



Speciation of chromium in beverages and seasoning samples by magnetic solid-phase extraction and microsample injection system flame atomic absorption spectrometry

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Abstract

In this research, a magnetic solid phase extraction based on the use of magnetic polyaniline-polythiophene copolymer ($\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$) nanoparticles is applied for chromium speciation from water, beverages and seasoning samples followed by microsample injection system-flame atomic absorption spectrometry(MIS-FAAS) analysis. The selective adsorption of Cr(III) in presence of Cr(VI) by $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$ in the pH range of 9.0-10.5 was obtained and the total Cr, after reduction of chromium(VI) to chromium(III) by adding 0.5 mL of concentrated H_2SO_4 and 10 mL of 5% (w/v) hydroxylamine hydrochloride, was determined. The detection limit, enhancement factor, and repeatability of the optimized method for Cr(III) were calculated to be $1.5 \mu\text{g L}^{-1}$, 38.5, and 1.78%, respectively. The method was validated by the analysis of TMDW-500 drinking water and LGC7162 Strawberry Leaves as certified reference materials. The relative error for total chromium was found to be lower than 4.6%. Recoveries were obtained quantitatively using this method ($\geq 95\%$).

Article info

History:

Received:07.04.2020

Accepted:04.06.2020

Keywords:

$\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$, chromium, speciation, water, beverages.

1. Introduction

Chromium is one of the commonly employed elements in various industries, such as leather, textile, paint, battery, ceramic, glass, metal, catalyst, and fungicide[1,2]. Therefore, large amounts of chromium species are emitted or discharged to the environment as waste. This leads to the pollution of farmlands and the pollution of irrigation and drinking water resources. Then, these species are gradually taken up by plants and they reach the human's body through the food chain.

Chromium is typically found in the environment in two oxidation forms: trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI). The naturally occurring Cr(III) is a less toxic and essential ion for the body and it plays a role in glucose and lipid metabolism[3,4]. While certain amounts of Cr(III) is essential, an excess amount of Cr(III) could create toxicity[3,4]. Then, this toxicity may cause some diseases such as cancer or damage to the nervous system[3,4]. On the contrary, Cr(VI) is highly toxic due to its carcinogenic and mutagenic properties[5,6]. Also, Cr(VI) is highly soluble and mobile in groundwater and surface water that could create problems for human health[7]. Thus,

EPA and WHO recommend the threshold value for total chromium as $100 \mu\text{g L}^{-1}$ and Cr(VI) as $50 \mu\text{g L}^{-1}$ in drinking water, respectively[8,9]. Chromium is mostly found in meat, fruit, vegetables, grains, and legumes. Cr(VI) content in many food samples is less than the content of Cr(III)[10]. Taking into account the potential toxicity of Cr(III) and the high toxicity of Cr(VI), it is important to monitor their concentrations in various samples. In real samples, low concentrations of both chromium ions and the complexity of matrix make the determination of these ions challenging. For this reason, an accurate quantification method including preconcentration/separation procedure is required to develop for speciation studies[11].

It is well known that flame atomic absorption spectrometry(FAAS) is widely used for the determination of the total concentration of a metal ion in aqueous samples. Nevertheless, due to its low sensitivity, this technique is not used directly for the determination of total chromium. Also, it lacks ion selectivity for speciation of the different oxidation states of chromium. For overcoming these problems, the speciation analysis is required by combining FAAS with ion selective preconcentration method. Many chromium speciation methods coupled with FAAS

