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# Deep eutectic solvents based assay for extraction and determination of zinc in fish and eel samples using FAAS

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ABSTRACT

A new assay based on effective (high recovery) extraction by means of deep eutectic solvents (DESs) was developed for ppb level determination of zinc in fishes and eel samples. Choline chloride and Phenol in a 1:2 M ratio was selected as optimal DES-based extraction solvent. 8-Hydroxy quinoline was used as a chelating agent for zinc ions. The optimized conditions were found at pH value of 8, ligand concentration of 10 mg/L, THF volumetric ratio in bulk solution of 0.5:10. The total time at optimal sample preparation conditions was 5 min for digested sample. Developed method fits to the purpose of routine analysis of fishes and eels. The LOD and LOQ were found 0.041 μg/kg and 0.136 μg/kg with pre-concentration factor of 25 and RSD 1.7%.



## 1. Introduction

Zinc is considered one of the most essential elements for the human body and its deficiency is a worldwide nutrition issue [28]. Zinc is acting as cofactor in more than 200 enzymes taking place in mechanisms of disturb energy metabolism, increased oxidative stress, disturb pregnancy and weight loss [30,31]. Zinc deficiency causes skin problems, slow healing, reduction in taste and smell sense, decreased fertility, susceptibility to infection, mental lethargy, loss of appetite and hairs, stunted growth [35]. Importantly, the US environmental protection agency (EPA) has recommended a zinc concentration in water over 5 mg/L [6], resulting in a regular monitor zinc concentration in drinking water and food materials.

Zinc usually appears at a very low concentration level in food samples, which are often below the limit of detection of the instrument. Thus, a proper sample preparation stage together with zinc enrichment as well as for the elimination of matrix effects is always required [3]. To date, a large number of pre-concentration methods have been investigated including cloud point extraction [37], solid-phase extraction [16], solid-phase microextraction [36], co precipitation method [15], adsorption methods [25], chromatographic methods[33], liquid phase microextraction[15] and many other methods.

Mostly these techniques are time-consuming and produce large amount of wastes [10]. Today, according to the "Twelve Principles of Green Chemistry" developed by Anastas and Warner, there is a need of implementing "green" processes and feed stocks. Therefore, in this study a new green method was proposed and investigated for the pre-concentration of zinc prior to its analysis through FAAS. Herein, deep Eutectic Solvents (DESs), considered as the new generation of green solvents, were selected for liquid-phase extraction. The application of DESs has proved to be an interesting alternative to classic organic solvents for several groups of compounds, including carboxylic acids [19], polycyclic aromatic hydrocarbons [20], sulfur [18], oxygen-containing organic compounds [21] among others. This paper presents a study on the extraction of zinc ions in fish and eel samples based on the addition of ligands combined with extraction using DESs.

## 2. Materials and methods

### 2.1. Materials

All chemicals were analytical grade and used without any prior purification. 1000 mg/L standard stock solution of Zn (II) was prepared by dissolving $ZnCl_2$ (DAEJUNG Korea) in deionized water. 100 mg/L

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solution of 8-hydroxyquinoline (DAEJUNG Korea) was prepared by dissolving an appropriate amount of reagent in analytical grade ethanol. Tetrahydrofuran (THF purity >99%, DAEJUNG Korea) was directly used without any purification. Standard solution of Ammonium chloride (purity >99.8%; BDH AnalaR) was prepared by dissolving in deionized water. DESs were prepared by mixing Choline chloride and Phenol in 1:1, 1:2, 1:3 and 1:4 M ratios. The resulting mixture was stirred and heated at 60 °C until obtaining a homogeneous mixture. Analytical grad Acetic acid (DAEJUNG Korea) was used for buffer formation. Sodium acetate, Ammonium hydroxide, Phosphoric acid, Sodium dihydrogen phosphate, and Ammonium acetate were purchased from Sigma Aldrich and used for buffer preparation.

