Effervescence assisted dispersive liquid-liquid microextraction for spectrophotometric determination of chromium (VI) in water, tannery effluent, milk, and orange juice samples

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ABSTRACT

In this paper, effervescence-assisted dispersive liquid-liquid microextraction was proposed for selective extraction and preconcentration of Cr (VI) prior to its quantitative determination by UV-Vis spectrophotometry. Before employing the method, Cr (VI) ions available in the samples were complexed with 1,5-diphenylcarbazide in an acidic medium. Experimental parameters influencing the performances of the method including pH, the concentration of the complexing agent, type and volume of both extraction solvent and effervescent agent, stability of the complex, and effect of extraction time were thoroughly studied and optimized. Calibration curve plotted from 0.005–2.0 mg L^{-1} demonstrated good linearity ($R^2 = 0.9992$). The limits of detection and quantification of the method were 0.001 and 0.005 mg L^{-1}, respectively. The method provided an enrichment factor of 21.4. Precision studies in terms of repeatability, intermediate precision, and reproducibility were conducted at three concentration levels and their RSD values were <6.2. The ruggedness of the method studied at different wavelengths (535–545 nm) had RSD values <3.3. The recoveries of the method were from 83.0–117.6%. Finally, the proposed method was successfully applied for the determination of Cr (VI) from various matrices including tap, well, and river water; tannery effluent; milk; and orange juice samples.

KEYWORDS

dispersive liquid-liquid microextraction; effervescence-assisted; UV-Vis spectrophotometry

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INTRODUCTION

Environmental contamination due to Cr has become a major concern due to its high concentration in the soil and water. Industrial applications such as electroplating, dyeing of textiles, leather processing, steel production and tanning factories release Cr containing effluents into the environment.[1,2] Chromium mainly exists in the environment as Cr (III) and Cr (VI). Cr (III) is essential for plants and animals as well as exhibits less toxicity and mobility. However, Cr (VI) is highly toxic to humans, animals, plants, and microorganisms.[3–7] Cr (VI) occurs as $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$, which are potent oxidant under acidic conditions. It has the ability to penetrate cells, and attached to proteins, DNA and membrane lipids.[6,8,9] The International Agency for Research on Cancer (IARC) classified Cr (VI) as Group 1 human carcinogen [10].

Cr (VI) is highly soluble in water and mobile in soil. Thus, it can easily contaminate water, soil and ultimately contaminate crop that may cause serious health hazards in humans and animals through food chain.[6,9] Exposure to Cr (VI) may cause human health problems such as internal hemorrhage, respiratory ailments (including lung cancer), teeth abnormalities, kidney and liver damage as well as skin rashes.[11,12] According to World Health Organization (WHO) and united states environmental protection agencies (USEPA) the allowed tolerable limit is 0.05 and 2 mg L^{-1} for Cr (VI) and total chromium in drinking water, respectively.[2,13]

Various analytical techniques such as flame atomic absorption spectrometry (FAAS),[3,14,15] dynamic reaction cell inductively coupled plasma mass spectrometry (DRC-ICP-MS),[16] anodic electrothermal atomic absorption spectrometry (EAAS),[17] ultraviolet-visible (UV-Vis) spectrophotometry[12,13,18–20] and high-performance liquid chromatography (HPLC) with UV detection[21,22] have been used for determination of Cr (VI). However, due to its low concentration and complexity of real samples selective extraction and/or preconcentration step is needed prior to its determination.

Several selective sample preparation methods including homogeneous liquid-liquid-extraction (HLLE),[3] salting-out liquid-liquid extraction (SA-LLE),[23] solid phase extraction (SPE),[14,15,16,22,24] supported liquid membrane (SLM),[25] electromembrane extraction (EME) combined with micro-EME (μ-EME),[17] and various versions of dispersive liquid-liquid microextraction (DLLME)[4,8,1318,19,21,26–31] have been used for extraction and/or preconcentration of Cr (VI) prior to its quantitative determination from various matrices. In the last couple of decades, DLLME has been widely used for extraction and/or preconcentration of organic and inorganic pollutants due to its simplicity, selectivity, greenness and other several advantages.

To improve the selectivity, simplicity, greenness, and/or speed of extraction and/or preconcentration process of DLLME method, several noteworthy alternative approaches, including deep eutectic solvent DLLME (DES-DLLME),[18] surfactant-assisted dispersive liquid-liquid microextraction (SA-DLLME),[19] emulsification-based dispersive liquid microextraction (EB-DLME)[21], ultrasound enhanced air-assisted surfactant liquid-liquid microextraction based on the solidification of a floating organic droplet (UA-DES-ELPME),[28] supramolecular dispersive liquid–liquid microextraction-based solidification of floating organic drops (UEAASLLM-SFO),[29] ultrasound-assisted emulsification microextraction (UAEME)[8,27,30] and so on have been reported. However, most of these procedures comparatively use higher volumes of disperser solvent which may increase the solubility of target analytes in aqueous samples. Some of these methods also require special equipment such ultrasound sonicator and vortex agitator.[8,27–31]