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such as solid phase extraction[12,13], coprecipitation[14,15], cloud point extraction (CPE)[16,17] and dispersive liquid-liquid microextraction (DLLME)[18,19] have been developed to simplify analytical approaches. Among these, solid-phase extraction (SPE) based on column technique is generally found to be a more efficient one with high preconcentration factor, easy automation, and commonly available commercial solid phase materials. However, it has some drawbacks like time consuming processes, relatively complicated operation, and slightly toxic organic solvent use. These drawbacks of conventional SPE technique have been avoided by using nanostructured magnetic adsorbents and nowadays, magnetic solid phase extraction(MSPE) have become more popular in preconcentration studies. The magnetic adsorbents have advantages such as easy preparation procedures, faster adsorption and desorption properties, low-cost, environmental friendliness and high surface area that makes them effective adsorbent in SPE. Additionally, by an external magnetic field, the magnetic adsorbent can be simply removed from the analysis solution that it is added. The core-shell magnetic nanoparticles such as Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, and some ferrites (MFe_2O_4 (M: Cu, Ni, Mn, Mg, etc.)) can be functionalized with various complexing agents on the particle surface to increase the specificity towards metal ions[20,21,22]. For this purpose, conductive polymers (CPs) with sulfur, oxygen, or nitrogen groups complexing with metal ions are promising for selective preconcentration of heavy metal ions without the need for any complexing agent[21]. Additionally, they are preferred due to their highly stable nature at different pH ranges, nontoxic properties, and rapid synthesis procedures. Various CPs, polyaniline(PANI) [23], polypyrrole(PPY) [24,25], polythiophene (PTH) [26,27] and their derivatives[28] have been applied in removal and preconcentration studies of heavy metal ions. In most of these works, only a single type of polymer is used except in a few examples copolymers such as PPY-PTH, PANI-PPY, and so on are used [29-32]. According to the literature search, there is no report seen on the use of PANI-PTH copolymer coated Fe_3O_4 NPs ($\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$) for chromium speciation.

Herein, I synthesized $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$ nanoparticles and successfully applied them as a nanosorbent for the MSPE of chromium speciation in real samples. Following the speciation, MIS-FAAS was used for chromium detection.

2. Materials and Methods

2.1. Instrumentation and apparatus

A flame atomic absorption spectrometer (Perkin Elmer AAnalyst 200, Norwalk, CT, USA) equipped with a chromium hollow cathode lamp was used with a handmade microsample injection system (MIS) installed on it. The spectrometer was set as recommended in the manufacturer's manual. The MIS provides acceptable absorbance to be obtained with 100 μL sample volume injected with a micropipette into the spectrometer nebulizer[14]. A pH meter (WTW pH720 model, Weilheim, Germany), a heating magnetic stirrer (Velp Scientifica ARE, Usmate, Italy), and an ultrasonic bath (Ultrasound Bendelin Electronic, Berlin, Germany) were used when necessary. The ultrapure (UP) quality water (resistivity, 18.2 $\text{M}\Omega\text{ cm}^{-1}$) was obtained with the reverse osmosis system (Human Corp., Seoul, Korea).

2.2. Reagents and solutions

All reagents used in this work were at least analytical reagent grade. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, St. Louis, MO, USA), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Panreac, Barcelona, Spain), aniline and thiophene (analytical grade, Merck, Darmstadt, Germany) were used in the synthesis of $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$. Nitric acid (65%,v/v), hydrochloric acid (37%,v/v), phosphoric acid (85%), acetic acid(glacial), sodium hydroxide, ammonia solution (25%) were purchased commercially (E. Merck, Darmstadt, Germany). Standard stock solutions of Cr(III) (LGC, Manchester, USA) and Cr(VI) (High Purity, North Charleston, USA) as 1000 mg L^{-1} , were used to prepare the daily test and calibration standard solutions. The pH adjustments of test and sample solutions were carried out using an $\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$ buffer to pH 2, $\text{CH}_3\text{COO}^-/\text{CH}_3\text{COOH}$ buffers to pH 4-6, with $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ buffers to pH 6.5-7.5 and $\text{NH}_4^+/\text{NH}_3$ buffers to pH 8-11.

Drinking water (TMDW-500) and Strawberry Leaves(LGC7162) were used to check the accuracy as the certified reference materials. The analyzed real samples were purchased from local markets in Denizli/Turkey.

