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Determination of copper (II) in seafood and water samples by ICP-OES using magnetic titanium aluminum carbide nanocomposite for solid phase microextraction

Nebiye Kizil [a,b], Furkan Uzcan [c], Buse Bozan Beydagi [b], Mislina Sahin [d], Bahar Asiye Tokum [d], Mehmet Lutfi Yola [e], Mustafa Soylak [c,*]

[a] Hasan Kalyoncu University, Faculty of Engineering, Department of Basic Sciences, Gaziantep, Turkiye
[b] Hasan Kalyoncu University, Environmental Application and Research Center, Gaziantep, Turkiye
[c] Department of Chemistry, Faculty of Sciences, Erciyes University, Kayseri 38039, Turkiye
[d] Hasan Kalyoncu University, Faculty of Engineering, Department of Industrial Engineering, Gaziantep, Turkiye
[e] Hasan Kalyoncu University, Faculty of Health Sciences, Department of Nutrition and Dietetics, Gaziantep, Turkiye

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ABSTRACT

This study presents a method for the quantitative determination of copper ions (Cu (II)) in various seafood using solid phase microextraction (SPME) with magnetized maximum phase titanium aluminum carbide (Ti_3AlC_2) nanocomposite (MAX phase-MSPE). The aim of this method is to separate copper from the complex matrix environment and ensure a measurable concentration level. Optimized extraction conditions were established, including pH, extraction time, sample volume, and eluent concentration. The analytical significant parameters of the MAX phase-MSPE method have been assessed through limit of detection (LOD), limit of quantification (LOQ), recovery (R%), and certified reference material studies to obtain high accuracy and sensitivity. The LOD, LOQ, preconcentration factor, and relative standard deviation were obtained as 0.37 and 1.2 μg/L, 10, and % 4.1, respectively. The developed method demonstrates high selectivity toward copper ions (Cu (II)) in both food and water samples. This makes the approach particularly suitable for applications in food safety monitoring and environmental analysis, where precise detection and quantification of copper ions are critical.

1. Introduction

Environmental pollution increases exponentially due to the rapid population growth, industrial and agricultural activities. Hence, waters, oceans and seas have also polluted in parallel (Hanifar et al., 2023). Leaching from natural sources into the ecosystems of all living things, these pollutants pose major threats to the universe. Pesticides, dyes, heavy metals and pesticide sources containing heavy metals seriously affect food safety. In particular, heavy metals come from both soil and fertilizers and pesticides, negatively affecting sustainability in environmental samples. Silver, zinc, nickel, copper, cadmium, mercury and chromium, which are classified as heavy metals, should be evaluated to control environmental threats and human health (Khan et al., 2020; Ruzmetov et al., 2025).

Copper is an essential element for living organisms due to its crucial functions such as iron uptake into the human body, remediation of reactive oxygen species, energy and cell signalling metabolism. Hence, copper deficiency expedites some symptoms of disease such as anemia, leukopenia and myeloneuropathy (Kaur and Garg, 2021; Wazir and Ghobrial, 2017). Additionally, copper controls plant development and reproduction in the agricultural sector. Because copper absence can affect photosynthesis, reproduction, and protein intake, it is important to increase the quantity of this element (Chandra et al. 2018). On the other hand, humans exposed to excessive metals may have health problems like hypertension, memory loss, and speech problems (Sesli et al., 2008; Abdelrahman et al., 2025). Among the environmental pollutants, copper can lead to liver and renal problems, lung cancer, gastrointestinal problems, and mucous irritation. On account of the fact that the excretion of copper from the body is very slow, only 10 per cent in 72 hours, high doses of are a permanent problem for humans (Osredkar and Sustar, 2011). Therefore, the acceptable level of copper ions (Cu(II)) in drinking water has been set at 1.3 mg L^{-1} by the US

* Corresponding author.
E-mail address: soylak@erciyes.edu.tr (M. Soylak).

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Environmental Protection Agency (USEPA). Environmental concentrations of Cu (II) can be hazardous at levels of up to 0.15 mg L^{-1} for fish and 0.01 mg L^{-1} for invertebrates (Manne et al. 2022). Consequently, Cu (II) must be ascertained in food and diet samples, pharmaceutical products, and biological and water samples due to their essential properties for body functions and toxic effects.

In order to determine Cu(II) ions spectrometric methods such as UV-Vis spectrophotometry, inductively coupled plasma-mass spectrometry (ICP-MS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-optical emission spectrometry (ICP-OES) and flame atomic absorption spectrometry (FAAS) are performed. However, the low concentrations and interference effects of heavy metals make these determinations difficult to be accurate. For this reason, different extraction methods are tried before analysis. The primary ones are liquid-liquid extraction (LLE) and solid phase extraction (SPE), chemical precipitation, cloud point extraction (CPE) are used for the determination of Cu (II) ions in food and water matrices (Alsohaimi et al., 2024; Vaezi and Dalali, 2024; Khan et al., 2020). However, the disadvantages are the long extraction time, the excessive use of solvents and the toxicity of chemicals. Micro-extraction methods developed on the basis of green chemistry principles, which do not have these disadvantages, have recently become popular (Soylak et al., 2024). Many studies related to solid phase microextraction (SPME) and liquid phase microextraction (LPME) methods have been optimized to investigate the analysis of Cu (II) ions (Kariri et al., 2025; Alsohaimi et al., 2024; Sun et al., 2023).

