Cloud point extraction for preconcentration of Pb(II), Fe(III), Cr(III) and determination by flame atomic absorption spectrometry

Pb(II), Fe(III), Cr(III)'ün önderiştirilmesi için bulutlanma noktası ekstraksiyonu ve alevli atomik absorpsiyon spektrometresi ile tayini

Research Article

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ABSTRACT

A cloud point extraction (CPE) method for preconcentration of Pb(II), Fe(III) and Cr(III) has been established. This is based on the complexation of the metal ions with p-nitrophenylazoresorcinol (Magneson I) at pH 6.5 in the presence of non-ionic surfactant of octylphenoxy polyethoxyethanol (Triton X-114), prior to their determination by flame atomic absorption spectrometry (FAAS). The main factors affecting CPE efficiency, such as sample pH, complexing agent concentration, Triton X-114 concentration, temperature and incubation time were investigated. Under the optimized conditions, the detection limits (3s, n = 10) of Pb(II), Cr(III) and Fe(III) were 2.5, 2.3 and 1.9 μg L^{-1}, respectively. The relative standard deviation for ten replicate determinations of the analytes was less than 2.4%. The validation of the procedure was carried out by analysis of certified reference materials. The proposed method has been applied to the determination of lead, chromium and iron in tap water and some food samples.

Key Words
Cloud point extraction, preconcentration of lead, iron, chromium, FAAS.

ÖZET

Pb(II), Fe(III) ve Cr(III)'ün önderiştirilmesi için bulutlanma noktası ekstraksiyonu (CPE) yöntemi geliştirilmiştir. Bu yöntem, alevli atomik absorpsiyon spektrometresi (FAAS) ile metal iyonlarının tayininden önce, non-iyonik yüzey aktif madde Triton X-114 varlığında, pH 6.5 de, metal iyonlarının p-nitrofenilazoresorsinol (Magneson I) ile kompleks oluşturması temeline dayanmaktadır. CPE verimini etkileyen pH, kompleksleştirici madde derişimi, Triton X-114 derişimi, sıcaklık ve inkübasyon süresi gibi temel etkenler incelenmiştir. Optimum koşullarda, Pb(II), Cr(III) ve Fe(III) için gözlenebilme sınırı (3s, n = 10) sırasıyla 2.5, 2.3 ve 1.9 μg L^{-1} dir. On tekrarlı ölçümlere ait bağıl standart sapma %2.4 den daha düşüktür. Yöntemin doğruluğunun belirlenmesi için sertifikalı referans maddelerin analizi yapılmıştır. Önerilen yöntem, musluk suyu ve bazı gıda numunelerinde kurşun, krom ve demir tayini için uygulanmıştır.

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INTRODUCTION

Heavy metals in the environment are actually increasing due to human activity. In particular, mining operations and heavy industry in the developing world is leading to the accumulation of high concentrations of toxic heavy metals in natural waters. Today, it is understood that exposure to heavy metals can seriously affect human health [1]. Therefore, determination of trace metals in various samples is important for monitoring environmental pollution and human health. The determination of trace lead and chromium in environmental samples is a great importance due to toxicity of these metals. Iron is a moderately toxic element when compared with other transition metals. However, high level of iron in cells can lead to the formation of reactive radicals and cause cell damage. Iron imbalance can contribute to the development of numerous iron disorders, neurodegenerative diseases and some cancers [2].

The World Health Organization (WHO) has established the maximum allowable limit of $10\,\mu g\,L^{-1}$ for lead in drinking water. The provisional limit of total chromium in drinking water is $50\ \mu g\ L^{-1}$. Chromium value is designated as provisional because of uncertainties in the toxicological database. Concentration of iron in drinking water is normally less than 0.3 mg L^{-1}. However, iron occurs as a natural constituent in plants. Rice and many fruits and vegetables have low iron contents (1–10 mg kg^{-1}) [3].

Flame atomic absorption spectrometry (FAAS) has been a useful tool for the determination of metal ions. However, the direct determination of metal ions at trace levels by FAAS is limited due to their low concentrations and matrix interferences. Consequently, separation and preconcentration of analyte from the matrix prior to measurement is necessary. A wide variety of preconcentration and separation methods have been developed to determine trace metal ion in water and food samples. Some method has been included solid phase extraction, solvent extraction and coprecipitation, etc. [4-6]. In the last decade, there has been an increasing interest on the use of aqueous micellar solution as an extraction method. Cloud point extraction (CPE) is a simple method for the preconcentration and extraction of hydrophobic species from water. Metal ions can be extracted to the surfactant-rich phase usually after formation of a hydrophobic complex with an appropriate chelating agent [7-11]. The solute molecule present in aqueous solution of non-ionic surfactant is distributed between the two phases above the cloud point temperature this phenomenon is known as cloud point extraction [12].