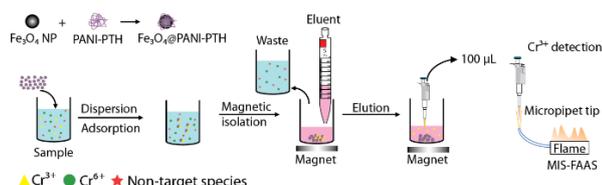
2.3. Synthesis of $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$

$\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$ nanoparticles as a magnetic adsorbent were prepared via in-situ chemical oxidative polymerization of aniline and thiophene monomers by using FeCl_3 in the presence of Fe_3O_4 , by modifying the

procedure from previous works [29,30-34]. The detail of the synthesis process and characterization data was reported in my earlier work [35]. However, after each synthesis of the magnetic copolymer, Fe₃O₄ and Fe₃O₄@coPANI-PTH IR spectra recorded by ATR-IR instrument (UATR two model, PerkinElmer, Waltham, MA, USA) and the results were compared. Once the peaks belonging to Fe₃O₄-Polyaniline and Fe₃O₄-Polythiophene recognized in synthesized Fe₃O₄@coPANI-PTH, these Fe₃O₄@coPANI-PTH nanoparticles were used as magnetic solid phase throughout the study.

2.4. General procedure using Fe₃O₄@coPANI-PTH magnetic nanoparticles

Particular volumes of Cr(III) solutions (5-100 mL) with concentrations from 10 to 100 µg L⁻¹ were placed into a beaker and buffered to desired pHs in the range of 2-12. 100 mg of Fe₃O₄@coPANI-PTH nanoparticles was added into the beaker and the resulting mixture was shaken by hand for 5 min to ensure the quantitative extraction of Cr(III) ions by the nanosorbent. After that, by applying an external magnet, the liquid is discarded. The remaining magnetic nanoparticles loaded with Cr(III) at the bottom of the beaker were treated with 0.5-5.0 mL of 0.2% thiourea solution in a mixture of 2 mol L⁻¹ HCl and 1 mol L⁻¹ HNO₃ and sonicated for 5 min. Then, the Fe₃O₄@coPANI-PTH nanoparticles were magnetically collected at the bottom of beaker, and the recovered Cr(III) ions in the clear solution were determined by a microsample injection system-flame atomic absorption spectrometry (MIS-FAAS) to investigate the adsorption behavior of the nanoparticles (Scheme 1).



Scheme 1. Magnetic solid phase extraction of Cr(III) ions using Fe₃O₄@coPANI-PTH

2.5. Cr(III) and Cr(VI) determination in real samples

The analyzed local beverages and seasoning samples were prepared according to a simplified and modified version of previous publications [36,37]. 0.6 mL conc. HNO₃ was added to a 40 mL sample in a 50 mL centrifuge tube (Isolab, Eschau, Germany) and the tube was carefully shaken and then centrifuged for 10 min at 10,000 rpm to remove solid particles. The acidic

supernatant solutions were buffered to pH 10 by adding conc. NH₃ dropwise by controlling pH values with a pH meter. Cr(III) concentration in the buffered sample solution was determined by the general procedure presented in Section 2.4.

After reducing Cr(VI) to Cr(III) by adding 1.0 mL of concentrated H₂SO₄ and 5.0 mL of 5% (w/v) hydroxylamine hydrochloride[38,39,40], total chromium concentration (Cr_T) was determined as Cr(III) by the procedure in Section 2.4. The given volumes of concentrated H₂SO₄ and 5% hydroxylamine hydrochloride were added into a 40 mL sample without any pretreatment in a 100 mL beaker and the solution was boiled for 30 min. Then, the solution was cooled to room temperature, and the pH of the solution was adjusted to 10 by adding conc. NH₃ dropwise. After pH adjustment, Cr_T was determined following the procedure given in Section 2.4. The Cr(VI) concentration was calculated by subtracting concentration of Cr_T from the concentration of Cr(III).

The dried and powdered LGC7162 Strawberry Leaves were weighed as 0.50 g into a beaker and treated with 4.0 mL of aqua regia for 3 h at 85 °C on a hot plate to extract chromium species from the sample[38]. To remove undissolved parts, the resulting solutions were filtered through a filter paper. 0.5 mL of conc. H₂SO₄ and 10 mL of 5% (w/v) hydroxylamine hydrochloride added filtrate were boiled for 30 min to ensure that Cr(VI) is completely reduced to Cr(III) [38,39,40]. The final solution cooled to room temperature was buffered to pH 10 by adding conc. NH₃ dropwise and then the procedure given in Section 2.4 was followed to determine Cr_T.