Recently, effervescence assisted DLLME (EA-DLLME) has been reported as another impressive alternative method to the existing DLLME approaches. EA-DLLME procedure was first reported in 2014 by Lasarte-Aragonés and coworkers.[32] The method is based on

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effervescent reaction; a reaction between an effervescent agent and a proton donor. The reaction generates CO_2 that disperses the extractant in aqueous samples. The EA-DLLME method has been used for extraction and/or preconcentration of silver and cobalt ions from cow milk, vitamin B_{12}, orange juice, and tap water;[33] copper ion from tap and lake water;[34] fungicides from apple juice [31] as well as vinegar and juices;[35] herbicides from water;[32] cationic and anionic surfactants from lake and river water;[36] synthetic dyes (sunset yellow and brilliant blue FCF) from jelly, fruity Pastel, smarties, ice cream and candy;[37] ketoprofen and diclofenac in liver;[38] benzoylurea insecticides from river water;[39] as well as copper and nickel ions from river, surface, and well water as well as peach and orange juices[40] prior to their quantitative determinations.

In this paper, EA-DLLME was proposed for the extraction and/or pre-concentration of Cr (VI) from tap and river water, tannery effluent, milk as well as orange juice samples prior to its determination by UV-Vis spectrophotometry. Different parameters affecting the extraction efficiency of the method were investigated and the optimal conditions were established. The analytical performance characteristics of the proposed method were compared with different DLLME approaches and other recently reported methods.

EXPERIMENTAL

Chemicals and reagents

Phosphoric acid, (H_3PO_4, 85%) was purchased from Thermo fisher (Kandel) GmbH (Kandel, Germany), sulfuric acid (H_2SO_4, 98%), sodium bicarbonate ($NaHCO_3$, 99%) and sodium carbonate (Na_2CO_3, 99%), calcium carbonate ($CaCO_3$), 1, 5-diphenylcarbazide (DPC), copper sulfate ($CuSO_4$), cobalt chloride ($CoCl_2$), and 1000 mg L^{-1} in 2% HNO_3 of each metal ion (Cd^{2+} in 2% HNO_3, Fe and V) were purchased from Merck (Darmstadt, Germany), nitric acid (HNO_3, 65%) was obtained from Blulux laboratories, P. Ltd (Haryana, India). Glacial acetic acid (99.9%) and hydrogen peroxide (H_2O_2, 30%) were purchased from Fisher Scientific UK, Ltd (Leicestershire, UK). Potassium dihydrogen phosphate (KH_2PO_4), citric acid ($C_6H_8O_7$), potassium hydroxide (KOH), and potassium dichromate ($K_2Cr_2O_7$ were obtained from BDH Chemicals Ltd (Poole, England). Methanol (CH_3OH), chloroform ($CHCl_3$), dichloromethane (Cl_2CH_2, and carbon tetrachloride (CCl_4) were supplied by Loba Chemie Pvt, Ltd (Mumbai, India).

Solution preparation

A standard solution of Cr (VI) (1000 mg L^{-1}) was prepared by dissolving 2.83 g of $K_2Cr_2O_7$ in 0.01 mol L^{-1} of HNO_3. Intermediate solution was prepared daily by dilution of the stock solution with distilled water. Then, working solutions were prepared by diluting the intermediate solution with distilled water. A stock solution of DPC, 1000 mg L^{-1}, was prepared in methanol and stored in the dark at 4 °C. Phosphate buffer was prepared from KH_2PO_4 and of K_2HPO_4. Solutions containing 3 mol L^{-1} of KOH, H_2SO_4, citric acid, ascorbic acid, and K_2HPO_4 were separately prepared and used during the study.

Instrument and apparatus

Absorbance measurements were carried out using double beam UV-Vis spectrophotometer Analytik Jena Specord 200 Plus (Analytik Jena GmbH, Jena, Germany), Portable pH meter from Hanna instruments (Póvoa d Varzim, Portugal), a Centrifuge, model 800 from Jiangsu Zhenji instruments Co., Ltd. (Jiangsu, China), Whatman filter paper (no. 542, 110 mm), purchased from Whatman International Ltd (Maidstone, England) were used during the study.

Sample collection and preparation

Milk sample

Milk samples were collected from local milk vendors at Abba Hassan village of Jimma town, Jimma, Ethiopia. The collected samples were transported to Jimma University Analytical Chemistry Research Laboratory and kept in refrigerator until analysis. Before the analysis, samples were pretreated following the reported procedure.[33] Accordingly, milk sample was first thawed and then, properly homogenized by manually shaking. Then, 10 mL of 2 N acetic acid was added to 10 g of milk sample. The mixture was placed in a refrigerator for 20 min; subsequently proteins were precipitated. Afterwards, the content was centrifuged for 10 min at 4000 rpm and as a result fat layer was formed on the top, and proteins were precipitated at the bottom of the solution. Finally, the supernatant solution containing the analyte of interest was collected and subsequently, extracted by the proposed EA-DLLME method after adjusting its pH to 3.