Dispersive micro-solid phase extraction (d-μSPE) for the determination and preconcentration of trace elements has become one of the favorite microextraction methods because it is simple, solvent-free, rapid and sensitive (Ozalp and Soylak, 2023). It is frequently preferred because it is more cost-effective than traditional methods (Dugheri et al., 2021). For instance, Alsohaimi and colleagues in 2023 have carried out magnetic ionic liquid-based d-μSPE method using sulfanilic acid-modified magnetic graphene oxide effervescent tablets for extraction of heavy metals from aqueous samples. In that study, the researchers have developed the d-μSPE method to analyze heavy metals using ICP-OES in fish samples (Bozorgzadeh et al., 2021). The most important step of these studies is the selection of the absorbent suitable for microextraction. Therefore, many adsorbents such as biosorbents, fibers, graphene, carbon nanotubes, metal oxides, magnetic nanoparticles, and metal-organic frameworks (MOFs) have been studied (Uzcan and Soylak, 2024; Verma et al., 2023; Escudero et al., 2016; Xu et al., 2016; Giakisikli and Anthemidis, 2013; Pyrzynska, 2010).

Max phases as crystalline layered carbides or nitrides with hexagonal symmetry are one of the sorbents used in the d-μSPE method. These compounds, also referred to as layered ternary compounds, have the general formula $Mn_{n+1}AX_n$, where M represents an early transition metal (e.g., Sc, Ti, V, Cr), A denotes a IIIA or IVA group element (e.g., Al, Si, Ga), X is either carbon (C) or nitrogen (N), and n ranges from 1 to 3 (Hu et al., 2013). They are similar to ceramics because of their thermal stability, high melting points and excellent strength. They have all the excellent properties sought after as a sorbent, such as environmental stability, non-toxicity, low cost and ease of synthesis (Ge et al., 2003; Hu et al., 2013). Additionally, the max phase has more different functional groups, high recovery performance, excellent processability, increased chemical resistance e.g. than other conventional adsorbents such as zeolites, silica gel, activated carbon, and some ion-exchange resins (Thaveemas et al., 2024). Another significant feature of MAX phases is their ability to form a wide range of isostructural compositions by substituting M, A, and X with different elements (Ali et al., 2021; Miao et al., 2020). The MAX phases have been employed in the extraction and analysis of a wide variety of organic and inorganic compounds, including polycyclic aromatic hydrocarbons (Li et al., 2023; Ghaemmaghami et al., 2020), bisphenol A (Sanko et al., 2022), pesticides (Khosrowshahi et al., 2022), triadimenol and iprodione (Esrafili et al., 2022), cadmium (Uzcan and Soylak, 2024; Khan et al., 2022), lead (Kori et al., 2024, Khan et al., 2022), chromium, palladium, lead (Kori et al., 2024, Khan and Soylak, 2023; Ullah et al., 2021), catecholamines (Yang et al., 2024), aromatic hydrocarbons, parabens (Jiang et al., 2024; Mousavi et al., 2024), fluorouracil (Sundaresan et al., 2024), heavy metals (Bagheri et al., 2022), and numerous other organic and inorganic species. On the other hand, the material was used as an adsorbent for the removal of azo dye Basic Red 46 from wastewater (Aksoy, 2024).

This study focuses on the synthesis of a magnetic Ti_3AlC_2 MAX-phase nanomaterial for the analysis of Cu (II) ions in various fish species and water samples. Following the characterization of the adsorbent, its performance in enriching the target analytes via d-μSPE microextraction was evaluated. After successfully applying the MAX phase-MSPE method, the concentrations of Cu (II) ions in real samples that were categorized and evaluated seafood as both packaged, frozen and fresh-seafood were determined using ICP-OES.

Our literature review indicates that the use of the magnetic Ti_3AlC_2 MAX-phase as an adsorbent in solid-phase extraction studies remains limited and even this adsorbent is almost not used in the analysis of Cu (II) ions. Given its broad applicability across in various fields, this material shows potential for the separation and determination of Cu(II) ions without ligand in complex matrices such as seafood. Its unique properties and ability to be easily magnetized have been the keys to the improvement of analytical performance.

2. Experimental

2.1. Reagents and instruments

The ultrapure water utilized in the ICP-OES measurements for this MSPE method, developed with all chemicals of analytical purity, was sourced from the Mp Minipure Dest water purification system (Ankara, Turkiye). The stock solutions containing Cu (II) ions were prepared by diluting solutions procured from VHG Labs, Inc., Manchester, New Hampshire, USA. Suprapure nitric acid (HNO_3, 65 %), employed as the eluent in all experiments, was obtained from Merck (Darmstadt, Germany). Sodium phosphate monobasic dihydrate ($NaH_2PO_4{\cdot}2H_2O$) from Carlo Erba Reagents (France) and sodium phosphate dibasic heptahydrate ($Na_2HPO_4{\cdot}7H_2O$) from Sigma-Aldrich (India) were used for the preparation of the buffer solution. Finally, the titanium aluminum carbide (Ti_3AlC_2) Max Phase with a purity of 99 % was supplied from Nanografi in Ankara, Turkiye.