Many azo reagents, such as *o*-hydroxyarylazo and *o,o'*-dihydroxyarylazo compounds, have been used for spectrophotometric determination of metals. In these azo reagents the oxygen atom of the *o*-hydroxyl group and the nitrogen atom of the azo group participate in complex formation with metal ions. *o,o'*-dihydroxyazo dyes are some of the more common chromogenic reagents and that have been used in metal determination by the ternary system (metal, dye, surfactant) [13,14]. Resorcinol-based dyes, 4-(2-pyridylazo)-resorcinol (PAR) and 4-(2-thiazolylazo)-resorcinol (TAR), include an ortho azo functional group, have been used as metal ion complexing agent as a function of pH [15]. *o*-hydroxyarylazo compounds are very weak acids. They have been used in dyestuffs, as spectrophotometric and titrimetric reagents, and in solvent extraction studies [16].

In this work, p-nitrophenylazoresorcinol (Magneson I) was used as complexing agent which is an *o*-hydroxyazo dye. Magneson I is specific reagent for the detection of magnesium. However, to our knowledge, there has been no report on using Magneson I as complexing agent for determination of lead, chromium and iron. This work reports the simultaneous preconcentration of lead, chromium and iron after the formation of a complex with Magneson I in slightly acidic media. In addition, the present work shows that the possible usage of the Magneson I, and its selectivity depends on pH. The experimental parameters affecting the CPE efficiency were investigated in detail. This method offers a procedure for determination of lead, iron and chromium at $\mu g\ L^{-1}$ levels by FAAS.

The proposed method has been directly applied to the determination of the lead, chromium and iron in water samples. For food samples, decomposition procedure was applied and then lead and iron content have been determined. Cr(III) has been probably oxidized to Cr(VI) when decomposition

procedure was applied to the food samples. Therefore Cr(III) has not been determined in food samples. Finally, the method was validated by analyzing the certified reference materials.

EXPERIMENTAL

Instrumentation

All measurements were carried out using an AAnalyst 800 flame atomic absorption spectrometer (Perkin Elmer, Norwalk, CT, USA). Deuterium background correction was employed to correct for non-specific absorption. Hollow cathode lamps for Pb, Cr and Fe (Perkin Elmer) were operated at 10 mA, 15 mA and 10 mA, respectively, with a spectral bandwidth of 0.7 nm for Pb and Cr, 0.2 nm for Fe. The selected wavelengths were 283.3 nm, 357.9 nm and 248.3 nm for Pb, Cr and Fe respectively. The acetylene flow rates and the burner height were adjusted in order to obtain the maximum absorbance signal by aspirating a solution containing the analyte in ethanol-nitric acid mixture. A Fisher scientific accumet model 15 pH meter was used to measure pH values. A Clifton model NE1-22 thermostatic bath, maintained at the desired temperature, was used for cloud point temperature experiments. A Hettich, EBA 21 model centrifuge was used to accelerate the phase separation.

Reagents

All chemicals used were of analytical reagent grade. All solutions were prepared with deionized water (18.1 MΩ cm) obtained from a Barnstead, Nanopure Diamond purification system. The non-ionic surfactant Triton X-114 (Sigma-Aldrich, Milwaukee, USA) was used without further purification. Stock standard solutions of metal ions at a concentration of 1000 mg L^1 were prepared from nitrate salts (Merck, Darmstadt, Germany). Working standard solutions were obtained daily by stepwise dilution of the stock standard solution with deionized water. Magneson I (Sigma-Aldrich) as a complexing reagent was dissolved in ethanol (Merck). Acetic acid-sodium acetate buffer was used to adjust the solution pH in the range of 4-6. HCl and NaOH were used for other pH values. Methanol and ethanol (Merck)

were used to decrease the viscosity of surfactant-rich phase. The laboratory glassware was kept overnight in 10% (v/v) nitric acid solution. Before use, the glassware was rinsed with deionized water and dried in dust free environment.

Samples and sample treatment

Multi grain bread, white bread, hazelnut, tomato paste and vegetable samples (spinach, lettuce and cabbage) were purchased for analysis from local supermarkets at Ankara in Turkey. First, vegetable samples were cleaned with tap water and deionized water. Then these samples, tomato paste and bread samples were dried to constant weight at 110°C. Dried samples and hazelnut samples were ground to reduce particle size. Triplicate samples of about 1.5 g were treated with 10 mL of concentrated nitric acid. The contents in the beaker were heated on a hot plate (130 °C) to near dryness. After cooling to room temperature, 5 mL of concentrated perchloric acid was added. To obtain clear solution, the beaker was heated gently until completion of sample decomposition. The solution left to cool down and then transferred into a 100 mL volumetric flask. Small portions of 0.1 mol L^1 nitric acid was added to the solution and diluted to the mark with deionized water. About 0.5 g wheat flour, rice and solid certified reference materials (NIST-1567a wheat flour, IRMM-804 rice flour and NCS ZC73008 rice) were taken and the same decomposition procedure was applied, finally diluted to 25 mL with deionized water. Tap water, TM-23.2 and TMDA 51.3 fortified water, LGC6010 hard drinking water and Seronorm 0511545 urine were direcly subjected to the cloud point extraction method as described below.

