



Analytical Methods

Synthesis of polystyrene-polyricinoleic acid copolymer containing silver nano particles for dispersive solid phase microextraction of molybdenum in water and food samples

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ABSTRACT

Polystyrene-polyricinoleic acid copolymer containing silver nano particles (AgPSruci) was synthesized and used in separation of molybdenum from different aqueous and foodstuff samples during a dispersive- μ -solid phase extraction approach. The synthesized nano particles were verified using Fourier transform infrared spectroscopy. An electrothermal atomic absorption spectrometry has been used for measurement of the studied ions. AgPSruci amount pH, sample volume, elution solvent kind, and the time of extraction were the effective parameters that were optimized by one-variable-at-one-time method. Analytical data of the method was calculated and limit of detection, relative standard deviation, limit of quantification were $0.022 \mu\text{g L}^{-1}$, 2.9%, 150, and $0.066 \mu\text{g L}^{-1}$, respectively. The synthesized adsorption capacity was obtained 170 mg g^{-1} . Accuracy of the method was studied by performing the method on certified reference materials and the presence of different interfering ions was studied. Molybdenum content of different water and foodstuffs was determined by the introduced method.

1. Introduction

Mo(VI) is an important biologically crucial trace element for human. It is essential for plants as it plays as a co-factor for various enzymes like xanthine, sulfite and aldehyde oxidase or nitrate reductase (Machado & Tissot, 2020; Tissot, Torres, & Knochen, 2017). Molybdenum is used in industrial process such as pigments, glass, metal alloys, ceramics, welding rods, lubricants, fertilizer, and fossil fuels. Mines containing molybdenum and pretreatment procedures are major sources of contamination (Shamsipur & Habibollahi, 2010). Required daily amount of it for adults is about $25 \mu\text{g}$ (Li, Zhao, Guan, & Liu, 2006). Low amounts of molybdenum are necessary element, but it can be toxic for plants, animal, or human at higher amounts (Kara & Karadas, 2015). It may cause gastroenterological disorders and cardiac failure (Snigur, Chebotarev, Duboviy, Barbalat, & Bevziuk, 2018). The other important molybdenum source is drinking water. World Health Organization (WHO) recommends maximum molybdenum concentration as $70 \mu\text{g L}^{-1}$

for drinking water (World Health Organization, 2006).

Inductively coupled plasma (ICP)-atomic emission spectrometry (Barros, Aguirre, Kovachev, Canals, & Nóbrega, 2016), ICP-mass spectrometry (Zhang et al., 2020), spectrophotometer (Snigur et al., 2018), adsorptive anodic stripping voltammetry (Rojas-Romo, Aliaga, & Arancibia, 2020), electrothermal atomic absorption spectrometry (ETAAS) (Machado & Tissot, 2020), atomic absorption spectrometry with flame atomization (Gürkan, Korkmaz, & Altunay, 2016) have been used in the determination of molybdenum in diverse matrices. Significant advantages of ETAAS like sensitivity, cheapness, automation for sampling and easy operation can be found in the determination of molybdenum.

There are main problems including low concentration levels of analytes and high matrix effects in the determination of molybdenum ions in the sample matrix by using ETAAS. To overcome these restrictions, extraction and preconcentration procedures consist of solid phase extraction (Nomngongo, Ngila, Kamau, Msagati, & Moodley, 2013), cloud point extraction (Gürkan et al., 2016), dispersive