Furthermore, several devices, such as Thermomac brand (MIO101002) vortex, Nuve brand water distiller ND-4, XB 220 A Precisa model brand ultrasonic bath model, NF 400 Nuve brand (Ankara, Türkiye) centrifuge, and Hanon Instrument Tank Basic microwave reaction system (Hanon, China), were employed in this SPME method, optimized for the separation and preconcentration of trace elements in seafood samples. Finally, the Perkin Elmer optima 8000 model of ICP-OES (PerkinElmer, Inc., Shelton, CT, USA) was utilized for determination of the trace level of Cu (II) ions.

2.2. Synthesis of Fe_3O_4/Ti_3AlC_2 MAX phase material

Magnetic nanoparticles (Fe_3O_4) were deposited on the Ti_3AlC_2 max phase using the in situ magnetization technique. In this procedure, 1.0 g of Ti_3AlC_2 max phase was gathered and added to 1.5 g of $FeCl_3$ and 2.75 g of $FeSO_4.5H_2O$ in double-distilled water. Then, this mixture was also exposed to ultrasonication for two hours at 80 °C. For the synthesis of the Fe_3O_4-Ti_3AlC_2 MAX phase, 20 mL of a 17 % ammonia solution was incrementally introduced to the reaction mixture through a dropwise addition. The final product was isolated from the aqueous solution employing a magnetic field and subsequently washed with water and ethanol to remove unreacted components. The MAX phase composite (Fe_3O_4-Ti_3AlC_2) was subjected to a temperature of 90 °C in an oven for a duration of twenty-four hours (Khan et al., 2022).

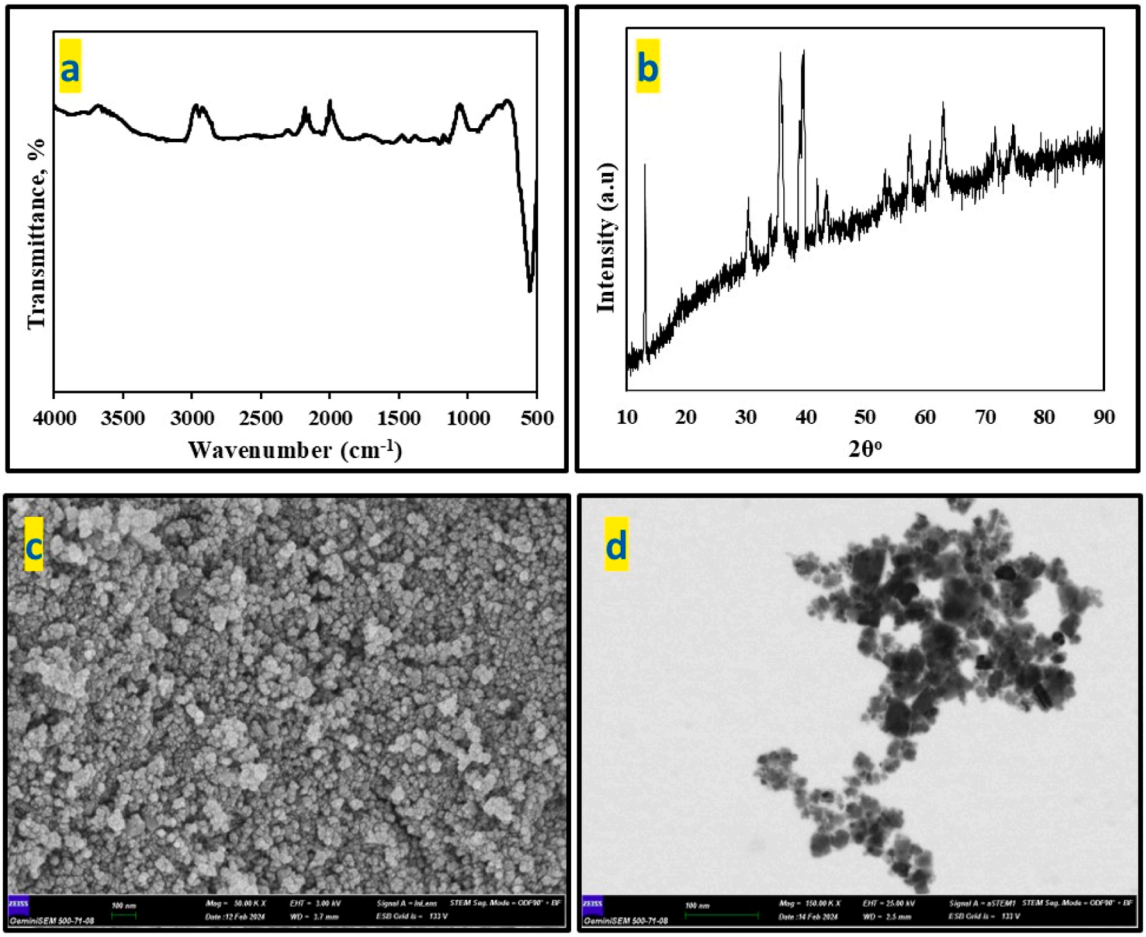

Fig. 1. FT-IR spectra (a), XRD image (b), SEM image (c) and STEM image of Fe_3O_4@Ti_3AlC_2 (d).