Procedure

For CPE, taken an aliquot of 25.0 mL of the standard or sample solution containing metal ions added 0.2% (v/v) of Triton X-114 and 0.04% (w/v) of Magneson I at pH 6.5 was prepared. This solution was shaken for 1 min and left to stand in a thermostated bath at 70°C for 45 min. The mixture was cooled in an ice bath to increase the viscosity of the surfactant rich phase and then separation of two phases was achieved by centrifugation for 5 min at 6000 rpm. The

supernatant aqueous phase was carefully removed with a pipette. In order to decrease the viscosity and facilitate sample handling prior to the FAAS assay, an ethanol solution containing 0.1 mol L^{-1} nitric acid was added to the surfactant-rich phase, in this step final volume was 1.5 mL. The resultant solutions were directly introduced by conventional aspiration into a FAAS. Blank solution was also submitted to similar procedure.

RESULTS AND DISCUSSION

Effect of pH

Separation of metal ions by CPE involves complex formation with sufficient hydrophobicity to be extracted into the small volume of the surfactant phase. The extraction yield depends on the pH at which complex formation occurs. The effect of pH on the complex formation and extraction of Pb(II), Fe(III), and Cr(III) was studied in the range of 3-12 (Figure 1).
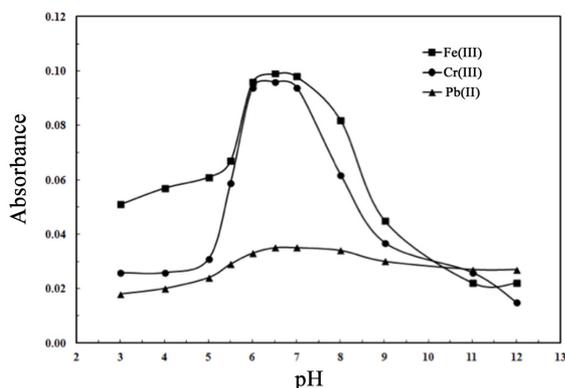

Figure 1. Effect of pH on the CPE of 200 μg L^{-1} Pb(II), Fe(III) and Cr(III). Other conditions: sample volume 25 mL, 0.04% (w/v) Magneson I, 0.2% (v/v) Triton X-114, dilution solvent 0.1 mol L^{-1} HNO$_3$ in ethanol, temperature 70 °C, time 45 min.

o-Hydroxydiarylazo compounds (H$_2$R) are very weak acids and they exist as HR$^-$ anion form between pH 6 and 8. In these azo reagents the oxygen atom of the o-hydroxyl group and the nitrogen atom of the azo group participate in complex formation with metal ions. This may be attributed to the presence of free lone pair of electrons on nitrogen and deprotonated oxygen atom [15,17,18].

Di -and mono-hydroxo complexes, Cr(OH)$_2^+$ and CrOH^{2+} are expected to be dominant forms of Cr(III) in weakly acidic and weakly alkaline solution

[19]. Considering the hydroxo complexes of Fe(III), in neutral region Fe(OH)$_2^+$ is predominant species. Furthermore, Fe(III) has a tendency to form mixed hydrolysis complexes with N, O-donor ligands [20]. Higher absorbance signals obtained at pH 6.5 for iron and chromium may be due to the electrostatic attractions between the charged cations and anionic form of azo dye. The absorbance is nearly constant in the pH range of 6.0-8.0 for Pb(II). Therefore, pH 6.5 was chosen for the subsequent experiments.

Effect of the complexing agent concentration

The effect of concentration of the Magneson I on the analytical respond was examined and the results are shown in Figure 2(a). The concentration of chelating agent was evaluated in the range of 0.002-0.06% (w/v). A concentration of 0.04% (w/v) was chosen as the optimum concentration of the chelating agent for extraction of three metal ions. The concentration above this value has no significant effect on the performance of the system.

Effect of Triton X-114 concentration

The effect of Triton X-114 concentration was investigated in the range 0.02-0.4% (v/v). Figure 2(b) shows the variation of the analytical signal as a function of Triton X-114 concentration. Analytical signal increases with increasing the concentration of the surfactant and reaches a maximum in the concentration range of 0.15-0.25% (v/v). At higher surfactant concentrations (> 0.25% v/v), the volume of the surfactant-rich phase increased that was obtained after centrifugation. Therefore surfactant-rich phase should be more diluted for directly introduced to the FAAS. The signals decreased, due to the increase of the final volume of extract, that decrease of concentration of analyte. At lower concentrations (< 0.15% v/v), the analytical signal was low probably because of the insufficient entrapment of metal complex quantitatively by micelles. A final concentration of 0.2% (v/v) Triton X-114 in total solution was chosen as optimum for the determination of lead, iron and chromium.