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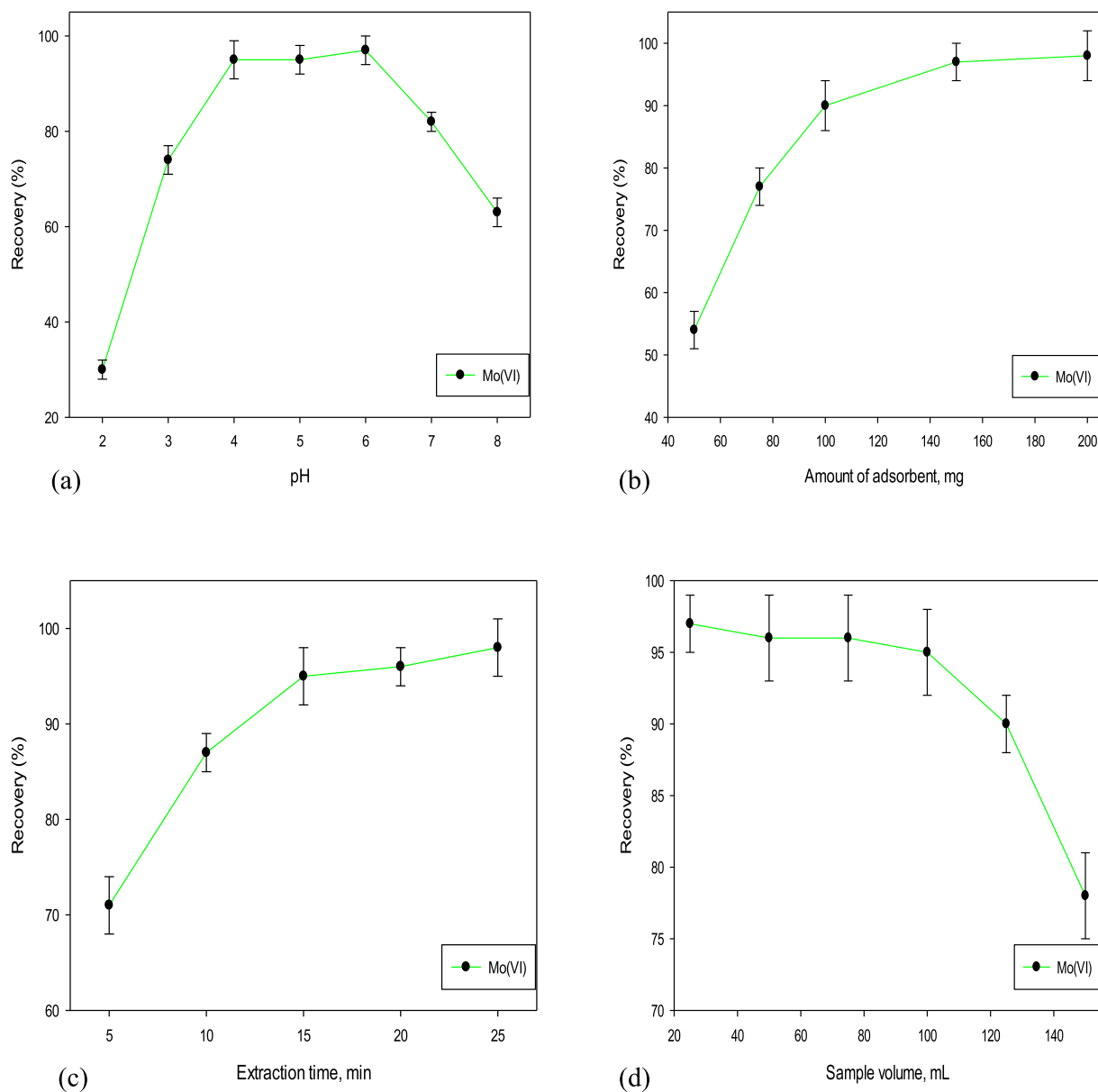


Fig. 1. (a) Effect of pH on the recovery of Mo(VI), (b) Effect of amount of adsorbent on the recovery of Mo(VI), (c) Effect of extraction time on the recovery of Mo(VI), (d) Effect of sample volume on the recovery of Mo(VI).

Table 1

Tolerant limits of foreign ions for the determination of $0.5 \mu\text{g L}^{-1}$ Mo(VI), $N = 3$.