### 2.2. Apparatus

Flame atomic absorption spectrophotometer, AAnalyst 700 model (Perkin Elmer) was used for quantitative analysis of zinc. CEM microwave synthesizer (UK) was used for sample digestion. Vortex F202A0175 (VELP SCIENTIFICA) was used for shaking during the extraction. A Centrifuge model (Wealtech Pakistan), was used to obtain a clear extract phase. Sonicator/ultrasonic bath made by IKON industries model IK/UTSB was used for sonication. A pH meter model ORION STAR A329 with a pH electrode model 8157BNUMD (Thermo Scientific) was used for measuring the pH. Water deionizer model LP-15/30/45 (FINETECH *water treatment technologies*) was used to obtain water meeting quality for the experiments.

### 2.3. Procedures

#### 2.3.1. Sample pre-treatment and digestion

Varieties of fishes are used in healthy human diet. Among all, two excessively using varieties *Scomberomorus cavalla*/King Fish and Anguilliform/eel were selected for determining zinc concentration. Fish and eel samples weighing 200 g to 600 g were collected from natural reservoirs of river Kabul. Edible parts (meat) of fishes and eels samples were dried in a thermostat oven and subsequently mixed/milled. From the composite samples 2 g of fish/eel sample was digested in a quartz tube of CEM microwave synthesizer under controlled conditions. Nitric acid, deionized water and Hydrogen peroxide were added at 1:3:2 mL ratio. Heating program was executed in three steps, as follows: step 1 (140 °C for 5 min), step 2 (180 °C for 8 min) and step 3 (220 °C for 3 min). While heating, the Nitric acid and Hydrogen peroxide decomposed and evolved to a form of NO2, H2O and O2 and when the samples were near to dry. The digested samples were transferred to falcon tubes, diluted with water up to 10 mL and were used for DES-based extraction.

#### 2.3.2. Preparation of buffer

Buffer systems ranging from pH 2 to 10 were used in this study. To set pH the following buffers were used. $H_3PO_3$-$NaHPO_4.2H_2O$ for pH 2, $CH_3COOH$-$CH_3COONa$ for pH 4,$CH_3COOH$-$CH_3COONH_4$ for pH 6, $NH_4OH$-$NH_4Cl$ for pH 8 and $NH_4Cl$-$NH_{3(aq)}$ for pH 10. A volume (2 mL) of buffer solution in reagents mixture was found enough for maintaining stable pH value.

#### 2.3.3. DES selection and preparation

Different combinations of DES with different mole ratios were prepared. DES made of Choline chloride + Phenol, Choline chloride + Urea, Choline chloride + Ethylene glycol and Choline chloride + Malonic acid were tested for zinc extraction. Choline chloride was mixed with the HBDs (Phenol, Urea, Ethylene glycol and Malonic acid) in molar ratio 1:1, 1:2 and 1:3. All the DES solvents were prepared under identical conditions. In a 50 mL polypropylene tube, the components of DESs were mixed, then heated in a water bath for 60 min at 60 °C. Results for this study are given in fig. S2. For each experiment freshly prepared DES solvents were prepared and directly used without any dilution or purification.

#### 2.3.4. Extraction by DES

2 mL pH 8 buffer solution was added to each sample (10 mL) and 0.1 mL standard zinc solution (zinc in solution 5 μg/Kg) in the falcon tube. 0.5 mL of ligand solution was added to obtain a final concentration of 10 mg/L in bulk solution. Next, 0.6 mL of DES was added to the sample solution followed by sonication (20 kHz and 1000 W) at 60 °C, for 80 s. The resulting mixture was looking cloudy and turbidity of DES solvent in aqueous mixture was visible. On standing for long time, DES solvent was partially separated as upper layer. To enhance the DES phase separation from aqueous phase, a 0.5 mL Tetrahydrofuran was added to a bulk mixture followed by shaking with vortex. Finally, the mixture was centrifuged for 30 s at 4000 rpm. DES layer was clearly separated on the top of aqueous medium. The upper DES layer (approximately 1 mL) was separated and diluted with methanol to 3 mL for FAAS analysis.

