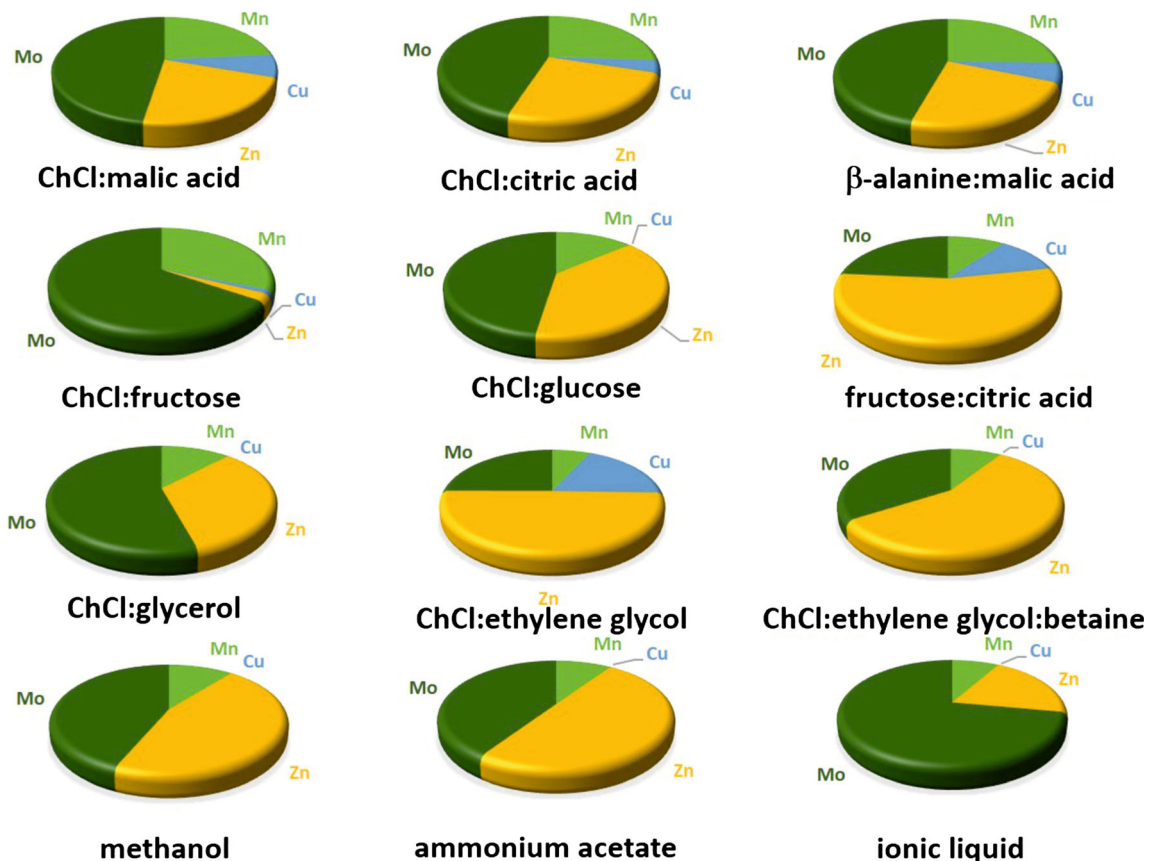
of yttrium ( $^{89}\text{Y}$ ) as an internal standard. The quantification (external calibration) was carried out by using calibration curves (relevant dilutions of multielement standard solution

with internal standard addition). Curves were linear in the investigated range from 0.5 to 100.0  $\mu\text{g L}^{-1}$  with  $r^2$  above 0.999.