Foreign ions	Tolerance limits	Recovery (%)
Cl^-	20,000	95 ± 2
Na^+	12,000	96 ± 3
$\text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$	4000	97 ± 2
SO_4^{2-}	3000	95 ± 2
NO_3^-	2500	95 ± 3
$\text{PO}_4^{3-}, \text{CO}_3^{2-}$	1000	95 ± 2
$\text{Pb}^{2+}, \text{Cd}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Mn}^{2+}$	100	96 ± 2
$\text{Cr}^{3+}, \text{Fe}^{3+}, \text{Co}^{2+}, \text{Ni}^{2+}$	50	95 ± 2
$\text{Al}^{3+}, \text{As}^{3+}, \text{Sb}^{3+}$	25	95 ± 2

liquid–liquid microextraction (DLLME) (Machado & Tissot, 2020; Silva, Sá, Higuera, & Nogueira, 2021), liquid–liquid microextraction (Salehi, Tavakoli, Aboutalebi, & Samim, 2019), and solidified floating organic drop microextraction (Tuzen, Shemsi, & Bukhari, 2017) are necessary prior to determination of molybdenum. DLLME method is contained

Table 2

Analytical results for determination of Mo in certified reference material ($N = 5$).

CRM	Reference value \pm standard deviation	Measured value \pm standard deviation	Recovery (%)
NIST-1568a Rice Flour ($\mu\text{g kg}^{-1}$)	1451 ± 48	1378 ± 66	95 ± 2
GBW 07,605 Tea ($\mu\text{g kg}^{-1}$)	38 ± 0.39	36.3 ± 2.4	96 ± 3

toxic organic solvents such as carbon tetrachloride, chloroform, tetrachloroethane, etc. These solvents are dangerous and harmful for environmental event at trace levels. A mixture of disperser and extraction solvent is used for extraction of the analyte ions from sample solution, during DLLME. The analyte ion must form a complex by a ligand to transfer into the organic extraction solvent. Dispersive solid phase microextraction (DSPME) has become popular as an alternative technique to other techniques that use organic solvent and involve the

Table 3

Standard addition approach and their recoveries for samples of water, beverage and milk N = 4.

Samples	Spiked ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water	–	$2.8 \pm 0.1^*$	–
	5	7.6 ± 0.4	97 ± 3
	10	12.2 ± 0.9	95 ± 3
Mineral water	–	10.5 ± 0.8	–
	5	14.7 ± 1.1	95 ± 3
	10	19.9 ± 0.8	97 ± 2
Orange juice	–	14.2 ± 0.6	–
	5	18.5 ± 1.3	96 ± 3
	10	23.7 ± 1.8	98 ± 3
Cow's milk	–	5.6 ± 0.1	–
	5	10.8 ± 0.7	97 ± 1
	10	15.1 ± 0.9	97 ± 2
Sheep's milk	–	8.9 ± 0.1	–
	5	13.2 ± 0.7	95 ± 2
	10	18.5 ± 1.2	98 ± 3

*mean \pm SD

Table 4

The determination of molybdenum in food samples after the application of the presented procedure, N = 4.

Samples	Molybdenum amount ($\mu\text{g kg}^{-1}$)
Cultivated mushroom	$35.1 \pm 2.3^*$
Rice	47.4 ± 3.8
Canned fish	98.1 ± 6.2
Canned tomato	49.1 ± 4.3
Green tea	115.2 ± 11.1
Black tea	189.4 ± 17.5
Cereal	53.8 ± 4.1
Egg	69.1 ± 3.7
Chicken meat	97.2 ± 7.6
Cow's meat	128.7 ± 10.5
Olive oil	49.3 ± 3.6
Boiled wheat	82.6 ± 5.1
Potato	94.8 ± 6.4
Onion	72.5 ± 3.3
Garlic	101.4 ± 8.2
Spinach	145.2 ± 11.8
Broccoli	55.7 ± 4.6
Corn	31.5 ± 1.8
Butter	17.3 ± 1.2

*mean \pm standard deviation

heating step. The DSPME has some advantages such as highly selective, high enhancement factor, fast, low cost, green and environmentally friendly and there is no need chelating reagent.

Table 5

Comparison of analytical performance of present DSPME method with other methods.