Orange juice sample

A procedure reported by Moghadam and coworkers[33] was used for pretreatment of a juice sample. Orange juice was prepared by compression of fresh oranges collected from local market in Jimma town. The juice sample was filtered through Whatman filter paper and centrifuged for 15 min at 4000 rpm. Subsequently, 6 mL of concentrated HNO_3 and 24 mL 10.0% (w/v) H_2O_2 were added to10 mL of the filtrate. The resulting solution was again filtered and the obtained filtrate was then transferred into a 100 mL volumetric flask and then filled to the mark with distillated water. Finally, its pH was adjusted to 3.0, and then, the proposed extraction method was performed.

Water samples

The tap water sample was taken from the Jimma University Analytical Chemistry Research Laboratory. Well and River water samples were collected from Abba Hassan village and Hawetu river (a river that cross the Jimma town). Water samples were filtered through a Whatman filter paper to remove suspended materials.[4,18,33] Then, the pH of the samples was adjusted to 3.0 and subsequently extracted by proposed method.

Tannery effluent

The tannery effluent sample was collected from Mojo Tannery industries area, using 2-L polyethylene plastic containers Mojo town, Oromia Regional State, Ethiopia. The collected sample was acidified by adding 1 mL of conc. HNO_3 at the sampling site and transported to the Jimma University Analytical Chemistry Research Laboratory and kept in refrigerator until analysis. Before analysis, 25 mL of the previously filtered tannery effluent through a Whatman filter paper was taken into a 100 mL volumetric flask. Then, the remaining volume was filled to the mark with distilled water.[41] Finally, its pH was adjusted to 3.0, and extracted by the proposed method.

EA-DLLME procedure

First, 10 mL aqueous solution containing 2 mg L^{-1} Cr (VI), 0.5 mL H_2SO_4 (0.05 mol L^{-1}) and 300 µL DPC (1000 mg L^{-1}) were taken into a 15 mL falcon tube. After standing for 5 min (for the complete complex formation), its pH was adjusted to 3 by adding 150 µL phosphate buffer. Subsequently, a mixture of 400 µL $CHCl_3$ and 750 µL $NaHCO_3$ (2 mol L^{-1}) were rapidly injected into the sample using medical syringe, with special needle. Then, 750 µL H_2SO_4 (3 mol L^{-1}) was slowly injected to release CO_2 bubbles. The generated CO_2 bubbles induced homogeneous distribution of the extraction solvent, $CHCl_3$, as fine droplets throughout the aqueous sample and thus, the metal–ligand complex was rapidly extracted into the fine droplets of the extraction solvent. After completing the effervescent reaction, the solution was allowed to stand for 3–5 min, to settle down the extraction solvent. Finally, the organic phase was withdrawn using medical syringe with a special needle, transferred to quartz cuvette and the absorbance was recorded at 542 nm.

RESULTS AND DISCUSSION

Spectral characteristics

The absorption spectra of 0.75 mg mL^{-1} Cr (VI) solution, DPC, and Cr (VI)-DPC complex were recorded in the range of 400–700 nm (Figure 1). It was observed that Cr (VI) solution and DPC have shown insignificant absorption compared to the Cr-DPC complex, which has shown the maximum absorbance at 542 nm. Thus, 542 nm was selected as a monitoring wavelength throughout the experiments.

Optimization of the EA-DLLME procedure

Effect of pH on extraction

The pH of sample solution plays a significant role on the extractability of the metal-ligand complex.[18] The effect of pH was studied in the range of 1–7. The obtained results demonstrated that the extraction efficiency increased with rise of pH of the sample solution up to 3 and then decreased gradually at higher pH values. Thus, pH 3 was selected for the subsequent experiment.

Effect of amount of complexing agent

The amount of the complexing reagent is an important parameter since it affects the formation of the complex. The amount of the complexing agent added should be enough to form the complex with the available metal ion in the sample solution.[42] Thus, different volumes of 1000 mg L^{-1} DPC, ranging from 100–600 µL were investigated. The absorbance of the complex increased with increasing of the volume of DPC up to 300 µL and then, remains constant up on addition of higher volumes. Thus, 300 µL of 1000 mg L^{-1} DPC was chosen as the optimum volume for subsequent works.

Effects of the type and volume of the extraction solvent

Selection of appropriate extraction solvent is an important parameter in EA-DLLME. Accordingly, to use as an extraction solvent, it should have higher density than water, low solubility in water, and high extraction capability for the target analyte/s.[31] In this work, $CHCl_3$, CH_2Cl_2, and CCl_4 were investigated as extraction solvents. The obtained results demonstrated that $CHCl_3$ exhibited the highest extraction efficiency than the other two solvents. Hence, it was selected as the extraction solvent in the subsequent experiments.

The volume of the extraction solvent is another important parameter that can influence the extraction performance of the presented method.[21,29,34,35] To attain an optimal volume, different volumes of chloroform ranging from 200–700 µL were tested. At lower volumes, phase separation was not clear and sufficient to take. The absorbance of a solution was increased up to 400 µL and then, declined at higher volumes. Hence, 400 µL was selected in the subsequent experimental work.