#### 2.3.5. Percent recovery

For calculating percent recovery, standard solutions of zinc ion concentrations were prepared. The standard addition method was used for determining zinc ions concentration in bulk solution to minimize the effect of interfering species. The standard addition method is extensively used in chemical instrumental analysis, such as atomic absorption spectroscopy, for determining metal ion concentration in matrix [2]. This method is usually preferred over calibration curve approach, in which analytical signal is affected by matrix effect and making the results [12]. Each sample was prepared in triplicate. In the first step, only a digested sample was analyzed followed by samples adding zinc ion standard solution in ascending order. All samples and standards were analyzed for zinc ion concentration under the same conditions using flame atomic absorption spectrophotometer. The percent recovery was determined as follows:

$$R(\%) = \frac{C\ quant}{C\ except} \times 100$$

Where *C quant* – found analyte concentration in spiked sample [μg/Kg], *C except* – analyte concentration added as spike [μg/Kg].

#### 2.3.6. FAAS analysis

The DES extract was diluted with methanol up to 3 mL. Standard solutions of zinc (0.25–15 μg/Kg) were also prepared. Samples were analyzed through flame atomic absorption spectrophotometer Perkin Elmer AAnalyst 700, using air-acetylene flame for excitation. Hollow cathode lamp with single wavelength (213.9 nm) was used as a light source. Gas flow rate was 2 L $min^{-1}$ for each gas. Standard addition method was used for analysis of zinc ions in fishes and eel samples. Absorption was determined for standard solutions of zinc ion and plotted as a standard curve.

## 3. Results and discussion

### 3.1. Selection of parameters for optimal sample preparation

The effect of temperature was studied in a temperature range between 20 and 80 °C. With increase of temperature, the viscosity of the DES solvents decreases, secondly it also affects metal ligand complex formation. Complexation reaction of 8-Hydroxyquinoline with Zinc follow endothermic kinetics, thus according to Van't Hoff equation $[(\frac{d}{dT} In\ K_{eq} = \Delta H^{-}/RT^2)]$ with increasing temperature the rate and yield of reaction increases [29]. With increase in temperature diffusion coefficient increases, this along with viscosity decrease allows to increase the overall mass transfer between the donor and acceptor phases. An effective extraction takes place in reduced time of the

process. These studies revealed that the best performance was obtained for a constant temperature of 60 °C and 80 s of sonication. Optimum temperature and time is illustrated in fig. S3 and fig. S4 respectively. At this condition 99.5% recovery of analyte was obtained.

For ligand optimization 5 sets of experiments were performed under the same reaction conditions differing the concentration of ligand ranged from 2.5 to 12.5 mg/L. Results for optimum ligand volume are illustrated in fig. S5. A continuous increase in % recovery was observed with the ligand concentration increase from 2.5 to 10 mg/*L. Maximum* recovery was obtained at 10 mg/L, so this concentration was selected as an optimum concentration for further experiments.

The effect of pH was studied by adding an appropriate amount of buffer solution, evaluating the extraction effectiveness based on percent recovery of the analyte. In this procedure deprotonating of 8-Hydroxyquinoline takes place, thus pH adversely affects this process. In basic medium, the deprotonating of 8-Hydroxyquinoline increases [17] and thus extraction increases.

This part of the study revealed an enhanced recovery percentage by changing the pH from 2 to 8. At pH 10 lesser recovery was observed. A precipitate formation occurs above pH 9, which it could be zinc ion precipitation in the form of zinc hydroxide [34], as suggested in following reaction:

$$Zn^{+2}_{(aq)} + 2NH_{3(aq)} + 2H_2O_{(l)} \rightarrow Zn(OH)_{2\ (s)} + 2NH^{+}_{4(aq)}.$$

Since the maximum recovery was observed at pH 8 (Fig. 1), so this pH was selected as an optimum pH for further studies.

THF can role as co-solvent and co-product in the extraction to increase extraction efficiency. It is moderately polar solvent and has the ability to dissolve a wide range of polar and non-polar compounds, together with low surface tension and low vaporization enthalpies thus helping in a more efficient separation [14]. THF penetrates easier than water in extracting complex thus improving solvent contact with extracting complex thus THF reduces the time required for extraction [5]. THF concentration was optimized by changing THF (99%) volume from 0.1 to 0.8 mL per 10 mL of bulk solution. A continuous increase of the recovery, as presented in fig. S6, was observed with an increase of THF volume from 0.1 to 0.5 Ml. *maximum* recovery was observed for 0.5 mL THF so this volume was selected as the optimum volume for further studies.