Analytical technique	Detection system	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	Enrichment factor	Time (min)	References
CPE	Ultraviolet–visible spectrophotometry	50	2.7–3.8	–	–	(Snigur et al., 2018)
SPE	ICP-OES	0.14	<4	120	–	(Nomngongo et al., 2013)
Solvent extraction	Spectrophotometry	17.7	–	–	>15	(Kara & Karadas, 2015)
VA-DLLME	ICP-AES	17	–	246	–	(Barros et al., 2016)
DLLME	ETAAS	0.03	4.7	200	5	(Machado & Tissot, 2020)
CPE	FAAS	2.18	2.36	100	>30	(Gurkan, Korkmaz, & Altunay, 2013)
DLLME	Ultraviolet–visible spectrophotometry	2.4	4.3	25	–	(Klochkova, Barbalat, Chebotarev, & Snigur, 2021)
HLLME-FA	ETAAS	0.1	9.7	66	1	(Rezaee, Mozaffari, Haddadi, Pourjavid, & Semnani, 2015).
VA-SFODME	FAAS	4.9	14.5	67	4	(Oviedo, Fialho, & Nóbrega, 2013).
DSPME	ETAAS	0.02	2.9	150	15	This study

DLLME: dispersive liquid liquid microextraction, CPE: cloud point extraction, FAAS: flame atomic absorption spectrometry, ETAAS: Electrothermal atomic absorption spectrometry, LLE: Liquid liquid extraction, VA: vortex assisted, SPE: solid phase extraction, SPME: solid phase microextraction, ICP-OES: inductively couple plasma optic emission spectrometry, HLLME-FA: Homogeneous liquid–liquid microextraction via flotation assistance, VA-SFODME: Vortex-assisted emulsification solidified floating organic drop microextraction.

Oxidation of unsaturated fatty acids or fatty acyls of triglycerides can produce free radicals because of allylic hydrogens abstraction (Brimberg & Kamal-Eldin, 2003; Porter, 2013). Vegetable oils are mainly packed in transparent plastic bottles with some headspace full of air because daylight and air oxygen in the headspace cause autoxidation, cooking oils undergo to rancidity and deterioration (Chen, Han, McClements, & Decker, 2010; Hazer & Ashby, 2021; Li, McClements, & Decker, 2020). In contrast, the autoxidized unsaturated oil can be used peroxidised macro initiators and polyols (Keleş & Hazer, 2009; Lligadas, Ronda, Galià, & Cádiz, 2013). Recently, we have reported the formation of the autoxidized soybean oil consist of Au and silver nanoparticles (AgNPs) (Hazer & Akyol, 2016; Hazer & Kalaycı, 2017). Organic/inorganic nanocomposites have been attracting the high interest of the scientists due to their different biological, optical and physicochemical characteristics. The surface plasmon resonance is a typical property of the metal nanoparticle embedded into polymer that causes displaying very intense colors (Alivisatos, 1996; El-Sayed, 2001; Millstone, Hurst, Métraux, Cutler, & Mirkin, 2009; Oren et al., 2009; Russo et al., 2020; Shani & Heikki, 2007).

Ricinoleic acid contains one hydroxyl and one –COOH functional groups. The autoxidation causes epoxidation and peroxidation. These all functional groups containing peroxide, carboxylic acid and hydroxyl groups attract the cationic species with help of the electrostatic interaction. Molybdenum ions can be adsorbed mainly by this oxide containing functional groups. Metal nanoparticles can cause the porosity inside the polymer matrix which helps the additional adsorption of the cations. Maximum adsorption capacity of maghemite nanoparticles was found 33.4 mg g^{-1} for Mo(VI) ions (Afkhani & Norooz-Asl, 2009). Chitosan sorbent was found 123 mg g^{-1} maximum adsorption capacity for molybdenum ions (Brion-Roby, Gagnon, Nosrati, Deschênes, & Chabot, 2018). Chemically modified persimmon residua was applied as the sorbent for adsorption and removal of Mo(VI). It was 53.72 mg g^{-1} adsorption capacity (Xiong et al., 2011). Orange peel was used as adsorbent for separation of molybdenum ions with 84.48 mg g^{-1} adsorption capacity (Shan et al., 2012). These adsorbents have low adsorption capacity. The adsorption capacity of sorbents is very important for adsorption, separation and quantitative removal of molybdenum ions from very complex matrix.