### Extraction Procedure

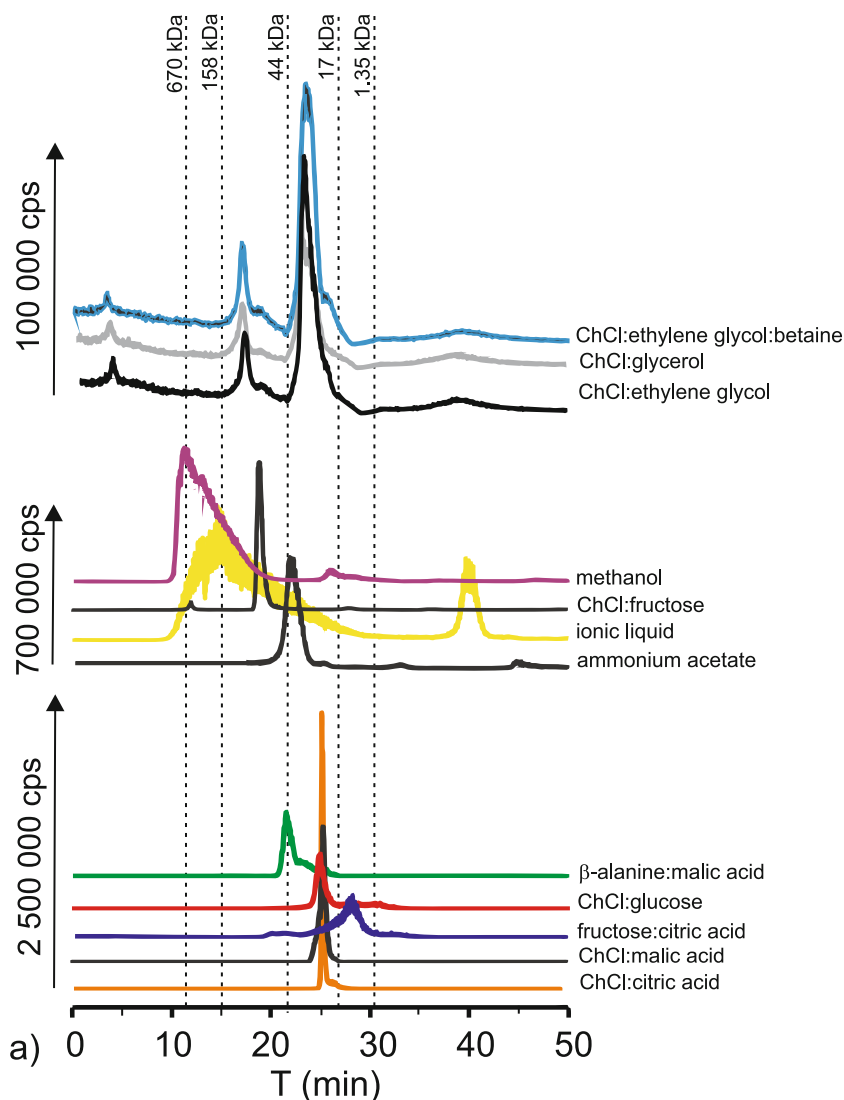
An initial step was carried out in order to determine the best solvent for extraction of metal complexes. To find the most suitable solvent for extraction of metal species, different solvents methanol, 10 mM ammonium acetate (pH 7.4), ionic liquid (IL), 1-*n*-butyl-3-methylimidazolium bromide [ $\text{C}_4\text{mim}$ ] $\text{Br}$ , and natural deep eutectic solvents (Table 2) were used.

Grounded samples (0.05 g of dry young barley powder) were extracted using vortexing for 30 min with 1 mL of each solvent. The obtained solutions were centrifuged for 20 min at 10,000 rpm at 21 °C. The final supernatant was filtered with 0.45- $\mu\text{m}$  syringe filter (Sigma-Aldrich, Bellefonte, PA, USA). The part of solutions was digested by microwave-assisted mineralization with a mixture of 5 mL of  $\text{HNO}_3$  and 3 mL of  $\text{H}_2\text{O}_2$ . The remaining part of the filtrate was injected on the size exclusion column.