3. Results and Discussion

3.1. Effect of pH

A suitable pH can improve the efficiency and selectivity of adsorbent as it influences both the surface chemistry of adsorbent and the solution chemistry of chromium ions. So, the pH optimization of the analyzed solution is primarily performed in the development of speciation/preconcentration methods based on solid phase extraction. So, the effect of pH on the adsorption of Cr(III) and Cr(VI) ions was controlled over a pH range of 2 to 12. The data in Figure 1 showed quantitative adsorption (recovery ≥95%) of Cr(III) ions over the pH ranges of 9–10.5. At the same pH range, the recovery values for Cr(VI) ions were found to be ≤10%. It was concluded that the suitable pH is 10 for distinguishing Cr(III) and Cr(VI) and this pH is chosen for the subsequent experiments.

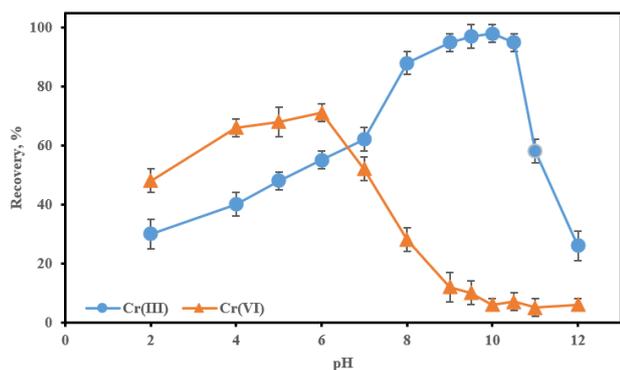


Figure 1. Effect of pH on recovery of Cr(III) and Cr(VI) ions using 100 mg $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$ (n:3, Sample vol.: 40 mL, Analyte conc.: $25 \mu\text{g L}^{-1}$, Eluent vol.: 2 mL)

The increase in the recovery of Cr(III) from pH 2 to 8 can be explained by the deprotonation of nitrogen and sulfur atoms on the surface of $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$. As a result of this deprotonation at pH 8 and beyond, the complex formation can be achieved between Cr(III) species ($\text{Cr}(\text{H}_2\text{O})_2(\text{OH})^{2+}$ or $\text{Cr}(\text{H}_2\text{O})(\text{OH})_2^+$) and the surface[41]. Below pH 8, since the ions are positively charged and the surface is protonated, a repulsion of charges is present. The decrease in the recovery of Cr(VI) above pH 6 can be explained by repulsion of Cr(IV) species due to the deprotonation of the surface[28]. Based on this behavior of the two chromium ions, pH 10 was selected for the analysis.

3.2. Effect of $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$ Amount

The amount of adsorbent required to achieve efficient extraction is an important factor in preconcentration studies. Compared to the conventional adsorbents, the surface area of nanoparticle adsorbents is larger. Thus, quantitative recovery of analytes is expected to be achieved with a smaller amount of nanoparticle adsorbents. The influence of $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$ amount as a magnetic adsorbent on the recovery of Cr(III) at pH 10 was investigated over the range of 50 to 200 mg for preconcentration of $100 \mu\text{g L}^{-1}$ Cr(III) from 20 mL solution. The quantitative recovery was obtained at 100 mg $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$ (Table 1). A similar amount of nanoadsorbent use is recorded by other groups as well [27,35,40]. The low recoveries achieved below and above 100 mg could possibly be attributed to the insufficient adsorbent amount and eluent volume, respectively.

Table 1. Effect of $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$ amount on extraction efficiency of Cr(III) (eluent: 2 mL of 0.2% thiourea solution prepared by $1 \text{ mol L}^{-1} \text{HNO}_3$ and $2 \text{ mol L}^{-1} \text{HCl}$, n:3)

$\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$, mg	Recovery, %
50	44.9 ± 6.5
75	82.3 ± 4.1
100	96.0 ± 4.3
125	65.5 ± 7.5
200	58.7 ± 2.0

3.3. Sample volume

To attain a high preconcentration factor, it is important to work with a maximum sample volume that ensures quantitative adsorption of an analyte by an adsorbent. Effect of sample volume on the adsorption efficiency of Cr(III) ion was studied by extraction of the analytes from 10 to 100 mL of $100 \mu\text{g L}^{-1}$ Cr(III) solution in the presence of 100 mg of $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$. The largest volume in which the quantitative recovery was obtained was found to be 80 mL (Table 2).