In this work, we have autoxidized ricinoleic acid containing hydroxyl and carboxylic acid functionality in the presence of AgNO₃ to achieve macroperoxide ricinoleic acid with AgNPs. This macroperoxide containing AgNPs was coded as PriciAg. Free radical copolymerization of styrene with PriciAg rendered polystyrene containing AgNPs and hydroxyl and carboxylic acid functionality. Polystyrene-polyricinoleic acid copolymer containing silver nano particles (AgPSrici) adsorbent has

high capacity for adsorption and it was effectively used for extraction of molybdenum at first time without using chelating reagent.

2. Experimental

2.1. Materials, reagents and standards

A standard solution of Mo(VI) was bought from E. Merck (Darmstadt, Germany). It was at a concentration of 1000 mg L^{-1} . $\text{Mg}(\text{NO}_3)_2$ and palladium were used as matrix modifiers supplied from E. Merck (Darmstadt, Germany). Working and standard solutions were prepared by ultrapure water. Also ultrapure water was used for dilution of real samples. The method accuracy was checked by performing the introduced method on certified reference materials (CRMs). pH adjustment was done using different buffer solutions (ammonia, borate, acetate and phosphate). Castor oil was bought from local markets in Turkey (originally made by India, purity: 86–90 wt%) (Hazer & Eren, 2019) and it was used to prepare ricinoleic acid by the hydrolysis of the basic alcoholic solution.

2.2. Apparatus

Determination of Mo in real samples was performed by an ETAAS (700 model Perkin Elmer, CT, USA). The wavelength and slit width of Mo hollow cathode lamp were 313.3 nm and 0.7 nm, respectively. The temperature of different steps (drying, ashing, atomization, and cleaning) was initially studied for ETAAS determination of Mo. For the optimization, $20 \mu\text{L}$ samples + $10 \mu\text{L}$ of mixture of $0.020 \text{ mg Pd} + 0.015 \text{ mg Mg}(\text{NO}_3)_2$ was used. Absorbances were measured as peak high and reading time was 7 s. pH values of the solutions were adjusted using Sartorius pp-15 model glass electrode. NF-200 model (Turkey) centrifuge was used for the centrifuge. A Thermolyne 37,600 vortex mixer (USA) was used during performing the method. The foodstuff samples were prepared by a microwave digestion system (Milestone Ethos D model, Sorisole-Bg, Italy). A Perkin-Elmer FTIR Spectrometer was used in transmissive mode for the characterization of the AgPSrCi at a scan rate 4000 to 650 cm^{-1} . Scanning electron microscopy (SEM) imaging (Zeiss EVO IS10) was used for the characterization of AgPSrCi.

2.3. Synthesis of polystyrene-polyricinoleic acid copolymer containing silver nano particles

2.3.1. Autoxidation of ricinoleic acid containing AgNPs

The mixture of ricinoleic acid (32 g) and AgNO_3 (1.49 g) was spread in a Petri dish ($\Phi = 20 \text{ cm}$, oil thickness $\sim 1.0 \text{ mm}$) and was kept at room temperature for 78 days according to the general autoxidation process described in the cited reference under atmospheric conditions (Hazer & Eren, 2019).

2.3.2. Polymerization of styrene with PriciAg

The mixture of styrene (11.2 g) and PriciAg (2.85 g) was thermally polymerized under argon at 95°C for 275 min. The obtained polymer was coagulated into the excess of methanol and then it was dried in a desiccator under vacuum at 40°C (for 24 h). After that, the polymer was dissolved in re-dissolved in chloroform and precipitated using methanol under the above mentioned conditions. Finally, 3.23 g of the polymer was obtained. FT-IR spectrum of the polystyrene-polyricinoleic acid copolymer containing silver nano particles (AgPSrCi) (Fig. S1) were observed in spectrum (Fig. S2). The signal at 1733 cm^{-1} disappears in the spectrum of AgPSrCi-2 since silver nanoparticles cause a decarboxylation of ricinoleic acid during styrene polymerization.