**Fig. 1** The extraction efficiency of selected metals from young barley powder

**Fig. 2** SEC-ICP-MS chromatograms for manganese, obtained for extracts of young barley with different solutions



The yield of extraction was calculated as follows:

Extraction<sub>efficiency</sub>

$$= \frac{\text{amount of metal in solution after extraction}}{\text{total amount of metal in young barley}} \times 100\%$$

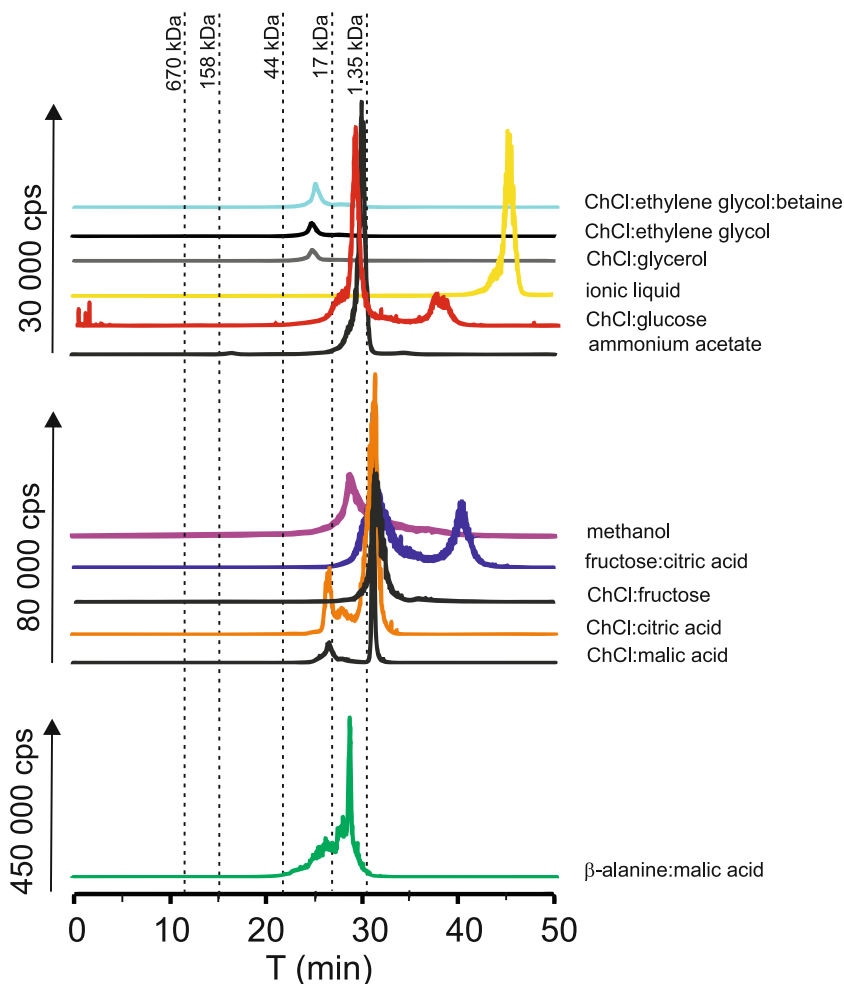
## Results and Discussion

### Total Content of Metals in Young Barley

The total amount of elements in young barley was established by means of ICP-MS as  $16.69 \pm 0.22 \mu\text{g g}^{-1}$  (RSD 1.36%) for copper,  $156.29 \pm 0.82 \mu\text{g g}^{-1}$  (RSD 0.52%) for manganese,  $155.35 \pm 1.29 \mu\text{g g}^{-1}$  (RSD 0.83%) for zinc,  $9.10 \pm 0.21 \mu\text{g g}^{-1}$  (RSD 2.36%) for molybdenum, and  $0.35 \pm 0.01 \mu\text{g g}^{-1}$  (RSD 1.63%) for cobalt. Total content of metals