2.3. Sample preparation

The Max phase-MSPME method was employed for analysis and preconcentration of Cu (II) ions in seafood types categorized as frozen, canned, and fresh-sea fish under optimal conditions. Prior to analysis, solid samples were converted to a homogeneous liquid form using a microwave-assisted sample preparation process. Before the analysis, the fish samples were stored at −20 °C without bones, skin and internal organs (Subotić et al., 2013). Hence, 1 g of fish samples were weighed, and then 16 mL of 65 % nitric acid (HNO_3) and 1 mL of hydrogen peroxide (H_2O_2) were added. And then, the microwave heating method was applied to them (400 PSI, 15 min., 180 °C). The solubilized samples were filtered through a 0.45 μm microfiber filter, diluted, and prepared for the SPME analysis.

The wastewater and well water samples were prepared by filtering for implementation of the Max phase method. Otherwise, the tap water and drinking water samples were analyzed without any treatment. The recovery studies were also conducted to these water samples.

2.4. SPME procedure

The MAX phase-MSPME method started with synthesis of the nanomaterial for the extraction of Cu (II) ions from seafood, water, and wastewater samples, followed by optimization and implementation on the mentioned samples. Detailed descriptions of the material synthesis can be found in the section synthesis of Fe_3O_4/Ti_3AlC_2 max phase material, and the comprehensive methodology is summarized below.

The procedure involves precise weighing of the Ti_3AlC_2 magnetized material, preparation of reference solutions and subsequent steps to provide efficient adsorption and desorption of analytes for analysis. Ti_3AlC_2 nanocomposite material was weighed 20 mg each into 50 mL test tubes. Afterwards, solutions containing Cu (II) ions at known concentrations were prepared by diluting 1000 mg/L stock solution. Test tubes, containing 8 mL of pure water, 1 mL of pH 7 buffer solution, 25 μg/L stock solution and 20 mg adsorbent, were filled up to 10 mL. The prepared model solutions were ultrasonically stirred for 5 min. for adsorption of Cu (II) ions on the surface of the material. Then, all mixtures were centrifuged for 3 min. to effectively separate the solid phase, which contained the adsorbed analyte, from the liquid phase. Following the decantation of the liquid phase, desorption was carried out by adding 3 mL of 0.1 M HNO_3 to the solid material. The final phase containing the extracted Cu (II) ions was analyzed by the ICP-OES analytical technique.

3. Results and discussion

3.1. Characterization results of Fe_3O_4/Ti_3AlC_2 maxphase nanocomposite

The adsorbent Fe_3O_4-Ti_3AlC_2 magnetic max-phase has been characterized via Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Scanning Transmission Electron Microscopy (STEM), and X-Ray diffraction (XRD) techniques.

The FTIR spectra of the generated sorbent sample are shown in Fig. (1a). Ti–C bonds are characterized by lower ionicity in the carbides. The charge states of carbon and titanium are nearly the same due to a small shift in electron density in the direction of the carbon atoms. As a result, in IR spectroscopy, the Ti–C (Me–C) bond vibrations are weakly active. Vibrations in the infrared spectrum can become more intense due

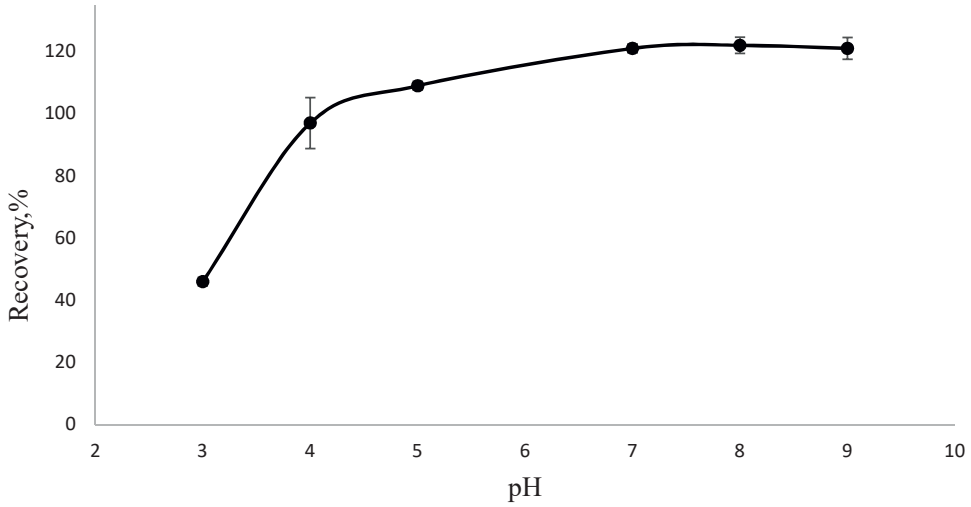

Fig.2. The optimization of pH (n: 3, adsorbent amount: 20 mg, eluent volume and concentration: 3 mL and 0.1 M).