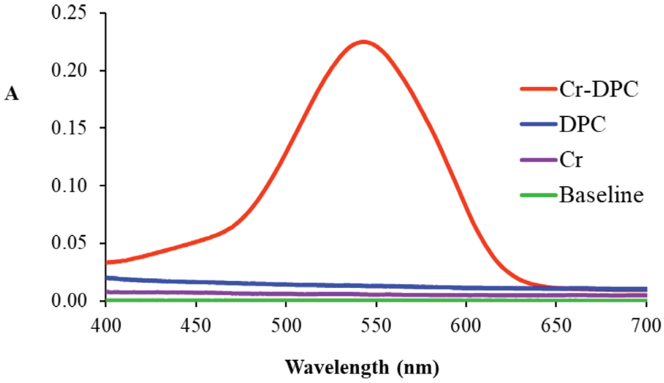

Figure 1. Spectra of Cr (VI), DPC and Cr (VI)-DPC complex

Type and amount of effervescence agents

Effervescence agents consisted of two constituents: a CO_2 source and a proton donor. The efficiency of EA-DLLME is highly influenced by the amount and composition of effervescent agents.[34,43] In this study, the effects of the type of proton donors and CO_2 sources were separately investigated. Different proton donors including H_2SO_4, citric acid, ascorbic acid, and K_2HPO_4 were investigated. To study their effects, 750 µL of 3 M of each proton donor, and 750 µL of 2 M Na_2HCO_3 as CO_2 source were used. The findings demonstrated that the highest extraction efficiency was recorded when H_2SO_4 was used (Figure 2). Therefore, H_2SO_4 was selected as a proton donor for subsequent experiments.

The effect of carbon dioxide source was also studied by using three different salts including Na_2CO_3, $NaHCO_3$ and $CaCO_3$. As can be seen from Figure 3, the highest extraction efficiency was obtained when $NaHCO_3$ was used and hence, it was selected in further study.

An effervesce reaction, i.e., the reaction that take place between CO_2 source and proton donor, is also strongly dependent on the concentrations (molar ration) of the two components. Thus, determining their appropriate concentration levels is important to achieve the maximum extraction efficiency of the method.[34,43] Accordingly, the amount of CO_2 source was investigated by varying its concentration from 1 to 5 M. The extraction efficiency was increased up to 2 M $NaHCO_3$ and then, slightly decreased at higher concentrations. Thus, 2 M was selected as optimum concentration in the subsequent experimental work. Similarly, the effect of concentration of the proton donor (i.e. H_2SO_4) was also studied by varying its concentrations from 1 to 5 M using 750 µL of 2 M $NaHCO_3$ as CO_2 source. It was observed that the extraction efficiency of the method increased with the concentration of H_2SO_4 up to 3 M and then abruptly decreased at higher concentrations. Therefore, 3 M of H_2SO_4 was selected as optimum concentration for further experiments.

Stability of complex (Cr-DPC)

The stability of the complex formed was investigated by standing the resulting extracts in dark for 10–180 min. It was observed that the absorbance of the complex formed was not significantly changed until 120 min, but above 120 min, the absorbance started to decrease indicating the decomposition of the complex. Mohammad and coworkers[18] also reported similar findings.

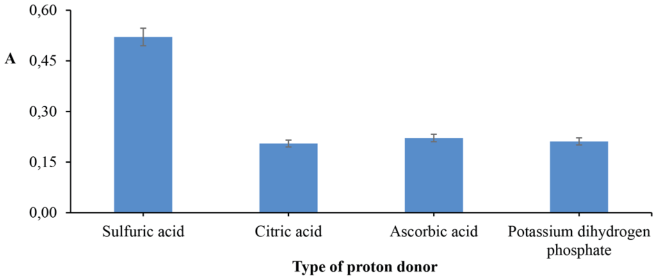

Figure 2. Effect of the type of proton donor

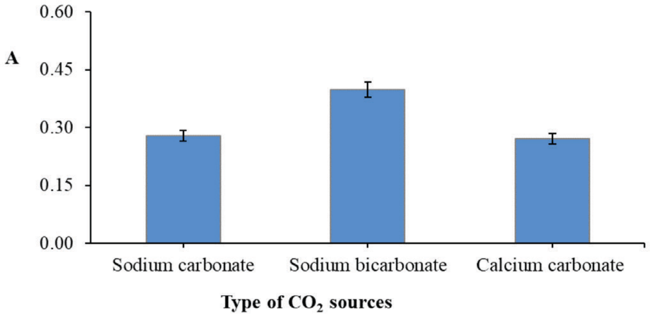

Figure 3. Effect of carbon dioxide source

Effect of extraction time

In EA-DLLME, extraction time is the time elapsed from cloudy solution formation to the start of centrifugation.[4] The effect of extraction time was investigated from 1.0–9.0 min. The findings demonstrated that the extraction efficiency of the method was slightly increased up to 3 min and then, became constant. In general, extraction time has limited effect on the extraction efficiency of the method. Hence, 3 min was selected for subsequent works.