was obtained from three independent experiments, and the mean value was calculated for each metal. Relative standard deviations among replicates of analysis of each sample were always lower than 5%. The limits of detection (LOD) and quantification (LOQ) are defined as the concentration corresponding to three and ten times of the standard deviation (SD) of the blank, respectively, divided by the slope of the calibration curve. The LOD was calculated for standard deviations (SD) of ten measurements for blank, and it was found to be  $0.05\text{--}1.2 \mu\text{g L}^{-1}$ . The LOD of analyzed elements were as follows ( $\mu\text{g L}^{-1}$ ): Mn 0.59, Co 0.05, Cu 0.33, Zn 1.2, and Mo 0.12. The LOQ of studied metals were as follows ( $\mu\text{g L}^{-1}$ ): Mn 1.9, Co 0.18, Cu 1.1, Zn 4.0, and Mo 1.4. The accuracy of the method was evaluated for the copper by spiking analyzed samples of barley with the standard of copper solution, and then, the extraction using NADES was carried out. Appropriate standard solution was added to the three samples, and recovery values were between 90 and 103%.

**Fig. 3** SEC-ICP-MS chromatograms for copper, obtained for extracts of young barley with different solutions



The results are not in good agreement with the earlier studies reported by other authors (Bell et al. 1991; Ariya Hymete 2015), but it should be pointed that to our knowledge, the difference in metal content in plant depends on the place of plant cultivation.

### NADESs in the Extraction of Metal—Extraction Efficiency

In order to investigate the effect of different NADES on the extraction efficiency, nine different mediums of DES and three of conventional medium were used. The results revealed that extracted amounts of metals were lower for conventional solvents compared to NADES.

The extraction of various metals from young barley indicated that depending on the composition of DES, different metals with different efficiencies are extracted from the plant (Table 3; Fig. 1). The extraction of manganese indicated that NADES comprised of choline chloride with citric/malic acid or fructose and  $\beta$ -alanine:malic acid with water were the most efficient solvents. The extraction of zinc indicated that NADES contained choline chloride with ethylene glycol, or

ethylene glycol with betaine (ternary system) and fructose: citric acid with water were the most efficient solvents. Note that for copper extraction, both choline chloride:ethylene glycol and fructose: citric acid also indicated the best efficiency. However, the extraction of molybdenum indicated that all NADES shows the similar extraction efficiency (40–60%).

It is important to mention that the presence of water in NADES reduces the viscosity of them in the extraction process (Dai et al. 2013a) and amount of water used in NADES had an immense influence on the extraction efficiency.