Effects of other experimental factors

In the CPE method, equilibration temperature and time should be optimized for completion of the
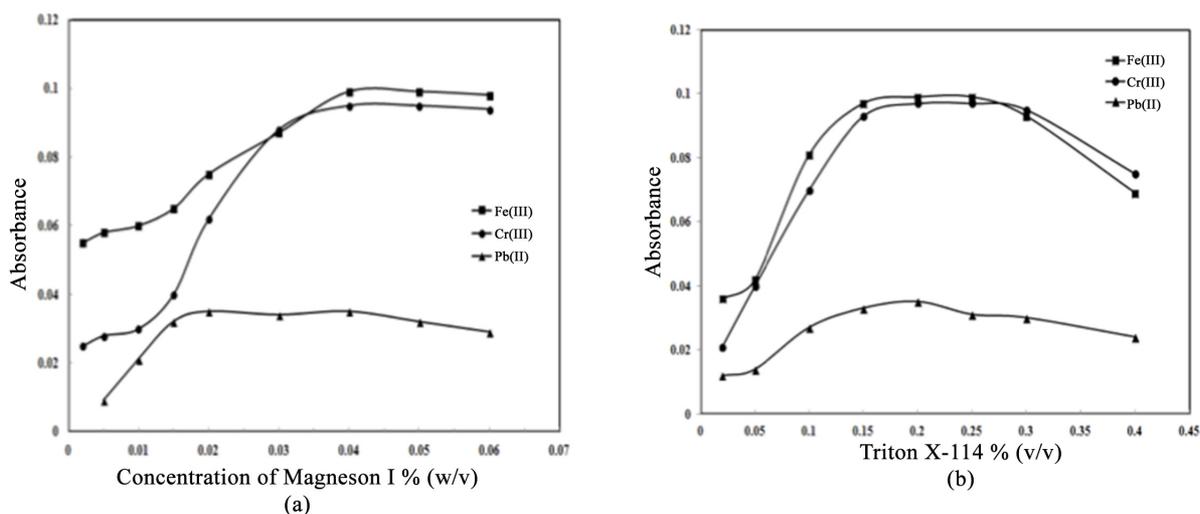
Figure 2. (a) Effect of Magneson I concentration, (b) Effect of TX-114 concentration on the CPE of 200 μg L^{-1} Pb(II), Fe(III) and Cr(III).

reaction and easy phase separation. The effect of the equilibration temperature and time were studied within a range of 30–80°C and 5–60 min. The results showed that an equilibration temperature of 70°C and a time of 45 min were adequate to obtain quantitative extraction.

The addition of a salt can markedly facilitate the phase-separation process, as demonstrated with some non-ionic surfactant systems, since it alters the density of the bulk aqueous phase. Ionic strength was tested within the interval of 0.005–0.05 mol L^{-1} NaCl concentration. It had no significant effect on CPE efficiency.

After cloud point preconcentration, it is necessary to decrease the viscosity of the surfactant-rich phase to facilitate handling and introduction into the atomizer. Different solvents such as ethanol, methanol and acidic solutions of ethanol and methanol were tried in order to select a diluting agent. In the presence of ethanol and methanol, surfactant rich phase could not be dissolved. On the other hand, in the presence of acidic ethanol, surfactant-rich phase was dissolved completely and maximum absorbance values were obtained. Therefore, 1 mL of ethanol solution containing 0.1 mol L^{-1} nitric acid was chosen as diluting agent.

Effect of foreign ions
The effect of typical potential interfering ions on the analytical signal was investigated. Different amounts of ions were added to the test solution containing 200 μg L^{-1} of Pb(II), Cr(III) and Fe(III) and then CPE procedure was applied as described previously. The tolerance limit was defined as the concentration of added ion that caused less than ±5% relative error in the determination of Pb(II), Cr(III) and Fe(III). Table 1 summarizes the maximum tolerances of the studied ions. It can be seen that common coexisting ions such as alkali and alkaline earth elements do not interfere at high concentrations. The effects of other ions at given concentrations are negligible. These results indicate the applicability of the developed procedure for Pb(II), Cr(III) and Fe(III) determination free of interference.