Interference studies

To investigate the selectivity of the proposed method, the effect of potentially interfering ions such as Cd (II), Cu (II), Co (II), Fe (III) and V was studied. It was studied by spiking known concentrations of each interfering species from 100–600 mg L^{-1} in to an aqueous sample containing 2 mg L^{-1} of Cr (VI). Each interfering ion was considered to be tolerable if it caused < 5% variation in the absorbance signal.[2,18]

It was observed that the tolerance limit of Cd (II) and Fe (III) was 500 mg L^{-1} whereas, the tolerance limit of Co (II) was 600 mg L^{-1}. V and Cu (II) exhibited relatively lower tolerance limits. But, the interfering effect of V was rapidly diminished after 20 min, indicating the instability of V-DPC complex after 20 min. Literature report also indicated that the interfering effect of Cu (II)-DPC complex is unstable after 40 min.[44] Therefore, V and Cu (II) could not interfere in the determination of Cr (VI) provided that their determination is made after 20 and 40 min, respectively.

Method validation

Calibration curves and analytical performance characteristics

A calibration curve was constructed using nine concentration levels ranging from 0.005–2 mg L^{-1} of Cr (VI) standard solution. Each level was extracted in duplicate and analyzed in triplicates. Calibration curve was obtained by plotting the absorbance as a function of the concentration of the target analyte. The obtained calibration curve has linear equation of $y = 0.213x + 0.0011$ and exhibited wide linear dynamic range, acceptable $r^2 = 0.999$. The LOD and LOQ of the proposed method which were determined from the standard deviation (SD) of the blank samples (n = 15) as 3SD and 10SD of the samples were 0.001 and 0.005 mg L^{-1}, respectively. The proposed method has also demonstrated satisfactory enrichment factor, EF = 21.44. The EF was obtained from the ratio of the analyte concentration after extract (C_e) to the concentration of analyte in the sample, before extraction (C_s).

Precision study

The precision of the proposed method was evaluated in terms of repeatability (intra-day precision), intermediate precision (inter-day precision) and reproducibility at three concentration levels (Level 1: 0.25, Level 2: 0.75, and Level 3: 1.25 mg L^{-1}). Repeatability was evaluated by extracting two samples for each concentration level twice in a day (in the morning and afternoon) and analyzing each in triplicate. Intermediate precision was evaluated for five consecutive days. Reproducibility was evaluated from the results of two analysts. The obtained results, which were reported as RSD, are presented in Table 1. As can be seen, the proposed method exhibited satisfactory precision, RSD below 6.5.

Table 1. Precisions study

Level	Intra-day (n = 12)	Inter-day (n = 30)	Reproducibility (n = 12)
1	1.1	5.4	1.6
2	1.9	4.6	2.0
3	1.3	6.2	1.7

Level 1: 0.25 mg L^{-1}; Level 2: 0.75 mg L^{-1}; Level 3: 1.25 mg L^{-1}

Ruggedness

Ruggedness is the capacity of an analytical procedure to produce unbiased results in the presence of small change in experimental conditions.[45] In this study, ruggedness was investigated by measuring absorbance of the three concentration levels at different monitoring wavelength ranging from 535–545 nm. The obtained RSD values for all concentration levels were less than 3.3, indicating the ruggedness of the developed method.

Applications of the method and recovery studies

Applicability of the proposed method has been evaluated by analyzing real samples and performing percent recovery (%RR) studies. Six different real samples including tap, well and river water, tannery effluent, milk and orange juice samples were used to evaluate the applicability of the method. %RR studies were performed by spiking each sample with three known concentration levels earlier used for the precision studies. Each concentration level was extracted in duplicates and analysed in triplicates. The obtained recoveries (%RR ± RSD) were ranged from 83.0–117.6% (Table 2). These values were within the acceptable range.

As can be observed from Table 2, except in milk sample, Cr (VI) was determined in all the studied samples. As expected the highest concentration of Cr (VI) (0.57 mg L^{-1}) was determined in tannery effluent. From water samples the river water contained relatively higher concentration of the analyte.

Comparison with other methods

The proposed EA-DLLME-UV-Vis method has been compared with other recently reported methods for the extraction and determination of Cr (VI) from water and other samples (Table 3). Compared to the conventional DLLME, EA-DLLME does not use organic disperser solvent. It also does not need special instruments or apparatus such as ultrasonic or vortex agitator to enhance dispersion of the extraction phase. The method demonstrated comparable analytical performance characteristics to those reported in the literature. The proposed method also uses conventional laboratory apparatus and small volume of organic solvent, which are available in any research laboratories. Thus, the proposed EA-DLLME-UV-Vis method could be used as alternative method for determination of Cr (VI) from different matrices such as orange juice, cow milk, water (tap water, river and well) and tannery effluent.