A DES used for extraction must meet several requirements like high affinity for analytes, liquid state at RT, no interference in analytical signal, different density from that of water, high stability and low solubility in aqueous medium. Among different DES made of Choline chloride + Phenol, Choline chloride + Urea, Choline chloride + Glycol and Choline chloride + Malonic acid were tested for zinc extraction. DES made of Choline chloride and phenol was found to provide highest efficiency for zinc extraction. Deep eutectic solvent (DES) was prepared from Choline chloride and Phenol at different molar ratios, e.g. 1:1, 1:2, 1:3 and 1:4. The preliminary studies revealed that the optimal molar ratio was 1:2 allowing the highest recovery (101%) of zinc ions. Results for extraction of zinc at different HBA-HBD molar ratios are given in Fig. S2 (Supporting Information). DES volume was studied in the range 0.1 to 0.8 mL. The results released that the optimum ratio DES to sample is 0.6:10 (*v*/v). Results of optimum volume ratio for DES are given in Fig. 2. At this ratio, a maximum recovery was obtained, which was subsequently selected as an optimum for further studies.

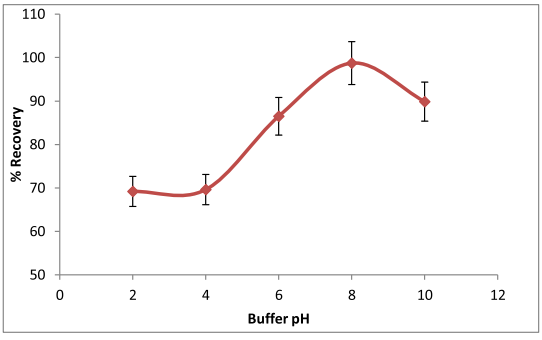


**Fig. 1.** Study of the effect of pH on zinc ion extraction. Sample volume 10 mL, ligand 10 mg/L, DES 0.6 mL, THF 0.5 mL, Zinc 5 μg/Kg, Temperature 60 °C, Sonication time 80 s.

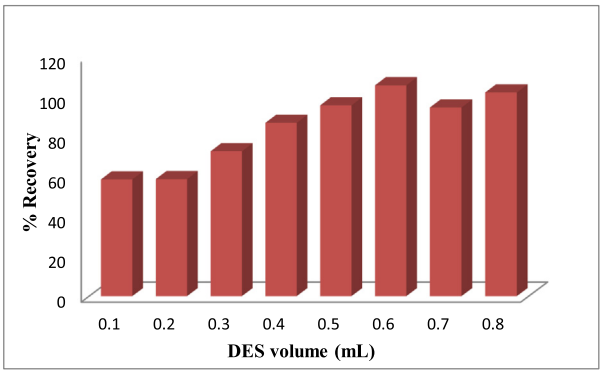


**Fig. 2.** DES volume optimization. Sample volume 10 mL, 2 ml pH 8 buffer, ligand 10 mg/L, THF 0.5 mL, Zinc 5 μg/Kg, Temperature 60 °C, Sonication time 80 s.

**Table 1**
Analytical parameters.

| Parameters | Value | |
|---|---|---|
| | Range 1 | Range 2 |
| Slope | 0.001 | 0.0016 |
| Intercept | 0.0024 | 0.0184 |
| Linearity range 1 | 0.24–1 μg/Kg | 1–15.2 μg/Kg |
| **Coefficient of determination** ($R^2$) | 0.9998 | 0.9997 |
| Standard error (SE) of intercept | 0.0077 | 0.1454 |
| LOD without preconcentration | 1.030 μg/Kg | |
| LOD with preconcentration | 0.041 μg/Kg | |
| LOQ without preconcentration | 3.420 μg/Kg | |
| LOQ with preconcentration | 0.136 μg/Kg | |
| Relative standard deviation (RSD) | 1.7% | |
| Enrichment factor (EF) | 25 | |