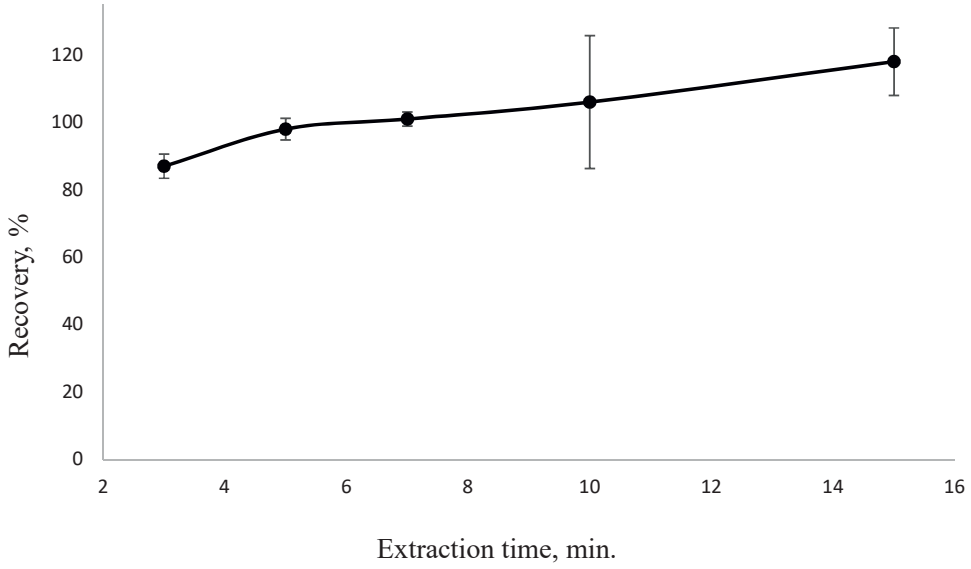

Fig. 3. The optimization of extraction time (pH:7, n: 3, adsorbent amount: 20 mg, eluent volume and concentration: 3 mL and 0.1 M).

to structural defects such as oxygen, TiO_x surface layers, or unoccupied places that change the polarity of the Ti-C bonds. Stretching vibrations of C═O bonds arise in the band about 1620 cm^{-1} (Uzcan and Soylak, 2024; Khan et al., 2022). In addition, the placed XRD patterns crystallographic planes and SEM image are similar to previous analysis (Fig.1b, c) (Uzcan and Soylak, 2024; Ullah et al., 2021). Every diffraction peak is consistent with JCPDS and shows a good match with the reference (Su et al., 2024; Deepthi et al., 2023). The STEM image indicates that the structure is nanoscale as well (Fig. 1d).

3.2. *Influence of pH*

Prior to the application of the Max phase MSPME procedure to real samples parameters such as adsorption-desorption duration, pH value, acid solution concentration, and sample volume have been optimized. Among these, the pH of the extraction medium is the most critical parameter owing to the fact that it can generally affects the interactions between Cu (II) ions and adsorbent. In order to commentate the pH effect on extraction efficiency of Cu (II) ions model solutions were prepared by adjusting the pH between 3 and 9. These experiments aimed to determine quantitative pH to obtain maximum Cu (II) ions recoveries from real samples. As illustrated in Fig. 2, quantitative results were obtained after pH 7 medium in the Max phase MSPME method. Subsequent optimization studies were conducted at this pH level to ensure consistency and efficacy in the Cu (II) ions extraction process.

3.3. *The optimization of extraction time*

The extraction time was another important optimization parameter as it affects removal efficiency of Cu (II) ions in the Max phase-MSPME method. Hence, the investigation focused on the optimization of both adsorption and desorption times to enhance the extraction efficiency. In this study, which was conducted via ultrasound assisted, model solutions were subjected to an ultrasonic bath for durations ranging from 3 to 15 min. The optimization of the extraction time curve illustrate that an extraction duration of 5 min is sufficient for this Max phase-MSPME method without any interferences (Fig.3). This means that the acid resistance of the max-phase and analyte adsorbent balance is good. Lastly, the acceptable recoveries of could be achieved up to 10 min. The dissolution of the adsorbent after 10 min. brings about an excessive increase in Cu (II) recoveries. Therefore, the adsorbent may have transformed into an unstable form. So, the Max phase-MSPME method