Table 2. Effect of varying sample volumes on recovery values of Cr(III) ions (eluent vol.: 2 mL, n:3)

Sample volume, mL	Recovery, %
5	98.5 ± 2.6
10	100.1 ± 1.7
25	99.1 ± 2.8
40	95.9 ± 3.7
80	96.4 ± 4.1
100	56.5 ± 3.8

3.4. Eluent type and volume

From the data in Figure 1, it can be estimated that quantitative elution would be possible to attenuate the polythiophene-Cr(III) interaction using a highly acidic eluent. Cr(III) as a hard acid is well known to preferentially bind to nitrogen (hard acid) and sulfur (soft acid) containing ligands such as thiourea. Therefore, the elution of preloaded Cr(III) from $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$ was controlled using 5.0 mL of thiourea solutions prepared with diluted HCl, HNO_3 , and their mixtures (Table 3). The best elution efficiency was obtained with 0.2% thiourea in 1 M $\text{HNO}_3 + 2 \text{ M HCl}$.

Table 3. Recoveries founded at various eluent volumes (sample vol.: 40 mL, $100 \mu\text{g L}^{-1}$ Cr(III), n:3)

Eluent volumes, mL	Recovery, %
5	95.3 ± 3.6
2	97.1 ± 4.1
1	67.2 ± 3.3
0.5	58.9 ± 3.8

To achieve the high preconcentration factor (PF), the elution efficiency of smaller volumes of this eluent was examined over the range of 0.5 to 5 mL. 2.0 mL of 0.2% thiourea in 1 M HNO₃ + 2 M HCl provided the quantitative elution of Cr(III) as the smallest required eluent volume. The ratio of the maximum sample volume (80 mL) to minimum eluent volume (2.0 mL) defines the PF and based on that PF was calculated to be 40.0.

3.5. Extraction time for Cr(III)

Another factor that requires to be optimized is the extraction time including adsorption and desorption times. Adsorption time is defined as the time required for complete adsorption of Cr(III) on the adsorbent surface. The effect of adsorption time was changed over the range of 2 to 15 min (Table 4). At 5 min, the recovery values for Cr(III) achieved to be quantitative ($\geq 95\%$), after that there is no remarkable change in the recovery of Cr(III). This short time can be attributed to the attractive surface properties of the adsorbent for rapid adsorption of Cr(III) from solution under operating conditions. Hence, 5 min was chosen as the adsorption time. A similar study was carried out for desorption time (elution time) by fixing the adsorption time to 5 min. It was also found to be 5 min. This fast extraction time can be explained by the fast adsorption kinetic between the surface and the analyte.

Table 4. Recovery changes found with varying adsorption and desorption times (sample vol.:80 mL, eluent vol.: 2 mL, Cr(III) conc.: 100 $\mu\text{g L}^{-1}$, n:3)

Time, min	Recovery, %	
	Adsorption ^a	Desorption ^b
2	36.2 \pm 3.6	42.2 \pm 4.2
4	85.7 \pm 4.1	79.1 \pm 3.8
5	96.9 \pm 3.4	97.7 \pm 3.2
10	98.9 \pm 3.9	96.8 \pm 4.2
15	97.2 \pm 2.9	96.2 \pm 3.6

^a at fixed desorption time of 5 min. ^b at fixed adsorption time of 5 min.

3.6. Cr(III) and Cr_T determination in sample solution

The usability of described methods in Section 2.4 and 2.5 were checked for the determination of Cr(III) and total chromium(Cr_T) in a solution mixed with Cr(III) and Cr(VI)(Table 5). Cr(III) ions from the solution containing Cr(III) and Cr(VI) were quantitatively adsorbed on Fe₃O₄@coPANI-PTH while Cr(VI) ions remained almost completely in the supernatant solution. On the other hand, Cr_T was determined after the reduction of Cr(VI) to Cr(III) by adding 0.5 mL of concentrated H₂SO₄ and 10 mL of 5% (w/v) hydroxylamine hydrochloride to a 40 mL sample solution containing Cr(III) and Cr(VI) at different amounts. Cr_T was quantitatively recovered. Cr(VI) amount was calculated by subtracting Cr(III) amounts from Cr_T amounts.