**Table 2**
Application of the method on real samples.

| Samples | Zn added (μg/Kg) | Zn found (μg/Kg) | % Recovery |
|---|---|---|---|
| Fish | 0 | <LOD | – |
| | 0.126 | 0.130 | 96.9 ± 3 |
| | 0.253 | 0.263 | 96.2 ± 2 |
| Eel | 0 | 0.042 | – |
| | 0.126 | 0.181 | 92.8 ± 2 |
| | 0.253 | 0.291 | 101.3 ± 5 |

### 3.2. Method validation and application for analysis of real samples

#### 3.2.1. Interference studies

DESs are considered as a highly selective extraction media for heavy metals, while flame atomic absorption spectroscopy is also a highly selective technique, however interference may be attributed to the pre-concentration steps. The selectivity for the proposed method was investigated under optimized conditions by evaluating interference effect for $Mn^{2+}$, $Mg^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Cl^{-}$, $SO_4^{2-}$, $Na^{+}$ and $K^{+}$. It was observed that the proposed method is highly selective. Table S6 illustrates results for interference study.

**Table 3**
Comparison of present method with reported methods in the literature.

| Method | Reagents used[a] | RSD (%) | Analytical technique | LOD (μg/Kg) | Real sample | References |
|---|---|---|---|---|---|---|
| Solid phase extraction | APDC, $HNO_3$, Acetone | 6 | FAAS | 25.3 | Fishes | [13] |
| Adsorption method | Amberlite XAD-7, Congo red | 6 | FAAS | 2.50 | Fishes | [1] |
| Electro-analytical | Ag/AgCl electrode, KCl, Modified glassy carbon electrode. | 2.3 | DPSA | – | Fishes | [27] |
| DES based extraction | Choline chloride, Oxalic acid | 1.14–20 | FAAS | 12 | Fishes | [11] |
| Solid phase extraction | Activated carbon, CMBM, DDTC, APDC | 0.9 | FAAS | 0.22 | Fishes | [23] |
| Solid phase extraction | HBDAHBDA | 1.4 | | 1.9 | Fishes | [4] |
| Cloud point extraction | PAN, Triton X-114 | – | FAAS | 2.3 | Water, fish | [8] |
| DES-assisted method | $^5$DES, 8-Hydroxy quinoline | 1.7 | FAAS | 0.041 | Fishes, eel | *This work* |

[a] APDC; Ammonium pyrrolidin edithiocarbamate, FAAS; Flame atomic absorption spectroscopy, DPSA: Derivative potentiometric stripping analysis, CMBM; 4,4′-[(4-Cyano-phenyl) methylene]bis (3-methyl-1-phenyl-1H-pyrazol-5-o, DDTC; diethyldithiocarbamate, APDC; Ammonium pyrrolidine dithiocarbamate, HBDAHBDA; 2[2,hydroxybenzylideneamino]2-hydroxybenzonitral, PAN; 1-(2-Pyridylazo)-2-naphthol, DES;Deep eutectic solvents.

*3.2.2. Determination of basic parameters of the developed method*

Under optimum conditions, the linearity of the method, the limit of detection as well as limit of quantification was investigated according to the European Union Reference Laboratory (EURL) report (2016) for Heavy Metals in Feed and Food (EURL HM). LOD and LOQ were calculated before and after pre concentration. The relative standard deviation was calculated as SD/mean×100% while enrichment factor was calculated as $EF = C_f/C_i$, where $C_f$ and $C_i$ are the final and initial concentrations, respectively. Results of method validation are given in Table 1.

A 6 points calibration curve was done with each calibration level in triplicate. Linearity was obtained within two ranges - range 1 for lower concentration (0.25–1 μg/Kg) and range 2 for higher concentrations (1–15 μg/Kg). Data presented in Fig. S7 indicate good linearity of the method. Thus, the proposed method is applicable in a range from 0.24 to 15.2 μg/Kg. Accuracy (mean ± SD) was 99.20%.