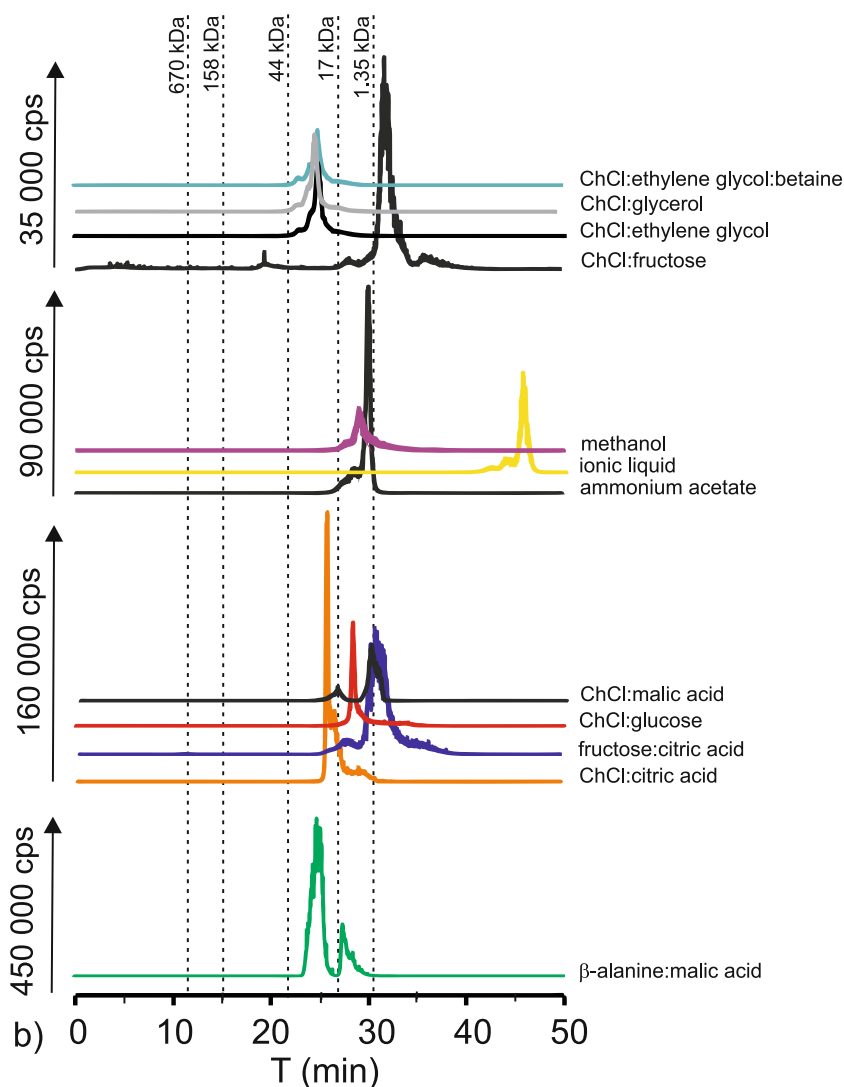
Also, there are many factors affecting the extraction efficiency, among which the concentration of solvent, extraction time, solid-liquid ratio and extraction temperature. In present investigation from the beginning, preliminary screening was performed to find out the most suitable solvent exhibiting significant influence on the yield of metals extraction.

### Effect of Solvent Type—SEC-ICP-MS Analysis

Since the main aim of the study was to find the most effective extraction conditions for analysis of metal complexes in plant (young barley), SEC-ICP-MS analysis was also performed.



**Fig. 4** SEC-ICP-MS chromatograms for zinc, obtained for extracts of young barley with different solutions



## Manganese

The one intensive peak in SEC-ICP-MS chromatograms was achieved for NADES contained choline chloride (with citric/malic acid, glucose) extracts at  $t_r = 25$  min; only one peak was observed in chromatograms at different time of retention for other extraction medium: fructose: citric acid at  $t_r = 28$  min and  $\beta$ -alanine: malic acid at  $t_r = 22$  min similar to ammonium acetate (Fig. 2). In the chromatogram obtained for choline chloride with ethylene glycol, glycerol, or betaine extracts, three signals from manganese complexes were observed with molecular mass in the range from approximately 200 to 20 kDa. Additionally, only one peak at  $t_r = 18$  min was observed for choline chloride with fructose. Just in these chromatograms, we could observe the high molecular mass compounds, probably from manganese complexes with proteins. This could indicate that non-polar NADES have significant tendency to extract hydrophobic compound with ability to bind studied elements.