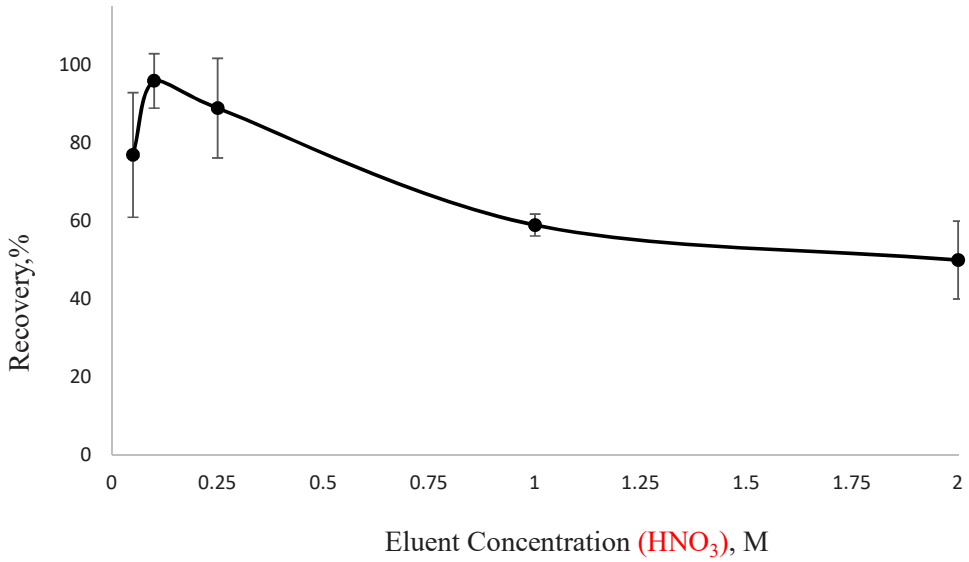

Fig. 4. The optimization of eluent concentration (pH:7, n: 3, adsorbent amount: 20 mg, eluent volume: 3 mL).

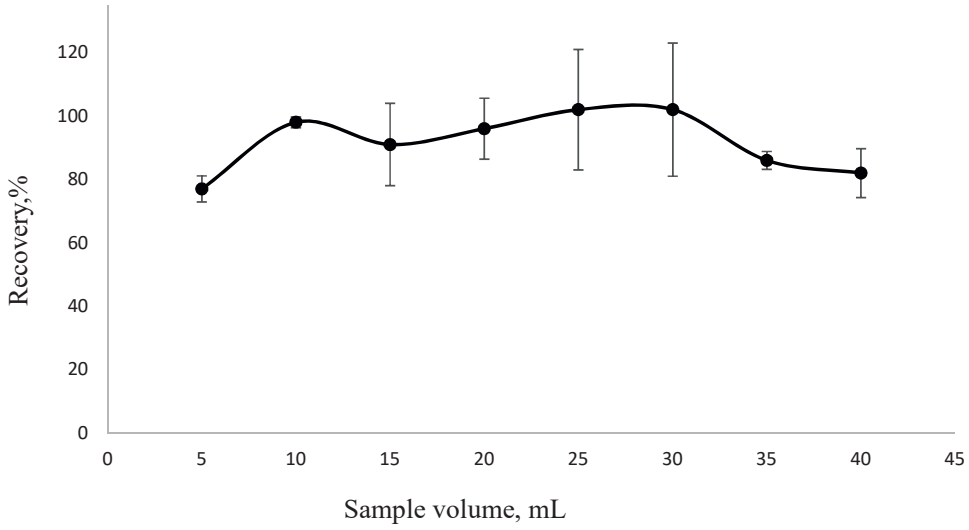

Fig. 5. The optimization of sample volume (pH:7, n: 3, adsorbent amount: 20 mg, eluent volume and concentration: 3 mL and 0.1 M).

was carried forward with sonication support for a duration of 5 min.

Furthermore, centrifugation times of 3–10 min. have been studied to eliminate the solid phase from the aqueous phase. Recoveries obtained in the range of % 106–118 proved that the centrifugation time was insignificant for the Max phase-MSPME method.

3.4. Optimal HNO_3 concentration for elution

Desorption studies for the SPME method were carried out by adjusting the molar concentration of the HNO_3 solution. The goal was to find a concentration that would efficiently separate the analyte from the adsorbent while avoiding any interference effects caused by dissolution of the material. To this end, the impact of HNO_3 elution solutions with molar concentrations ranging from 0.05 to 2.0 M was evaluated. Fig. 4 indicates that the highest recovery rates were achieved with a concentration of 0.1 M HNO_3. In contrast, higher concentrations proved detrimental to the effectiveness of Maxphase-MSPME method, probably owing to the dissolution of the metal-based material.

3.5. Optimizing sample volume for effective results

The determination of peak sample volume is vital to figure out application of the Max phase-MSPME method to extract trace concentrations of Cu (II) ions at the highest sample volumes. Furthermore, the sensitivity and efficiency of the Maxphase-MSPME method are improved by increasing the sample volume to achieve high preconcentration/enrichment factor (Soylak et al., 2007; ALOthman et al., 2016; Anyat et al., 2025).

To address sample volume affect, model solutions were prepared with volumes ranging from 5 to 40 mL. Aftermath, the Maxphase-MSPME method was applied to these mixtures. Quantitative recoveries were successfully obtained for volumes up to 30 mL, as illustrated in Fig. 5. Since the final eluent volume was 3 mL, a 10-fold preconcentration factor was calculated.

3.6. Influence of matrix effects on analytical results

In order to validate the selectivity of the Fe_3O_4@Ti_3AlC_2 Max phase MSPME procedure, the highest concentrations that can be studied in the

Table 1
Tolerance concentration of foreign ions for analysis of copper ion (pH:7, n: 3, adsorbent amount: 20 mg, eluent volume and concentration: 3 mL and 0.1 M).

Matrix ion	Concentration, μg L^{-1}	Recovery, %
Na^{+}	10000	100 ± 9[a]
K^{+}	10000	85 ± 5
Ba^{2+}	1000	112 ± 1
Co^{2+}	5000	100 ± 2
Fe^{+2}	1000	100 ± 5
Pb^{+2}	1000	87 ± 5
Cr^{+3}	100	93 ± 4
Mn^{+2}	10000	116 ± 4

[a] Mean ± standard deviations

Table 2
Real sample analyses results performed with the Max phase-MSPME method (pH:7, n: 3, adsorbent amount: 20 mg, eluent volume and concentration: 3 mL and 0.1 M).