*3.2.3. Determination of zinc ions in real samples*

This newly developed method was used for determining zinc concentration in fish (*Scomberomorus cavalla*) and eel (Anguilliform) samples. Standard addition method was followed to reduce the interference effect. Percent recovery higher than 92% was observed. The results for zinc concentration in fishes and eels are compiled in Table 2. It's recommended by WHO, that men need to eat 11 mg of zinc per day, while women need 8 mg per day. However, pregnant women need 11 mg per day, and if she is breastfeeding, then she will need 12 mg per day. This study revealed that zinc concentration in king fish (*Scomberomorus cavalla*) was found to be below the limit of detection, while in eel (Anguilliform) samples zinc concentration was 0.042 μg/Kg. Although fishes and eels are considered as rich sources of zinc however these studies revealed that these foodstuffs have a very low concentration of zinc. This low concentration is probably due to unavailability of supplementary foods in natural reservoirs. As this part of experiments was performed mainly to prove the applicability of the developed method, further routine studies on zinc concentration in fishes and eels should be performed. According to obtained LOD, recovery and repeatability, this method seems to fit this purpose.

*3.3. Comparison with other methods*

There are several methods reported in the literature dealing with the extraction of zinc ions, which were compared with this developed method. Many methods have been reported for zinc extraction including cloud point extraction [8], liquid phase micro extraction [7], solid phase micro extraction [15], selective back extraction [26], micelle mediated extraction [32], dispersive liquid-liquid micro extraction [24], adsorption [9] and co precipitation methods [22]. Among these methods cloud point extraction methods have been excessively used. Cloud point extraction methods are more sensitive and frequently used however these methods are associated with limitations. Cloud point extraction methods are more sensitive and effected by conditions such as ionic strength, pH, temperature, extraction and pressure [38], so any small change in these conditions may lead to a decrease in metal recovery. Our new method presented in this paper is more sensitive than the reported CPE methods with LOD 0.041 μg/Kg. Furthermore this method is quite faster than cloud point extraction where CPE takes more than 20 min for a single experiment [8]. The comparison of our novel method with other reported methods is shown in Table 3.

## 4. Conclusions

The paper presents a new assay for determination of zinc in fish and eel samples, based on zinc extraction by means of a DES-based system. It is based on green solvents (DES) which are easily prepared, biodegradable, less toxic than organic solvent, highly selective and remain liquid over a wide range of temperature. The determined validation parameters proved the usefulness of the developed procedure for analysis of real samples having complex matrix such as fishes and eels. This method is characterized by a very good percent recovery as well as precision. The sample preparation stage allows to easily obtain an enrichment factor of 25, resulting in low limits of detection (LOD) and quantification (LOQ) 0.041 μg/Kg and 0.136 μg/Kg respectively. Studies performed on real fish and eel samples proved its applicability for routine practice. The application of selected DESs is a step forward for the elimination of toxic organic solvents commonly used in sample preparation, making this procedure environmentally friendly.

## Declaration of Competing interest

The authors declare no conflict of interest.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.115930.

## References

[1] G. Alpdoğan, N. San, Ş. Dinç Zor, Analysis of some trace metals in fish species after preconcentration with Congo red on amberlite XAD-7 resin by flame atomic absorption spectrometry, J. Chem. (2016) 2016.