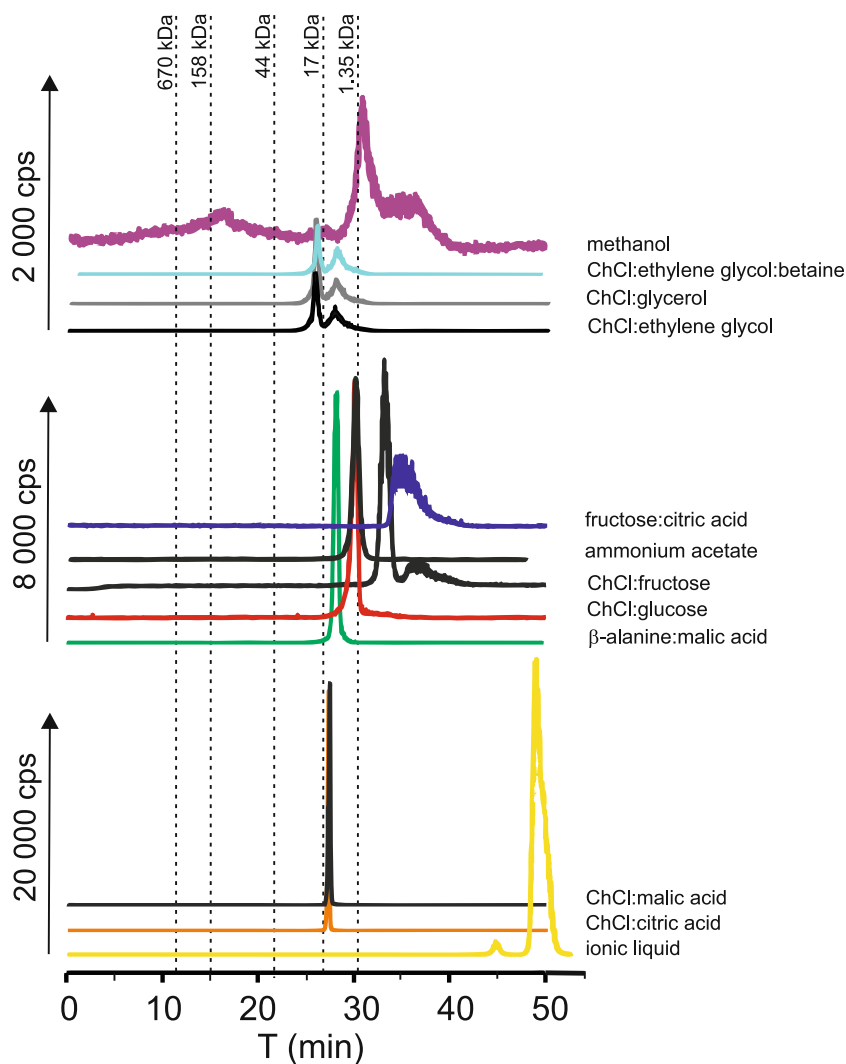
The yields of manganese extraction obtained after using of choline chloride with ethylene glycol or glycerol have been much lower than those obtained with choline chloride with citric/malic acid and fructose with citric acid but extracted the different manganese compounds.

## Copper

The one intensive peak in SEC-ICP-MS chromatograms was achieved for NADES containing choline chloride with citric/malic acid, glucose and fructose with citric acid extracts at  $t_r = 31$  min (close to 1.35 kDa molecular weight compounds). One peak was also observed at  $t_r = 24$  min in chromatograms of choline chloride extracts with ethylene glycol, glycerol, and citric/malic acid similar to ammonium acetate (Fig. 3).

Note that SEC-ICP-MS chromatograms achieved for choline chloride with malic/citric acid obtained two different peaks. Furthermore, in the chromatogram obtained for  $\beta$ -alanine with malic acid, one peak at the different retention time

**Fig. 5** SEC-ICP-MS chromatograms for molybdenum, obtained for extracts of young barley with different solutions



than other solvents at  $t_r = 27$  min was observed. Also, in SEC-ICP-MS chromatograms obtained for fructose with citric acid, one additional peak at  $t_r = 40$  min was detected this could indicate the complexes of copper with low molecular weight compounds are present.

## Zinc

In SEC-ICP-MS chromatograms obtained for zinc compounds, three groups of peaks were observed. The first is at  $t_r = 24$  min for NADES of  $\beta$ -alanine:malic acid, choline chloride: citric acid/malic acid, choline chloride:ethylene glycol, choline chloride:glycerol, and choline chloride:ethylene glycol:betaine (Fig. 4).

The second peak at  $t_r = 27$  min for NADES of  $\beta$ -alanine:malic acid, choline chloride:glucose, and choline chloride:malic acid (similar to ammonium acetate extracts). The third peak at  $t_r = 32$  min was obtained for NADES of fructose: citric acid and choline chloride:fructose. There was

additional peak detected at  $t_r = 45$  min but only for ionic liquid extracts.