CONCLUSIONS

An EA-DLLME, technique was developed for extraction and/or preconcentration of Cr (VI) from different matrices, prior its determination by UV-Vis spectrometry. In the procedure, homogeneous dispersion of the extraction solvent into the aqueous sample is easily achieved by addition of appropriate amount of

Table 2. Recovery study

Sample type	Level 1	Level 2	Level 3	Conc. in sample (mg L^{-1})
Milk	108.4 ± 1.9	98.8 ± 1.9	97.5 ± 0.1	DNQ
Orange	83.1 ± 0.2	83.0 ± 2.2	92.3 ± 1.7	0.02 ± 0.0003
Tannery Effluent	91.4 ± 2.5	88.1 ± 2.4	83.4 ± 5.4	0.57 ± 0.03
River water	101.3 ± 0.3	117.6 ± 2.1	96.4 ± 3.5	0.13 ± 0.04
Well Water	102.6 ± 4.9	112.4 ± 3.5	96.1 ± 5.4	0.08 ± 0.002
Tap water	100.3 ± 1.7	106.7 ± 2.6	106.9 ± 2.1	0.03 ± 0.002

DNQ: Detected but not quantifiable

Table 3. Comparison of applied method with other reported methods

Method	Matrix	LDR (μg L^{-1})	LOD (μg L^{-1})	LOQ (μg L^{-1})	RSD	%RR	R^2	EF	Ref.
DLLME-FAA	Tap, river and waste water as well as milk samples	1–50	0.7	2.3	2.7	99.0–102.0	0.9990	20	4
UAEME-GFAAS	Water	0.002–0.07	0.0008	0.0028	3.5	90	0.9940	76.5	8
LLME-UV-VIS	Water	25–950	7.48		2.16	91	0.9888	15.87	13
DMSPE-FAAS	Water	0–100	1.1	3.6	5.5	103	0.9970	16	14
SPE- DRC-ICP-MS	Cow's milk	**	0.085	**	2.67	96.4–99.2	**	**	16
EME-µ-EME-EAAS	Food samples (milk powder, *Ocimum basilicum*, and fish samples)	0.01–5.0	0.003	0.010	≤11.8	73.7	**	584	17
DLLME-UV-VIS	Water	5.0–200	1.5	5.0	5.01	≥90	**	73	18
HLLE-FAAS	Water	0.001–0.007	0.001	0.003	2.8	103	0.9990	10	20
SALLME-IL-FAAS	Water, saline and food	3–150	1.25	4.16	1.0	97.6–102.4	0.9994	100	23
UADLLME-ETAAS	Water	0.005–0.2	0.002	0.006	7.2	108	**	240	30
SPE-GFAAS/ICPAES	Water	2–400	0.32	1.1	1.9	95	0.9999	400	47
Moringa oleifera husks as the solid phase in a FI*-FAAS	Water	**	2.45	2.5	1.2	81	0.9948	71	48
DSPE-FAAS	Water	20–700	7.1	23.6	2.7	88.5	0.9979	6.6	49
EA-DLLME-UV-Vis	Tap, river and well water, tannery effluent, milk and orange juice	5–2000	1.0	5.0	≤5.4	83.02–117.6	0.9992	21.4	This study

**flow injection system, **not given*

effervescence agents. Different parameters affecting the extraction efficiency of the proposed method have been evaluated and the optimal conditions have been established. The optimized method has demonstrated satisfactory analytical performance of characteristics such as wide linear dynamic range; with coefficient of determination, $r^2 = 0.999$; LOD = 0.001 mg L^{-1}; LOQ = 0.005 mg L^{-1}; and EF = 21.4. Intra-day, inter-day precision and reproducibility of the method were less than 6.5%. The ruggedness of the method studied at various wavelengths ranging from 535-545 nm was less than 3.3% indicating its ruggedness in the studied wavelength range. The method has shown its applicability for determination of Cr (VI) in orange juice, cow milk, tap water, well water and river water as well as tannery effluent. The obtained recoveries of Cr (VI) in these real samples were ranging from 83.0-117.6%. Generally, the proposed method could be used as simple and attractive alternative for determination of Cr (VI) from different matrices.