[2] M. Bader, A systematic approach to standard addition methods in instrumental analysis, J. Chem. Educ. 57 (1980) 703.
[3] J. Borkowska-Burnecka, A. Szymczycha-Madeja, W. Żyrnicki, Determination of toxic and other trace elements in calcium-rich materials using cloud point extraction and inductively coupled plasma emission spectrometry, J. Hazard. Mater. 182 (2010) 477–483.
[4] K. Chalapathi, Analysis of heavy metals in fish samples after preconcentation on activated carbon modified with 2 [2-hydroxybenzylideneamino] 2-hydroxybenzonitral, Int. J. Anal. Bioanal. Chem. 2 (2012) 122–128.
[5] W. Cheong, P.W. Carr, The surface tension of mixtures of methanol, acetonitrile, tetrahydrofuran, isopropanol, tertiary butanol and dimethyl-sulfoxide with water at 25 C, J. Liq. Chromatogr. 10 (1987) 561–581.
[6] U. EPA, Quality Assurance Guidance Document-Model Quality Assurance Project Plan for the PM Ambient Air, United States Environmental Protection Agency, 2001 2.
[7] Z. Es'haghi, A. Nezhadali, H.A. Hosseini, S. Mohammadi-Nokhandani, Preconcentration and determination of zinc in water samples by ligand assisted pseudo stirbar hollow fiber solid/liquid phase microextraction, Arab. J. Chem. 10 (2017) S3840–S3847.
[8] R. Galbeiro, S. Garcia, I. Gaubeur, A green and efficient procedure for the preconcentration and determination of cadmium, nickel and zinc from freshwater, hemodialysis solutions and tuna fish samples by cloud point extraction and flame atomic absorption spectrometry, J. Trace Elem. Med. Biol. 28 (2014) 160–165.
[9] P. Galiatsatou, M. Metaxas, V. Kasselouri-Rigopoulou, Adsorption of zinc by activated carbons prepared from solvent extracted olive pulp, J. Hazard. Mater. 91 (2002) 187–203.
[10] A. Gonzales, M. Firmino, C. Nomura, F. Rocha, P. Oliveira, I. Gaubeur, Peat as a natural solid-phase for copper preconcentration and determination in a multicommuted flow system coupled to flame atomic absorption spectrometry, Anal. Chim. Acta 636 (2009) 198–204.
[11] E. Habibi, K. Ghanemi, M. Fallah-Mehrjardi, A. Dadolahi-Sohrab, A novel digestion method based on a choline chloride–oxalic acid deep eutectic solvent for determining Cu, Fe, and Zn in fish samples, Anal. Chim. Acta 762 (2013) 61–67.
[12] D.C. Harris, Calibration methods, in: D.C. Harris (Ed.), Quantitative Chemical Analysis, 6th editionWH Freeman and Company, New York 2003, pp. 80–98.
[13] A. Imyim, P. Daorattanachai, F. Unob, Determination of cadmium, nickel, lead, and zinc in fish tissue by flame and graphite furnace atomic absorption after extraction with pyrrolidine dithiocarbamate and activated carbon, Anal. Lett. 46 (2013) 2101–2110.
[14] A. Kageyama, A. Motoyama, M. Takayama, Influence of solvent composition and surface tension on the signal intensity of amino acids in electrospray ionization mass spectrometry, Mass Spectrometry 8 (2019) A0077.
[15] I. Komjarova, R. Blust, Comparison of liquid–liquid extraction, solid-phase extraction and co-precipitation preconcentration methods for the determination of cadmium, copper, nickel, lead and zinc in seawater, Anal. Chim. Acta 576 (2006) 221–228.
[16] A. Kraut-Vass, J. Thoma, Performance of an extraction disk in synthetic organic chemical analysis using gas chromatography—mass spectrometry, J. Chromatogr. A 538 (1991) 233–240.
[17] W.J. Lennarz, M.D. Lane, Encyclopedia of Biological Chemistry, Academic Press, 2013.
[18] P. Makoś, G. Boczkaj, Deep eutectic solvents based highly efficient extractive desulfurization of fuels–Eco-friendly approach, J. Mol. Liq. (2019) 111916.
[19] P. Makoś, A. Fernandes, A. Przyjazny, G. Boczkaj, Sample preparation procedure using extraction and derivatization of carboxylic acids from aqueous samples by means of deep eutectic solvents for gas chromatographic-mass spectrometric analysis, J. Chromatogr. A 1555 (2018) 10–19.
[20] P. Makoś, A. Przyjazny, G. Boczkaj, Hydrophobic deep eutectic solvents as "green" extraction media for polycyclic aromatic hydrocarbons in aqueous samples, J. Chromatogr. A 1570 (2018) 28–37.