SEM technique was used to evaluate the topology and silver nanoparticles inclusion of the AgPSrCi nanocomposite. SEM micrograph shows the fiber like appearance of the nanocomposite (Fig. S3). Bigger size silver nanoparticles were observed in Fig. S4. Silver nano clusters with roughly sizes from 100 nm to 400 nm heterogenic distributed into

the continuous polymer matrix without 3 to 4 bigger size $1 \mu\text{m}$ micro-particles. Silver nano cluster presence in the polymer matrix were confirmed using X-ray technique (EDX). Fig. S5 shows the strong characteristic signals of the silver nanoparticles at 0.01, 3.1, and 22 keV in the EDX spectrum of the nanocomposite. Gold signals on the EDX spectrum come from the used gold in the covering process of the nanocomposite.

2.4. D- μSPE procedure

A 25 mL aliquot of Mo(VI) standard solution ($0.5 \mu\text{g L}^{-1}$) was added into 50 mL centrifuge tube containing pH 5 acetate buffer solution. Then, 150 mg newly synthesized AgPSrCi adsorbent was poured into sample solution and the mixture was vortexed for 10 min at 1500 rpm. In this step, analyte ions were adsorbed on AgPSrCi nanoparticles. Adsorbent was separated from aqueous solution by centrifugation at 3500 rpm for 5 min. The aqueous phase was decanted by using micro-pipette and Mo(VI) ions were eluted from AgPSrCi adsorbent by 1 mol L^{-1} HCl (2 mL). Using the same procedure, the blank solution was measured in parallel with the samples and calibration solutions. Finally, molybdenum ions were determined by using ETAAS and peak height mode was used for the measurement of molybdenum signals.

2.5. Sampling and digestion

Water samples were collected from Tokat city (Turkey) and transferred the laboratory. The samples were passed through a blue band filter paper ($0.45 \mu\text{m}$ pore size) and the clear solution was of each sample were stored in a refrigerator at 4°C before analysis. NIST SRM 1568a Rice Flour and GBW 07605 Tea (0.1 g), orange juice, cow's milk, sheep's milk) (1.0 mL), cultivated mushroom, rice, canned fish, canned tomato, green tea, black tea, cereal, egg, chicken meat, cow's meat, olive oil, boiled wheat, potato, onion, garlic, spinach, broccoli, corn, butter (1.0 g) were digested in microwave digestion system with 2 mL H_2O_2 (30%) and 6 mL HNO_3 (65%) (Tuzen et al., 2017) and diluted to 50 mL using distilled deionized water. The method described above was done on the prepared samples.

3. Result and discussion

3.1. Effect of pH

In order to obtain quantitative phase separation and acceptable analytical data, analyte ions must be effectively adsorbed onto the polystyrene-polyricinoleic acid copolymer containing AgPSrCi. To achieve this goal, the first factor to be optimized is the pH of the sample solution. Silver nano particles are an imperative factor for extraction of Mo(VI) ions onto the adsorbent. (Khajeh & Dastafkan, 2014). Adsorption efficiency of molybdenum ions is increased because nano particles have high specific area in AgPSrCi. The pH effect on the adsorption of the analyte was investigated by performing various experiments in the range of 2–8. The tests were done on 100 mL Mo(VI) solutions at a concentration of $0.5 \mu\text{g L}^{-1}$ and 150 mg, 15 min, and 2 mL was selected for AgPSrCi amount, extraction time, 1.0 mol L^{-1} HCl solution (as the eluent), respectively. The obtained recovery for each pH was in the range of 30–97% (Fig. 1a). It is noted that the analyte extraction was relatively constant at pH range of 4–6. Decreasing the extraction recovery of Mo(VI) ions at acidic (<3) and alkaline pHs (>7) can be related to protonation of AgPSrCi and formation of metal hydroxides, respectively. Therefore, the subsequent experiments were performed on the solution adjusted at pH = 5 using acetate buffer solution.