Analytical figures of merit
Using the optimized experimental condition, the calibration graphs were linear in the range of 20–1500 μg L^{-1} Pb(II) and 10–500 μg L^{-1} Cr(III) and Fe(III). The regression equations for Pb(II), Cr(III) and Fe(III) were A = 1.37 x 10^{-4} C + 6.9 x 10^{-3} (R^2 = 0.999), A = 3.62 x 10^{-4} C + 1.90 x 10^{-2} (R^2 = 0.998) and A = 5.10 x 10^{-4} C - 2.8 x 10^{-4} (R^2 = 0.999) respectively, where A is the absorbance and C is the metal ion concentration in solution (μg L^{-1}). The equation obtained by direct aspiration in FAAS without the preconcentration, the linear equations for Pb(II), Cr(III) and Fe(III) were A = 7.9 x 10^{-6} C + 3.0 x 10^{-3} (R^2 = 0.996), A = 2.17 x 10^{-5} C + 9.9 x 10^{-3} (R^2 = 0.997) and A = 2.91 x 10^{-5} C – 3.87 x 10^{-3} (R^2 = 0.998) respectively. Enrichment factors were calculated as the ratio of the slopes of the calibration graphs with and without CPE and

Table 1. Tolerance limits of interfering ions on the recoveries of Pb(II), Fe(III), Cr(III) (n=3)[a]

Ions	Analytes to interferents ratio		
	Pb(II)	Fe(III)	Cr(III)
Na^+	1:6000[b]	1:6000[b]	1:6000[b]
Cl^-	1:9000	1:9000	1:9000
K^+, Ca^{2+}, Mg^{2+}, NO_3^-, CO_3^{2-}	1:1000	1:1000	1:1000
SO_4^{2-}	1:500	1:500	1:500
Ni^{2+}, Co^{2+}	1:100	1:100	1:100
Cu^{2+}, Zn^{2+}	1:50	1:100	1:100
Al^{3+}	1:50	1:50	1:50
Cd^{2+}	1:10	1:50	1:50
Pb^{2+}	-	1:10	1:100
Fe^{3+}	1:500	-	1:100
Cr^{3+}	1:100	1:100	-

[a] ≤±5% Relative standard deviation
[b] Maximum ratio tested.

enrichment factors were 17 for Pb(II), 16 for Cr(III) and 18 for Fe(III). The precision of this method was calculated as the relative standard deviation (RSD %) of ten independent measurements of 200 μg L^{-1} Pb(II), Cr(III) and Fe(III) solutions and found as 2.4% for Pb(II), 2.2% for Cr(III) and 2.3% for Fe(III). The limit of detection (LOD) was calculated by the 3s criterion as the concentration that gives a response equivalent to three times the standard deviation (SD) of the blank (n = 10). The detection limits were found to be 2.5, 2.3 and 1.9 μg L^{-1} for Pb(II), Cr(III) and Fe(III) respectively. The limit of quantification (LOQ) is the lowest level of analyte that can be accurately and precisely measured. LOQ defined as ten times the SD of the blank measurements (n = 10) were found as 8.3 μg L^{-1} for Pb(II), 7.8 μg L^{-1} for Cr(III) and 6.3 μg L^{-1} for Fe(III).

Accuracy of the method

In order to evaluate the accuracy of the method, the following certified reference materials were submitted to preconcentration procedure: TM 23.2 (Fortified Water), LGC6010 (Hard Drinking Water), TMDA 51.3 (Fortified Water), Seronorm LOT 0511545 (Urine), NIST-1567a (Wheat Flour), IRMM-804 (rice flour) and NCS ZC73008 (Rice). The results for three individual determinations are shown in Table 2. As seen Table 2, there is no significant difference between results obtained by developed procedure and the certified values

for metal ions.

Analysis of real samples

The CPE procedure was applied to the determination of lead, chromium and iron content in tap water (Beytepe, Ankara, Turkey). Tap water was spiked with Pb(II), Cr(III) and Fe(III), and the recoveries were also studied. As shown Table 3, the recoveries ranged from 97 to 103%, demonstrating the applicability of the method.

The proposed CPE procedure was applied to the determination of lead and iron contents in rice, wheat flour, tomato paste, multi grain bread, white bread, hazelnut, spinach, lettuce and cabbage samples. Digestion of food samples was performed by using the procedure described in Section *samples and sample treatment* and these samples were subjected to the CPE procedure. The results are given in Table 4.

The metal concentrations determined were based on dry weight for all food samples. Lead was found to be below the detection limit of method in the analyzed food samples, except for the spinach and lettuce. Lead content of leafy vegetable samples were obtained as 2.2 μg g^{-1} for spinach and 1.9 μg g^{-1} for lettuce, respectively. The contents of lead in the spinach and lettuce samples are close to the reported by Oymak et al. [4]. On the other hand, the contents of lead in these samples are higher than those detected in Egypt [21]. The maximum limit value of lead recommended by Turkish Food Codex [22] for leafy vegetables is 0.3 μg g^{-1} (wet weight).