Samples name/Type of supply	Concentration (μg g^{-1})
Mackerel/ Frozen	2.88 ± 0.06
Anchovy/ Frozen	2.80 ± 0.24
Sardine/ Canned	2.02 ± 0.07
Tuna fish/ Canned	2.02 ± 0.03
Smelt fish/ fresh-sea fish	1.94 ± 0.03
Leerfish/ fresh-sea fish	1.94 ± 0.03
Shrimp/ fresh-sea fish	2.52 ± 0.16
Atherina fish/ fresh-sea fish	2.02 ± 0.03
Sea bream/ fresh-sea fish	2.48 ± 0.70
Crab leg/ fresh-sea fish	2.20 ± 0.09

[a] N.D.: Not Detected

presence of some inorganic species (metal ions) were determined. For this, the matrix effect of the method was interpreted (Ghaedi et al., 2010) according to the results obtained by increasing the concentrations of ions such as Ba^{2+}, Co^{2+}, Fe^{+2}, Pb^{+2}, Cr^{3+}, Mn^{2+}. The tolerance concentration values for the matrix medium listed in Table 1 were calculated such that the lowest recoveries were 87 %. The calculated high recovery findings indicate that the Max phase-MSPME method demonstrates good performance in the presence of these interfering ions, confirming its selectivity and effectiveness for the extraction of trace concentration of 25 μg/L Cu (II) ions in complex matrices.

3.7. Validation and analytical performance of the method

The optimized Max phase-MSPME method proved effective to separate and preconcentrate Cu (II) ions in various seafood, including mackerel, anchovy, sardine, tuna, shrimp, sea bream, and crab. According to the results presented in Table 2, Cu (II) ions have been detected in all fish species analyzed. The analyte concentration was calculated to be higher in frozen fish products than in sea fish. Some research articles have also ascertained similar results. For instance, the highest level of copper was found as 4.93 mg/kg in a study (Bilandžić et al., 2012). Also, the calculated results were similar to average copper concentration levels in fish samples (mg/kg) ranging from: 1.4–2.4 (Turkiye), 0.918–2.314 (Spain), 0.68–8.78 (Spain, the Netherlands and Portugal), 0.05–4.43 (Turkiye), 0.346–1.840 (Turkiye), 0.40–3.59 (Libya) (Attaf et al., 2025; Artar et al., 2024; Töre et al., 2021; Olmedo et al., 2013; Mendil et al., 2010). The average copper levels in the analyzed fish samples were calculated to be lower than the maximum copper content limit of 20 mg/kg created by the MAFF (Ministry of Agriculture, Fisheries and Food) and 30 mg/kg by WHO (1996) (Bilandžić et al., 2012).

Furthermore, environmental water, drinking water, and wastewater samples were tested in order to assess the accuracy of the Fe_3O_4@-Ti_3AlC_2 Max phase MSPME procedure. The wastewater samples have been pretreated by filtration using a 0.45 μm cellulose membrane.

Table 3
Addition-recovery application for recovery verification in water samples (pH:7, n: 3, adsorbent amount: 20 mg, eluent volume and concentration: 3 mL and 0.1 M).

Samples	Added (μg mL^{-1})	Found (μg mL^{-1})	Recovery (%)
Drinking water	0.000	N.D[a]	-
	0.042	0.047 ± 0.020	112
	0.083	0.070 ± 0.012	84
	0.167	0.188 ± 0.001	112
Tap water	0.000	0.150 ± 0.003	-
	0.083	0.233 ± 0.002	100
	0.167	0.337 ± 0.001	112
Wastewater1	0.000	0.018 ± 0.010	-
	0.027	0.044 ± 0.000	96
	0.056	0.074 ± 0.003	100
Wastewater2	0.000	N.D	-
	0.027	0.024 ± 0.001	89
	0.056	0.053 ± 0.010	95
Well water	0.000	0.004 ± 0.000	-
	0.007	0.010 ± 0.003	86
	0.028	0.034 ± 0.001	107

[a] N.D.: Not detected

Table 4
CRM analysis by using presented method (pH:7, n: 3, eluent volume: 3 mL, adsorbent amount: 20 mg, eluent concentration: 0.1 M).

CRM Sample	Certified Value (μg/g)	Found (μg/g)	Recovery, %
NIST 1549 Milk Powder	0.638 ± 0.049	0.66 ± 0.05	103.4

Firstly, water samples have been analyzed without spike Cu (II) solutions. On account of the fact that the wastewater is dyeing factory wastewater, Cu (II) ions are calculated at low concentrations. On the other hand, the level of analyte was ascertained high concentration in tap water due to the pollution of the equipment used for water transmission. Furthermore, addition/recovery studies were conducted by spiking known concentrations of analytes into the water samples. The recoveries, ranging from 86 % to 112 %, as shown in Table 3, indicate that the SPME method is reliable for water sample applications, demonstrating successful extraction and quantification of the target metals.