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REFERENCES

1. Singh HP, Mahajan P, Kaur S, Batish DR, Kohli RK. Chromium toxicity and tolerance in plants. Environ Chem Lett. 2013;11(3):229–254. https://doi.org/10.1007/s10311-013-0407-5.
2. Lace A, Ryan D, Bowkett M, Cleary J. Chromium monitoring in water by colorimetry using optimised 1,5-diphenylcarbazide method. Int J Environ Res Public Health. 2019;16(10):1803. https://doi.org/10.3390/ijerph16101803.
3. Abkenar SD, Hosseini M, Dahaghin Z, Salavati-Niasari M, Jamali MR. Speciation of chromium in water samples with homogeneous liquid-liquid extraction and determination by flame atomic absorption spectrometry. Bull Korean Chem Soc. 2010;31(10):2813–2818. https://doi.org/10.5012/bkcs.2010.31.10.2813.
4. Adibmehr M, Sadeghi HB, Dehghan S. Preconcentration and speciation of chromium using dispersive liquid-liquid microextraction; application to milk and different water samples. Anal. Bioanal. Chem. Res. 2014;1(1):20–28.
5. Rakhunde R, Deshpande L, Juneja HD. Chemical speciation of chromium in water: a review. Crit Rev Environ Sci Technol. 2012;42(7):776–810. https://doi.org/10.1080/10643389.2010.534029.
6. Sharma A, Kapoor D, Wang J, Shahzad B, Kumar V, Bali AS, Jasrotia S, Zheng B, Yuan H, Yan D. Chromium bioaccumulation and its impacts on plants: an overview. Plants. 2020;9(1):100. https://doi.org/10.3390/plants9010100.
7. Tumolo M, Ancona V, De Paola D, Losacco D, Campanale C, Massarelli C, Uricchio VF. Chromium pollution in European water, sources, health risk, and remediation strategies: an overview. Int J Environ Res Public Health. 2020;17(15):5438. https://doi.org/10.3390/ijerph17155438.
8. de Andrade JK, de Andrade CK, Felsner ML, dos Anjos VE. Ultrasound-assisted emulsification microextraction combined with graphite furnace atomic absorption spectrometry for the chromium speciation in water samples. Talanta. 2019;191:94–102. https://doi.org/10.1016/j.talanta.2018.07.067.
9. Shanker AK, Cervantes C, Loza-Tavera H, Avudainayagam S. Chromium toxicity in plants. Environ Int. 2005;31(5):739–753. https://doi.org/10.1016/j.envint.2005.02.003.
10. WHO [World Health Organization]. WHO Guidelines for Drinking-Water Quality, Vol. 1, World Health Organization (WHO), Geneva, Switzerland, 2003.
11. Dominik J, Vignati DAL, Koukal B, Pereira de Abreu MH, Kottelat R, Szalinska E, Baś B, Bobrowski A. Speciation and environmental fate of chromium in rivers contaminated with tannery effluents. Eng Life Sci. 2007;7(2):155–169. https://doi.org/10.1002/elsc.200620182.
12. Onchoke KK, Sasu SA. Determination of hexavalent chromium (Cr(VI)) concentrations via ion chromatography and UV-Vis spectrophotometry in samples collected from Nacogdoches wastewater treatment plant, East Texas (USA), Adv Environ Chem., 2016, ID 3468635. https://doi.org/10.1155/2016/3468635.
13. Ahmad W, Bashammakh AS, Al-Sibaai AA, Alwael H, El-Shahawi MS. Trace

determination of Cr(III) and Cr(VI) species in water samples via dispersive liquid-liquid microextraction and microvolume UV–Vis spectrometry. Thermodynamics, speciation study. J Mol Liq. 2016;224:1242–1248. https://doi.org/10.1016/j.molliq.2016.10.106.