Table 5. Determination of Cr(III) ions and total chromium in the mixture of Cr(III) and Cr(VI) ions (Sample volume:40 mL, eluent vol. 2 mL, n:3)

Added, μg			Found, μg ; Recovery%		
Cr(III)	Cr(VI)	Cr _T	Cr(III) ^a	Cr(VI) ^b	Cr _T ^c
5	5	10	4.8 \pm 0.1; 96.0	4.7 \pm 0.2; 94.0	9.6 \pm 0.2; 96.0
5	20	25	4.7 \pm 0.1; 94.0	19.5 \pm 0.2; 97.5	24.2 \pm 0.2; 96.8
10	5	15	9.9 \pm 0.1; 99.0	4.8 \pm 0.2; 96.0	14.7 \pm 0.2; 98.0
20	5	25	19.9 \pm 0.4; 99.5	5.0 \pm 0.4; 100.0	24.9 \pm 0.2; 99.6

^aCr(III): Determined amount of Cr(III) in presence of Cr(VI), ^bCr(VI): Amount of Cr(VI) ions founded by subtracting Cr(III) amount from Cr_T amount. ^c Cr_T: determined after reducing Cr(VI) to Cr(III) ions in sample solutions

3.7. Analytical performance figures

Analytical performance figures of the established MSPE method, combined with MIS-FAAS were evaluated under the optimum conditions (pH 10.0, 100 mg of Fe₃O₄@coPANI-PTH, 80.0 mL sample volume, 2 mL eluent volume and 10 min extraction time). The linear calibration equation in a range of 5-15 $\mu\text{g L}^{-1}$ was $A = 0.2272 C_{\text{Cr(III)}} - 0.0009$ ($R^2=0.997$), where A and $C_{\text{Cr(III)}}$ are the absorbance of chromium and

concentration of chromium ion in $\mu\text{g L}^{-1}$, respectively. The established calibration equation without the preconcentration was $A=0.0059 C_{\text{Cr(III)}}-0.0003$ ($R^2=0.996$) in range of 0.2-5.0 $\mu\text{g mL}^{-1}$ for Cr(III) ions. The enhancement factor (EF) was calculated to be 38.5 from the ratio of the slope of the calibration equation after preconcentration to that without preconcentration. The preconcentration factor(PF) was 40. The close PF and EF values confirm the accuracy of the method with the quantitative sorption and

elution cycle of the analyte recovered as 96.2% which is calculated as the ratio of the preconcentration factor to the enrichment factor. Nevertheless, the accuracy of the optimized method for real sample analysis was checked by applying to TMDW-500 drinking water and LGC7162 Strawberry Leaves as certified reference materials (Table 6). The student t-test was applied; the obtained t_{test} values (1.667 for TMDW-500 and 2.474 for LGC7162) is lower than the $t_{\text{critical}}=4.303$ (n:3 and 95% confidence level); therefore, there is no significant difference between certified and found values, and the presented method is applicable for real sample analysis.

Table 6. Analysis of certificated reference materials using proposed method (TMDW-500 vol.: 50 mL, LGC7162 Strawberry Leaves: 0.5 g, n:3)

Certified reference materials	Total chromium conc., mean \pm standard deviation		
	Certified	Found	Error, %; RSD, %
TMDW-500 Drinking water, $\mu\text{g L}^{-1}$	20.0 \pm 0.1	19.3 \pm 0.6	-3.5; 3.1
Strawberry Leaves, $\mu\text{g g}^{-1}$	2.15 \pm 0.34	2.05 \pm 0.07	-4.6; 3.4

The reproducibility of the overall preconcentration method was calculated to be 1.85% (n=7,

Table 7. Analysis of water, fruit juice, soft drink and vinegar samples spiked with Cr(III) and Cr(VI) ions (n:3)