## Molybdenum

In SEC-ICP-MS chromatograms obtained for molybdenum compounds peaks at different time of retention were observed, this could indicate possibility of extraction of different metal compounds. At  $t_r = 25$  min, the peak in the SEC-ICP-MS chromatogram obtained for choline chloride:ethylene glycol, choline chloride:glycerol and choline chloride:ethylene glycol:betaine extracts was observed (Fig. 5).

Another peak at  $t_r = 27$  min was detected for choline chloride:ethylene glycol, choline chloride:glycerol and choline chloride:ethylene glycol:betaine extracts and additionally for choline chloride with citric/malic acid and  $\beta$ -alanine:malic acid. At  $t_r = 30$  min, the peak was obtained for choline chloride:glucose extracts. In the SEC-ICP-MS chromatogram obtained for choline chloride:fructose, the only peak was observed at  $t_r = 33$  min. At  $t_r = 37$  min, the peak obtained for



choline chloride:fructose and fructose with malic acid was present. The last peak was observed at  $t_r = 50$  min only for ionic liquid extract.

To conclude, the NADES are based on (1) the choline chloride solution with citric acid, malic acid and/or glucose are dedicated to extraction of metal compounds with medium molecular weight (MMW)—in the chromatograms obtained for this extractant, the signal in the region of medium molecular weight compounds were observed; (2) choline chloride with ethylene glycol, glycerol, and ethylene glycol:betaine are dedicated to extraction of metal compounds with high molecular weight (HMW) compounds—in the chromatograms obtained for this extractant, the signals were obtained at retention time from the compounds with higher molecular mass (44–17 kDa); (3) the  $\beta$ -alanine extracts are dedicated also for metal with HMW compounds, and the signals were observed in the chromatogram at retention time from metal complexes with molecular mass in the range from 44 to 17 kDa; and (4) the sugar NADES has ability for extraction of metal complexes with small bioligands, for example organic acids. Analysis of NADES based on fructose extracts led to detecting a signal after 35 min, which indicated the presence of a small compounds (LMW).

From the results presented, it can be seen that the use of different NADES allow the extraction of various metals from one sample. In addition, the use of different NADES let to extract different species of the same metal. The use of different combinations of choline chloride allows the extraction of other group of metal compounds than the use of NADES which is based on alanine or fructose. These differences allow to plan the appropriate sequential extraction of metals from plants to extract important compounds from starch, and it also allows for speciation analysis of compounds that are affixed to the insoluble part of plants. In addition, the use of sequential extraction combining NADES with ionic liquids will allow for efficient extraction of metals for speciation analysis of biological and medical materials.

## Conclusions

The first step of this study was to determine the total concentration of selected trace elements—essential for human—manganese, zinc, copper, molybdenum, and cobalt. In the next step, choosing the most suitable natural deep eutectic solvents and conventional solvents of metal and metal species from young barley was optimized. This optimization showed that in order to obtain high yields of extraction of metals, different NADES for selected metal should be chosen. The NADES possessed great advantages in extracting metal complexes, in comparison with the conventional extraction approaches.

The use of size exclusion chromatography in combination with inductively coupled plasma mass spectrometry (SEC-ICP-MS) allowed on separation of extracted metal-containing compounds according to their size. SEC-ICP-MS analysis showed that extraction with NADES in optimized conditions lead to the multiplicity of the peaks in the obtained chromatogram. The results allow to conclude that NADES have an ability to extract of different group of compounds in comparison with other solutions.

Obtained results suggest that extraction of metal and metal species from young barley with NADES was an effective and simple method. In order to identify extracted metal species, use of more advanced techniques of mass spectrometry will be necessary.

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## Compliance with Ethical Standards

**Conflict of Interest** Natalia Osowska declares that she has no conflict of interest. Lena Ruzik declares that she has no conflict of interest.

**Ethical Approval** This article does not contain any studies with human participants or animals performed by any of the authors.

**Informed Consent** Not applicable.

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