Iron content ranged from 8.15 μg g^{-1} in rice to 144 μg g^{-1} in spinach samples. Iron levels have been reported in the range of 5.74 to 260 μg g^{-1} in vegetables and 7.48 to 34.3 μg g^{-1} in cereals [23]. Iron contents for vegetable samples from Egypt have been reported in the range of 17.6–257 μg g^{-1} and iron contents in bread and rice samples have been reported as 26.9 and 27.0 μg g^{-1} respectively. The contents of iron in the spinach, rice and bread samples are lower than those reported in Egypt [24]. Iron level in tomato paste sample was found to be higher than the legal limit the maximum iron level permitted for canned food is 15 μg g^{-1} according to Turkish Food Codex [22].

Table 2. Analysis of standard reference materials (n=3).

Sample	Ion	Certified value ($\mu g\ L^{-1}$)	Found[a] ($\mu g\ L^{-1}$)	Recovery (%)
TM-23.2 Fortified water	Pb(II)	3.8	BDL	-
	Cr(III)	6.5	BDL	-
	Fe(III)	12.7	12.3 ± 1.2	96.8
TMDA-51.3 Fortified water	Pb(II)	73.3	72.6 ± 2.3	99.0
	Cr(III)	67.5	66.2 ± 4.2	98.1
	Fe(III)	109	112 ± 2.6	103
LGC 6010 Hard drinking water	Pb(II)	95	96 ± 0.9	101
	Cr(III)	48	48 ± 1.0	100
	Fe(III)	236	236 ± 1.0	100
Seronorm LOT 0511545 urine	Pb(II)	40.3	42.2 ± 1.6	105
	Cr(III)	19.7	20.3 ± 0.5	103
	Fe(III)	12.3	12.0 ± 0.8	97.5
		Certified value ($\mu g\ g^{-1}$)	Found[a] ($\mu g\ g^{-1}$)	Recovery (%)
NIST-1567a Wheat flour	Pb(II)	NA[b]	-	-
	Fe(III)	14.1	13.8 ± 0.5	97.9
IRMM-804 Rice flour	Pb(II)	0.42	0.40 ± 0.3	95.2
	Fe(III)	NA[b]	-	-
NCS ZC73008 Rice	Pb(II)	0.08	BDL	-
	Fe(III)	7.6	7.7 ± 0.1	101

[a]mean: ±standard deviation
[b]NA: Not available for this reference material
BDL: Below detection limit

CONCLUSION

A cloud point extraction procedure for preconcentration of lead, chromium and iron ions by using a resorcinol-based dye (Magneson I) and nonionic surfactant Triton X-114 is developed. Table 5 gives the comparison of the purposed method with other CPE methods for determination of iron, chromium and lead using several reagents. The detection limits of method are comparable level with the works in literature including the combination of CPE-FAAS [7,8,10,11,25-28].

The proposed method offers a procedure for determination of lead, iron and chromium at μg L^{-1} levels by FAAS. The method was successfully applied to the determination of lead, chromium and iron in certified (water) reference materials and tap water. Lead and iron have been determined in certified food materials and real food samples.

Table 3. Determination of iron, chromium and lead ions in tap water (n = 5).

Ion	Added (µg L^{-1})	Found^a (µg L^{-1})	Recovery (%)
Fe(III)	0	18.9 ± 0.5	-
	10	28.6 ± 0.5	99
	50	70.6 ± 0.5	102
Cr(III)	0	BDL	-
	30	31.0 ± 1.2	103
	50	48.0 ± 1.6	96
Pb(II)	0	BDL	-
	30	29.2 ± 0.5	97
	50	48.3 ± 0.5	97

^{a}mean: ± standard deviation
BDL: Below detection limit

Simultaneous separation and preconcentration of these metal ions is one of the important advantages. In our previous work, Magneson I was used as complexing agent for CPE of nickel and manganese, pH value of around 11.5 found to be optimum for the quantitative extraction [29]. In this work the optimum pH value is 6.5 for quantitative extraction of lead, chromium and iron. The results for this work demonstrate the possibility of using the Magneson I - TX-114 system for the preconcentration of metal ions prior to flame atomic absorption spectrometric assay.