3.2. Amount of AgPSrCi adsorbent

In solid phase adsorbent studies, effective separation and pre-concentration of analyte ions in sample solution directly depends on the

amount of adsorbent. Therefore, to monitor the effect of AgPSrCi amount on the recovery of Mo(VI) ions, the AgPSrCi in the range of 50–200 mg were added to the sample solution. Mo(VI) ions recovery was improved with increasing amount of the adsorbent in range of 50–150 mg and then remained constant at higher amounts. Fig. 1(b) shows these analytical results. So, 150 mg AgPSrCi adsorbent was chosen as optimum for the subsequent experimental studies to achieve quantitative recovery.

3.3. Effect of extraction time

After adding the newly synthesized adsorbent to the model solution, the time required for the adsorption of Mo(VI) ions in the sample to the AgPSrCi should be optimized. If sufficient time is not determined, Mo(VI) ions cannot be adsorbed onto the AgPSrCi. Therefore, no quantitative recovery can be achieved. In addition, an extraction procedure should be as fast and practical as possible. The extraction time was evaluated in the range of 5–25 min by using vortex. Results were shown in Fig. 1c. After extraction, AgPSrCi adsorbent collection was done by centrifugation at 3500 rpm for 5 min. Extraction recovery for the analyte was quantitative in the range of 15–25 min. So, 15 min extraction time was found sufficient for the Mo(VI) ions to adhere to the surface of AgPSrCi adsorbent.

3.4. Effect of eluent solution

After vortex assisted extraction and centrifugation procedures, optimization of the eluent type and its volume is a critical variable both for separating the molybdenum ions from the AgPSrCi and for achieving high sensitivity. In this context, the effect of eluent solvents such as acetone, HNO₃ and HCl on the recovery of molybdenum ions was studied. Recovery values of molybdenum ions from AgPSrCi adsorbent were found to be 75, 80, 87, 90, and 96% for acetone, 1 mL HNO₃ solution (1.0 mol L⁻¹), 2 mL HNO₃ solution (1.0 mol L⁻¹), 1 mL HCl solution (1.0 mol L⁻¹), and 2 mL HCl solution (1.0 mol L⁻¹), respectively. So, 2 mL of 1.0 mol L⁻¹ HCl was selected to use as the elution solution. Minimum volume of elution solvent is important to reach high pre-concentration factors (PFs).

3.5. Sample volume optimization

Due to the fact that the volume of sample solution has inevitable effect on the recovery and PF of an extraction method, it should be optimized. In the present study, sample solution volume was evaluated by performing different tests in the range of 25–150 mL (Fig. 1d). The obtained results illustrated that, quantitative recovery has been increased up to 100 mL and high samples volumes can cause decrease to recoveries of molybdenum ions. It may be related to the insufficient capacity of the AgPSrCi adsorbent for extraction of molybdenum ions. Therefore, 100 mL was selected for the other steps. PF was found 50 according to above definition.

3.6. Effect of matrix ions

The tolerance limit of foreign ions is considered for the ions that can increase or decrease the analyte signals lower or greater than 5 % (Tuzen, Sahiner, & Hazer, 2016). Foreign ions were spiked to Mo(VI) ions solutions at a concentration of 0.5 µg L⁻¹, 150 mg AgPSrCi, 15 min extraction time, 100 mL sample volume adjusted at pH = 5, 2 mL of HCl solution (1.0 mol L⁻¹) and present method was applied. The foreign ions tolerance limits are given in Table 1. The high tolerance limit and quantitative recoveries obtained from these studies indicate that the prepared AgPSrCi has high efficiency for Mo(VI) ions. It is also clear from the results that there is no significant matrix effect. The intraday (N:3, 5 and 0.5 µg L⁻¹ Mo(VI) ions) and inter-day (N:3 × 3, 5 and 0.5 µg L⁻¹ Mo(VI) ions) precisions for matrix ions were found in the range of

2.6–3.2% and 2.9–3.8%, respectively.