Samples	Added, $\mu\text{g L}^{-1}$		Found ^a , $\mu\text{g L}^{-1}$		Recovery, %			
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr _T	Cr(III)	Cr(VI)	Cr _T
Bottled mineral water	0	0	n.d. ^b	n.d.	n.d.	-	-	-
	50	50	50.4 \pm 3.7	50.8 \pm 3.9	101.2 \pm 1.2	100.8	101.6	101.2
Spicy-turnip juice	0	0	8.6 \pm 0.8	\leq LOQ ^c	9.4 \pm 0.6	-	-	-
	50	50	62.4 \pm 6.8	48.6 \pm 9.9	110.0 \pm 9.7	107.6	97.2	100.6
Non-spicy turnip juice	0	0	10.5 \pm 1.2	\leq LOQ	12.8 \pm 0.9	-	-	-
	50	50	60.8 \pm 0.8	50.4 \pm 8.5	111.2 \pm 3.8	100.6	100.8	98.4
Apple juice	0	0	n.d.	n.d.	n.d.	-	-	-
	50	50	46.2 \pm 6.3	48.2 \pm 6.6	94.4 \pm 2.1	92.4	96.4	94.4
Apple vinegar	0	0	n.d.	n.d.	n.d.	-	-	-
	50	50	48.4 \pm 3.3	50.8 \pm 4.1	99.2 \pm 2.4	96.8	101.6	99.2
Grape vinegar	0	0	14.3 \pm 3.6	\leq LOQ	16.5 \pm 4.2	-	-	-
	50	50	64.1 \pm 3.5	49.2 \pm 4.4	113.3 \pm 3.7	99.6	98.4	96.8

^a Mean \pm standard deviation, ^b Not detected, ^c lower than limit of quantitation (5.0 $\mu\text{g L}^{-1}$), ^cCr_T: total chromium

recovery%:97.5, s=1.78) in terms of RSD% based on recoveries obtained for different samples and eluent volumes in Table 2 and 3. The limit of detection and limit of quantitation based on $3s_b/m$ and $10s_b/m$ was found to be as 1.5 and 5.0 $\mu\text{g L}^{-1}$, respectively.

3.8. Real sample analysis

The applicability of the proposed MSPE method was also controlled by Cr(III) and Cr(VI) spiking analysis of commercially available mineral water, apple juice, turnip juice, and vinegar samples. The recoveries for both ions from the real samples spiked with Cr(III) and Cr(VI) ions were achieved as above 95% (Table 7). The quantitative recovery values indicate that the proposed method is free from interferences and applicable.

On the other hand, the found contents of Cr(III) and Cr(VI) in water, fruit juice, and vinegar samples were evaluated relative to values for drinking water set out by EPA [8] and WHO [9], respectively. The concentrations of Cr(III) and Cr(VI) were both below the maximal permissible levels as 100 $\mu\text{g L}^{-1}$ total chromium and 50 $\mu\text{g L}^{-1}$ Cr(VI) (Table 7). Therefore, it can be concluded that the consumption of analyzed real samples cannot cause any adverse effects on human health.

4. Conclusions

The proposed magnetic solid phase extraction method for the preconcentration and speciation of chromium is simple, selective, and accurate. The recovery of Cr(III) from real samples and test solutions in the presence of Cr(VI) is quantitative at $\geq 95\%$. The extraction time was fairly short as 10 minutes. Due to the use of $\text{Fe}_3\text{O}_4@\text{coPANI-PTH}$ MNPs as adsorbent, Cr(III) ions were conveniently and rapidly collected on the adsorbent surface and then quickly desorbed from the adsorbent isolated with an external magnetic field. The method for selective determining Cr(III) revealed good analytical figures such as low LOD ($1.5 \mu\text{gL}^{-1}$), high precision (1.85%), and good preconcentration factor (40). Compared to the other research conducted in the literature, this method allows rapid extraction, low RSD, and comparable or higher PF [28,29,40,42-44]. Also, the figure of merits showed that the proposed MSPE-MIS-FAAS method was suitable for the rapid preconcentration, speciation, and determination of chromium in other beverages and various plant leaves.

Acknowledgment

The author thanks to Pamukkale University, Faculty of Art and Sciences, Chemistry Department, Analytical Chemistry Research laboratory for allowing use of instrument and lab space.

Conflicts of interest

The authors state that did not have conflict of interests

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