The Certified Reference Material (CRM) was analyzed in order to assess the accuracy of the method. Hence, the CRM was selected with known concentrations. The CRM was homogenized like section sample preparation using the microwave-assisted sample preparation method (400 PSI, 200 °C, 20 min.). Specifically, 1 g. of each CRM sample was weighed into a beaker and then 10 mL of nitric acid (HNO_3) was added to them. After the formation of yellow acid fumes, 1 mL of hydrogen peroxide (H_2O_2) was added to eliminate them. All the CRMs were filtered for the Fe_3O_4@Ti_3AlC_2 MAX phase MSPME procedure. The results are presented in Table 4.

The analytical performance of the Maxphase-MSPME method was evaluated using key parameters such as relative standard deviation (RSD), limit of detection (LOD), limit of quantification (LOQ), and preconcentration factor (PF). The calibration curve of Cu (II) ions for ICP-OES was given in Supplementary Figure S1. For copper, the RSD, LOD (liquid), LOD (solid), and LOQ (liquid), LOQ (solid) were determined to be % 4.1, 0.37 μg/L, 1.11 μg/kg, 1.24 μg/L, 3.72 μg/kg respectively. The preconcentration factor (PF) of the Maxphase-MSPME method was calculated as 10, calculated by dividing the maximum feasible sample volume by the final volume obtained through optimization. Furthermore, the Maxphase-MSPME method has been implemented to the model solutions in 10 replicates in order to evaluate the reusability of magnetic max-phase adsorbent. After 6th use of the max-

Table 5
The analysis of the Other Studies Comparison of MAX phase-MSPME method.

Extraction Metod	Type of adsorbent	Analytical method	pH	LOD[a]	PF[b], (EF)[c]	Recovery, %	Sample	References
Magnetic solid phase microextraction	Magnetic graphene oxide hybrid material	AAS	5–7	4.0 μg L^{-1}	20	95–103	Water, black tea and diet supplements	(Ozkantar et al., 2020)
Membrane solid phase microextraction	Alumina hollow fiber	ICP-OES	8.5	0.88 ng. mL^{-1}	10	87.4–110.2	Water samples	(Cui et al., 2011)
Dispersive solid-phase microextraction	Magnetic MoS_2-Fe_3O_4 nanocomposite	FAAS	6–8	1.8 μg·L^{-1}	35	98–104	Chamomile poppy seed and water samples	(Baghban et al., 2017)
Magnetic solid-phase extraction	β-cyclodextrin decorated magnetic composite	FAAS	6	2.2 μg L^{-1}	50	92.7–102.5	Water and food samples	(Shan et al., 2024)
Magnetic Dispersive Solid Phase Extraction	Magnetic XAD−16 chelating resin	AAS	6	10.24 μg L^{-1}	25	90–101	Water and food samples	(Ozalp and Soylak, 2021)
Solid Phase Extraction	Silica gel with the Schiff base	FAAS	7	0.45 μg L^{-1}	28.2	98–114	Water samples	(Imamoglu, 2023)
Maxphase-MSPME method	Max phase magnetic titanium aluminum carbide nanocomposite	ICP-OES	7	0.37 μg L^{-1}	10	86–112	Water and seafood samples	This study

LOD [a]: Limit of detection, PF [b]: Preconcentration factor, EF [c]: Enrichment factor

phase, the recovery of Cu (II) ions has decreased to 60.4 %. The results were shown in Fig. S2.

4. Conclusions

The Fe_3O_4@Ti_3AlC_2MAX phase adsorbent was synthesized in this novel microextraction approach. The Max phase-MSPME method was utilized to amend different real sample mediums in the analysis of Cu (II) ions process. Furthermore, the method was applied to mackerel, anchovy, sardine, tuna, shrimp, sea bream, and crab samples to define Cu (II) ion concentration levels. The addition and recovery experiments were implemented on various water samples (drinking water, tap water, wastewater, and well water) in order to prove the accuracy of the microextraction procedure. All experiments have been successfully performed under optimum circumstances. The other separation and preconcentration procedures for Cu (II) ions have been remarkably delved into to compare the analytical parameters of this study. Innovative materials have been synthesized in recent studies in order to analyze Cu (II) ions. According to a set of results listed in Table 5, the current study offers lower LOD and higher recovery values. This result demonstrates the outstanding performance of the Max phase-MSPME method in the analysis of some organic and inorganic species at low concentrations. In addition, Cu (II) analysis was carried out in different comprehensive matrix mediums, such as seafood samples categorized as frozen, canned, and fresh- sea fish, under optimal conditions. After all, a pH 7 experimental environment offers the advantage of a potential use of the method even in complex matrices as well. The Max phase-MSPME method has some pros, including low solvent consumption, good adsorption and desorption capability without ligand, and a short time compared to conventional methods.

CRediT authorship contribution statement

Kizil Nebiye: Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition. **Uzcan Furkan:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Beydagi Buse Bozan:** Writing – original draft, Investigation. **Sahin Mislina:** Writing – review & editing, Writing – original draft, Investigation. **Tokum Bahar Asiye:** Writing – original draft, Investigation. **Yola Mehmet Lutfi:** Writing – review & editing, Writing – original draft, Investigation. **Soylak Mustafa:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2025.107541.

Data Availability

No data was used for the research described in the article.

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