References

1. I. Jaric, Z.V. Jeftic, G. Cvijanovic, Z. Gacic, L. Jovanovic, S. Skoric, M. Lenhardt, Determination of differential heavy metal and trace element accumulation in liver, gills, intestine and muscle of sterlet (acipenser ruthenus) from the Danube river in serbia by ICP-OES, Microchemical Journal, 98 (2011) 77.
2. P.T. Lieu, M. Heiskala, P.A. Peterson, Y. Yang, The roles of iron in health and disease, Molecular Aspects of Medicine, 22 (2001) 1.
3. WHO (World Health Organization), http://www.who.int/water_sanitation_health/dwq/chemicals/iron.pdf, Accessed 15.04.13, 2008, 2.
4. T. Oymak, Ş. Tokalıoğlu, V. Yılmaz, Ş. Kartal, D. Aydın, Determination of lead and cadmium in food samples by the coprecipitation method, Food Chemistry, 113 (2009) 1314.
5. S.G. Özcan, N. Şatiroğlu, M. Soylak, Column solid phase extraction of iron(III), copper(II), manganese(II) and lead(II) ions food and water samples on multi-walled carbon nanotubes, Food and Chemical Toxicology, 48 (2010) 2401.
6. S. Saçmacı, S. Kartal, M. Saçmacı, Selective separation and preconcentration of Fe(III) and Zn(II) ions by solvent extraction using a new triketone reagent, Clean - Soil, Air, Water, 39 (2011) 584.
7. J. Chen, K.C. Teo, Determination of cadmium, copper, lead and zinc in water samples by flame atomic absorption spectrometry after cloud point extraction, Analytica Chimica Acta, 450 (2001) 215.
8. J.L. Manzoori, A.B. Tabrizi, Cloud point preconcentration and flame atomic absorption spectrometric determination of Cd and Pb in human hair, Analytica Chimica Acta, 470 (2002) 215.
9. N. Şatıroğlu, Ç. Arpa, Cloud point extraction for the determination of trace copper in water samples by flame atomic absorption spectrometry, Microchimica Acta, 162 (2008) 107.
10. M. Ghaedi, H. Tavallali, A. Shokrollahi, M. Zahedi, K. Niknam, M. Soylak, Preconcentration and determination of zinc and lead ions by a combination of cloud point extraction and flame atomic absorption spectrometry, Clean, 37 (2009) 328.
11. D. Citak, M. Tuzen, A novel preconcentration procedure using cloud point extraction for determination of lead, cobalt and copper in water and food samples using flame atomic absorption spectrometry, Food and Chemical Toxicology, 48 (2010) 1399.
12. Z. Wang, F. Zhao, D. Li, Determination of solubilization of phenol at coacervate phase of cloud point extraction, Colloids and Surfaces A, 216 (2003) 207.
13. M. Dakiky, I. Nemcova, Aggregation of o,o- dihydroxy azo dyes III. Efect of cationic, anionic and non-ionic surfactants on the electronic spectra of 2-hydroxy-5-nitrophenylazo- 4-[3-methyl-1-(400-sulfophenyl)-5-pyrazolone, Dyes and Pigments, 44 (2000) 181.
14. M.S. Masoud, H.H. Hammud, H. Beidas, Dissociation constants of eriochrome Black T and eriochromeblue black RC indicators and the formation constants of their complexes with Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), and Pb(II), under different temperatures and in presence of different solvents, Thermochimica Acta, 381 (2002) 119.
15. A.E. Visser, S.T. Griffin, D.H. Hartman, R.D. Rogers, Naphthol and resorcinol based azo dyes as metal ion complexants in aqueous biphasic systems, Journal of Chromatography B, 743 (2000) 107.

Table 4. Determination of iron and lead ions in some food samples (n = 3).

Sample	Added (µg g⁻¹)	Fe (III) (µg g⁻¹)ᵃ	Recovery (%)	Pb(II) (µg g⁻¹) ᵃ	Recovery (%)
Wheat flour	0	13.1 ± 0.1	-	BDL	-
	10	23.5 ± 1.1	102	9.6 ± 0.8	96
Rice	0	8.15 ± 0.9	-	BDL	-
	10	17.6 ± 1.3	97	10.5 ± 1.0	105
Multigrain bread	0	19.6 ± 1.8	-	BDL	-
	10	30.5	103	9.1 ± 0.5	91
White bread		10.8 ± 1.3	-	BDL	-
	10	21.4 ± 0.9	103	10 ± 0.9	100
Hazelnut	0	41.2 ± 1.7		BDL	-
	10	52.5 ± 1.3	103	10.4 ± 1.6	104
Tomato paste	0	66.2 ± 3.1	-	BDL	-
	10	74.0 ± 2.0	97	9.8 ± 1.1	98
Spinach	0	144 ± 4.5	-	2.2 ± 0.7	-
	10	157 ± 1.7	102	11.6 ± 0.9	95
Lettuce	0	46.3 ± 0.9	-	1.9 ± 0.9	-
	10	56.0 ± 1.5	99	11.2 ± 1.5	94
Cabbage	0	60.3 ± 1.5	-	BDL	-
	10	70.8 ± 2.2	101	9.8 ± 0.8	98

ᵃmean: ± standard deviation
BDL: Below detection limit

16. R. Carballo, A. Castineiras, B. Covelo, J. Niclos, E.M. Vazquez-Lopez, Synthesis and characterization of a potassium complex of magneson: [K(HL)(OH$_2$)$_2$]$_¥$ [H$_2$L=4-(4-nitrophenylazo) resorcinol (magneson)], Polyhedron, 20 (2001) 2415.