3.7. Analytical figure of merits

Calibration curve of molybdenum ions was linear within the range of 0.07–10 µg L⁻¹ after preconcentration. Correlation coefficient was found as 0.9992 from the calibration graph. The limits of detection (LOD) and quantification (LOQ), which defined as 3S_b/m and 10 S_b/m, respectively, (S_b: standard deviations of the blank; b: slope of the calibration curves) was 0.02 and 0.066 µg L⁻¹, respectively. The enhancement factor, defined as m₁/m₂ (m₁: calibration curve slope before performing the method; m₂: calibration curve slope after the micro-extraction method) was 150. PF was found as 50 by dividing initial sample volume to the volume of final phase. Relative standard deviations (RSD%, N:5) of 2.9% were obtained at 0.50 µg L⁻¹ of Mo(VI). The adsorption capacity of the AgPSrCi adsorbent was found as 170 mg g⁻¹ and calculated from our previous study (Acikkapi, Tuzen, & Hazer, 2019). AgPSrCi adsorbent can be used for 60 times in the adsorption/desorption approach effectively. Recovery of Mo(VI) ions in DSPME method was found to be 97 ± 3 at 95% confidence level.

3.8. Application results

Analysis of NIST SRM 1568a Rice Flour and GBW 07605 Tea certified reference materials by the method was used for evaluation of the method accuracy after digestion in closed vessel microwave system. The certified and experimental values of molybdenum were found as 1451 ± 48 and 1378 ± 66 µg kg⁻¹ in NIST SRM 1568a Rice Flour and 38 ± 0.39 and 36.3 ± 2.4 µg kg⁻¹ in GBW 07605 Tea. The recovery molybdenum ions were found in the range of 95–96 % in the values of certified reference materials (Table 2). The data were in agreement with the certified amounts for the analysis of molybdenum ions in ETAAS.

Present DSPME method was performed on to tap and mineral waters, orange juice, cow's milk and sheep's milk samples. Standard of 5.0 µg L⁻¹ and 10 µg L⁻¹ Mo(VI) was spiked to water, juice and milk samples and mean relative recoveries were found in the range of 95–98 % for molybdenum ions (Table 3).

Due to the importance of the molybdenum as essential trace element for human life, the introduced DSPME approach was performed on foodstuff samples including cultivated mushroom, rice, canned fish, canned tomato, green tea, black tea, cereal, egg, chicken meat, cow's meat, olive oil, boiled wheat, potato, onion, garlic, spinach, broccoli, corn, butter (Table 4). The obtained data were confirmed suitability of the studied foods for human from point of view of nutritional and toxic levels. Molybdenum was determined at trace levels in analyzed beverage, water, and foodstuffs.

4. Conclusions

A newly synthesized polystyrene-polyricinoleic acid copolymer containing AgPSrCi was used for the DSPME of molybdenum ions from the selected samples. Vortex assisted extraction and centrifugation procedures were used for extraction of molybdenum ions in a short time. The present DSPME procedure has outstanding benefits such as simple, fast, low cost, environmentally friendly, high enhancement factor, sensitive and selective. The present DSPME procedure is comparable with other published studies. Lower LOD and RSD values, shorten extraction time, and higher enhancement factor were found in present DSPME procedure than literature values reported in Table 5. High adsorption capacity of AgPSrCi adsorbent was found as 170 mg g⁻¹ for Mo(VI) ions. AgPSrCi adsorbent was first time used for separation, preconcentration and ETAAS determination of molybdenum without using chelating reagent. AgPSrCi adsorbent can be used at least 60 times for the adsorption and desorption steps without decrease of its sorption properties. The presented DSPME procedure can be easily application to water, beverage and food samples containing very complex matrix for the

separation, preconcentration and determination of molybdenum.

CRedit authorship contribution statement

Mustafa Tuzen: Investigation, Validation, Writing – original draft, Writing - review & editing, Software. **Nail Altunay:** Investigation, Validation, Writing – original draft, Writing - review & editing, Software. **Baki Hazer:** Supervision, Investigation, Validation, Writing – original draft, Writing - review & editing, Software, Conceptualization. **Mohammad Reza Afshar Mogaddam:** Investigation, Validation, Writing – original draft, Writing - review & editing, Software.

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. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2021.130973>.

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