[21] P. Makoś, A. Przyjazny, G. Boczkaj, Methods of assaying volatile oxygenated organic compounds in effluent samples by gas chromatography—A review, J. Chromatogr. A 1592 (2019) 143–160.
[22] A. Miller, T. Wildeman, L. Figueroa, Zinc and nickel removal in limestone based treatment of acid mine drainage: the relative role of adsorption and co-precipitation, Appl. Geochem. 37 (2013) 57–63.
[23] S. Nekouei, F. Nekouei, J.P. Canselier, Solid-phase extraction for simultaneous separation and preconcentration of Fe (III) and Zn (II) traces using three chelatants and Ramelak bark-derived activated carbon as a new bio-sorbent, Sep. Sci. Technol. 52 (2017) 824–833.
[24] M. Rajabi, S. Asemipour, B. Barfi, M.R. Jamali, M. Behzad, Ultrasound-assisted ionic liquid based dispersive liquid–liquid microextraction and flame atomic absorption spectrometry of cobalt, copper, and zinc in environmental water samples, J. Mol. Liq. 194 (2014) 166–171.
[25] P.S. Roldan, I.L. Alcântara, C.C. Padilha, P.M. Padilha, Determination of copper, iron, nickel and zinc in gasoline by FAAS after sorption and preconcentration on silica modified with 2-aminotiazole groups, Fuel 84 (2005) 305–309.
[26] Ş. Saçmac, Ş. Kartal, M. Saçmac, Selective back-extraction and preconcentration of zinc (II) from metal-1, 3, 5-triketone extracts prior to its determination by flame atomic absorption spectrometry, Int. J. Environ. Anal. Chem. 92 (2012) 1626–1637.
[27] S.S. Saei-Dehkordi, A.A. Fallah, Determination of copper, lead, cadmium and zinc content in commercially valuable fish species from the Persian Gulf using derivative potentiometric stripping analysis, Microchem. J. 98 (2011) 156–162.
[28] M.J. Salgueiro, M. Zubillaga, A. Lysionek, M.I. Sarabia, R. Caro, T. de Paoli, A. Hager, R. Weill, J. Boccio, Zinc as an essential micronutrient: a review, Nutr. Res. 20 (2000) 737–755.
[29] L.S. Sapochak, F.E. Benincasa, R.S. Schofield, J.L. Baker, K.K. Riccio, D. Fogarty, H. Kohlmann, K.F. Ferris, P.E. Burrows, Electroluminescent zinc (II) bis (8-hydroxyquinoline): structural effects on electronic states and device performance, J. Am. Chem. Soc. 124 (2002) 6119–6125.
[30] H. Seiler, A. Sigel, H. Sigel, Handbook on Metals in Clinical and Analytical Chemistry, CRC Press, 1994.
[31] A.B. Tabrizi, Cloud point extraction and spectrofluorimetric determination of aluminium and zinc in foodstuffs and water samples, Food Chem. 100 (2007) 1698–1703.
[32] M.A. Tarighat, A. Hasaninejad, G. Abdi, Chemometrics-enhanced micelle-mediated extraction spectrophotometric method for simultaneous determination of cu 2+ and Zn 2+ in medicinal plant, Rice and water samples using continuous wavelet transform, Food Anal. Methods 9 (2016) 1928–1938.
[33] L.S.G. Teixeira, E.S. Santos, L.S. Nunes, Determination of copper, iron, nickel and zinc in ethanol fuel by energy dispersive X-ray fluorescence after pre-concentration on chromatography paper, Anal. Chim. Acta 722 (2012) 29–33.
[34] L.P. Wang, J. Ponou, S. Matsuo, K. Okaya, G. Dodbiba, T. Nazuka, T. Fujita, Selective precipitation of copper and zinc over iron from acid mine drainage by neutralization and sulfidization for recovery, Int. J. Soc. Mater. Eng. Resour. 20 (2014) 136–140.
[35] S. Yılmaz, Ş. Tokalioğlu, S. Şahan, A. Ülgen, A. Şahan, C. Soykan, On-line preconcentration/determination of zinc from water, biological and food samples using synthesized chelating resin and flame atomic absorption spectrometry, J. Trace Elem. Med. Biol. 27 (2013) 85–90.
[36] Z.-Y. Zhang, M. Yang, J. Pawliszyn, S.-P. Microextraction, A solvent-free alternative for sample preparation, Anal. Chem. 66 (1994) 844A–853A.
[37] L. Zhao, S. Zhong, K. Fang, Z. Qian, J. Chen, Determination of cadmium (II), cobalt (II), nickel (II), lead (II), zinc (II), and copper (II) in water samples using dual-cloud point extraction and inductively coupled plasma emission spectrometry, J. Hazard. Mater. 239 (2012) 206–212.
[38] N. Zheng, Automated and High-Throughput Extraction Approaches, Elsevier, Solid-Phase Extraction, 2020.