17. Z. Marczenko, M. Balcerzak, Separation and spectrophotometric determination of elements, second edition, New York: Elsevier, Chapter 4, 2000.

18. K. Alizadeh, B. Rezaei, B. Maddah, Spectrophotometric determination of aqueous acidity constants of three azo dyes, Central European Journal of Chemistry, 8 (2010) 392.

19. J. Kotas, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, Environmental Pollution, 107 (2000) 263.

20. H. Filik, B.D. Öztürk, M. Doğutan, G. Gümüş, R. Apak, Separation and preconcentration of iron(II) and iron(III) from natural water on a melamine-formaldehyde resin, Talanta, 44 (1997) 877.

21. M.A. Radwan, A.K. Salama, Market basket survey for some heavy metals in Egyptian fruits and vegetables, Food and Chemical Toxicology, 44 (2006) 1273.

22. Turkish Official Gazette, Regulation of setting maximum levels for certain contaminants in foodstuffs, Iss:24908, October 16, 2002.

23. Ş. Tokalıoğlu, F. Gürbüz, Selective determination of copper and iron in various food samples by the solid phase extraction, Food Chemistry, 123 (2010) 183.

Table 5. Comparison of several CPE methods for metal ions.

Reagent	Surfactant	Sample volume (mL)	Metal ion	PF[a]	LOD[b] ($\mu g\ L^{-1}$)	Sample	Ref.
BPIMI [c]	Triton X-114	15	Pb(II)	30	2.5	Food, soil	10
BIES [d]	Triton X-114	15	Pb(II)	30	2.8	Radiology waste vegetable, blood, urine	26
PAN [e]	Triton X-114	50	Cr(III)	48	0.7	Water	28
Ligangless	Tween-80	50	Pb(II)	-	7.2	Water, food, mineral tablet	25
		50	Cr(III)	-	2.8		
o,o-Diethyl dithophosphate	Triton X-114	10	Pb(II)	43	2.86	Human hair	8
TAN [f]	Triton X-114	50	Pb(II)	55.6	1.1	Water	7
1-PTSC [g]	Triton X-114	50	Pb(II)	25	3.42	Water, food	11
PHBI [h]	Triton X-114	15	Fe(III)	30	2.8	Food, blood	27
Magneson I	Triton X-114	25	Pb(II)	17	2.5	Water, food	This work
		25	Cr(III)	16	2.3		
		25	Fe(III)	18	1.9		

[a]Preconcentration factor, [b]Limit of detection, [c]3-[(4-bromophenyl) (1-H-inden-3-yl)methyl]-1H–indene, [d]Bis((1H-benzo [d] imidazol-2yl) ethyl) sulfane,[e]1-(2-pyridilazo)-2-naphtol, [f]1-(2-thiazolylazo)-2-naphthol, [g]1-phenylthiosemicarbazide, [h]2-phenyl-1H-benzo[d] imidazole

24. S.M. Abdel-Azeem, N.R. Bader, H.M. Kuss, M.F. El-Shahat, Determination of total iron in food samples after flow injection preconcentration on polyurethane foam functionalized with N,N-bis(salicylidene)-1,3-propanediamine, Food Chemistry, 138 (2013) 1641.

25. S. Candir, I. Narin, M. Soylak, Ligandless cloud point extraction of Cr(III), Pb(II), Cu(II), Ni(II), Bi(III), and Cd(II) ions in environmental samples with Tween 80 and flame atomic absorption spectrometric determination, Talanta, 77 (2008) 289.

26. M. Ghaedi, A. Shokrollahi, K. Niknam, E. Niknam, A. Najibi, M. Soylak, Cloud point extraction and flame atomic absorption spectrometric determination of cadmium(II), lead(II), palladium(II) and silver(I) in environmental samples, Journal of Hazardous Materials, 168 (2009) 1022.

27. M. Ghaedi, A. Shokrollahi, K. Niknam, M. Soylak, Cloud point extraction of copper, zinc, iron and nickel in biological and environmental samples by flame atomic absorption spectrometry, Separation Science and Technology, 44 (2009) 773.

28. G.D. Matos, E.B. dos Reis, A.C.S. Costa, S.L.C. Ferreira, Speciation of chromium in river water samples contaminated with leather effluents by flame atomic absorption spectrometry after separation/preconcentration by cloud point extraction, Microchemical Journal, 92 (2009) 135.

29. Ç.A. Şahin, M. Efeçınar, N. Şatıroğlu, Combination of cloud point extraction and flame atomic absorption spectrometry for preconcentration and determination of nickel and manganese ions in water and food samples, Journal of Hazardous Materials, 176 (2010) 672.