14. Diniz KM, Tarley CRT. Speciation analysis of chromium in water samples through sequential combination of dispersive magnetic solid phase extraction using mesoporous amino-functionalized Fe_3O_4/SiO2 nanoparticles and cloud point extraction. Microchem J. 2015;123:185–195. https://doi.org/10.1016/j.microc.2015.06.011.
15. Moghimi A. Solid phase extraction and determination of chromium species using multiwalled carbon nanotubes by solid phase extraction: flame atomic absorption spectrometry (FAAS). African J. Pure Appl. Chem. 2013;7(4):146–156. https://doi.org/10.5897/AJPAC2013.0487.
16. Ambushe AA, McCrindle RI, McCrindle CME. Speciation of chromium in cow's milk by solid-phase extraction/dynamic reaction cell inductively coupled plasma mass spectrometry (DRC-ICP-MS). J Anal At Spectrom. 2009;24(4):502–507. https://doi.org/10.1039/b819962k.
17. Goodarzi L, Bayatloo MR, Chalavi S, Nojavan S, Rahmani T, Azimi SB. Selective extraction and determination of Cr(VI) in food samples based on tandem electromembrane extraction followed by electrothermal atomic absorption spectrometry. Food Chem. 2022;373:131442. https://doi.org/10.1016/j.foodchem.2021.131442.
18. Pourmohammad M, Faraji M, Jafarinejad S. Extraction of chromium (VI) in water samples by dispersive liquid–liquid microextraction based on deep eutectic solvent and determination by UV–Vis spectrophotometry. Int J Environ Anal Chem. 2020;100(10):1146–1159. https://doi.org/10.1080/03067319.2019.1650920.
19. Sobhi HR, Azadikhah E, Behbahani M, Esrafili A, Ghambarian M. Application of a surfactant-assisted dispersive liquid-liquid microextraction method along with central composite design for micro-volume based spectrophotometric determination of low level of Cr(VI) ions in aquatic samples. Spectrochim Acta A Mol Biomol Spectrosc. 2018;202:36–40. https://doi.org/10.1016/j.saa.2018.05.031.
20. Chen W, Zhong G, Zhou Z, Wu P, Hou X. Automation of liquid-liquid extraction-spectrophotometry using prolonged pseudo-liquid drops and handheld CCD for speciation of Cr(VI) and Cr(III) in water samples. Anal Sci. 2005;21(10):1189–1193. https://doi.org/10.2116/analsci.21.1189.
21. Zahedi MM, Rezaei A. Optimization of emulsification-based liquid phase microextraction of chromium in seawater of Chabahar Bay for its speciation by high-performance liquid chromatography. J Chromatogr Sci. 2016;54(10):1851–1857. https://doi.org/10.1093/chromsci/bmw168.
22. Bittner M, Broekaert JAC. Speciation of chromium by solid-phase extraction coupled to reversed-phase liquid chromatography with UV detection. Anal Chim Acta. 1998;364(1-3):31–40. https://doi.org/10.1016/S0003-2670(98)00124-X.
23. Majidi B, Shemirani F. Salt-assisted liquid-liquid microextraction of Cr(VI) ion using an ionic liquid for preconcentration prior to its determination by flame atomic absorption spectrometry. Mikrochim Acta. 2012;176(1):143–151. https://doi.org/10.1007/s00604-011-0711-3.
24. Andrle CM, Jakubowski N, Broekaert JAC. Speciation of chromium using reversed phase-high performance liquid chromatography coupled to different spectrometric detection methods. Spectrochim Acta B At Spectrosc. 1997;52(2):189–200. https://doi.org/10.1016/S0584-8547(96)01586-8.
25. Nawaz R, Ali K, Ali N, Khaliq A. Removal of chromium(VI) from industrial effluents through supported liquid membrane using trioctylphosphine oxide as a carrier. J Braz Chem Soc. 2016;27(1):209–220.
26. Abadi MDM, Chamsaz M, Arbab-Zavar MH, Shemirani F. Supramolecular dispersive liquid-liquid microextraction based solidification of floating organic drops for speciation and spectrophotometric determination of chromium in real samples. Anal Methods. 2013;5(12):2971–2977. https://doi.org/10.1039/c3ay00036b.
27. Ezoddin M, Abdi K, Esmaeili N. Ultrasound enhanced air-assisted surfactant liquid-liquid microextraction based on the solidification of an organic droplet for the determination of chromium in water, air and biological samples. Microchem J. 2016;129:200–204. https://doi.org/10.1016/j.microc.2016.07.005.
28. Yilmaz E, Soylak M. Ultrasound assisted-deep eutectic solvent based on emulsification liquid phase microextraction combined with microsample injection flame atomic absorption spectrometry for valence speciation of chromium(III/VI) in environmental samples. Talanta. 2016;160:680–685. https://doi.org/10.1016/j.talanta.2016.08.001.
29. Nourbala Tafti E, Dadfarnia S, Haji Shabani AM. Supramolecular dispersive liquid–liquid microextraction-based solidification of floating organic drops combined with electrothermal atomic absorption spectrometry for determination of chromium species. Int J Environ Anal Chem. 2017;97(5):444–455. https://doi.org/10.1080/03067319.2017.1321743.
30. López-García I, Briceño M, Vicente-Martínez Y, Hernández-Córdoba M. Ultrasound-assisted dispersive liquid-liquid microextraction for the speciation of traces of chromium using electrothermal atomic absorption spectrometry. Talanta. 2013;115:166–171. https://doi.org/10.1016/j.talanta.2013.04.052.
31. Jiang W, Chen X, Liu F, You X, Xue J. Effervescence-assisted dispersive liquid-liquid microextraction using a solid effervescent agent as a novel dispersion technique for the analysis of fungicides in apple juice. J Sep Sci. 2014;37(21):3157–3163. https://doi.org/10.1002/jssc.201400695.
32. Lasarte-Aragonés G, Lucena R, Cárdenas S, Valcárcel M. Effervescence assisted dispersive liquid-liquid microextraction with extractant removal by magnetic nanoparticles. Anal Chim Acta. 2014;807:61–66. https://doi.org/10.1016/j.aca.2013.11.029.
33. Moghadam AG, Rajabi M, Hemmati M, Asghari A. A. Development of effervescence-assisted liquid phase microextraction based on fatty acid for determination of silver and cobalt ions using micro-sampling flame atomic absorption spectrometry. J Mol Liq. 2017;242:1176–1183. https://doi.org/10.1016/j.molliq.2017.07.038.
34. Arpa Ç, Albayati S, Yahya M. Effervescence-assisted dispersive liquid-liquid microextraction based on deep eutectic solvent for preconcentration and FAAS determination of copper in aqueous samples. Int J Environ Anal Chem. 2018;98(10):938–953. https://doi.org/10.1080/03067319.2018.1517872.
35. Jing X, Zhang J, Zhu J, Chen Z, Yi L, Wang X. Effervescent-assisted dispersive liquid-liquid microextraction based on the solidification of floating organic droplets for the determination of fungicides in vinegar and juice. Food Addit Contam Part A Chem Anal Control Expo Risk Assess. 2018;35(11):2128–2134. https://doi.org/10.1080/19440049.2018.1496281.
36. Vakh C, Evdokimova E, Pochivalov A, Moskvin L, Bulatov A. Effervescence assisted dispersive liquid-liquid microextraction followed by microvolume UV-Vis spectrophotometric determination of surfactants in water. Toxicol Environ Chem. 2017;99(4):613–623. https://doi.org/10.1080/02772248.2016.1205069.
37. Ghorbani Ravandi M, Fat'hi MR. Green effervescence assisted dispersive liquid–liquid microextraction based on a hydrophobic deep eutectic solvent for determination of Sunset Yellow and Brilliant Blue FCF in food samples. New J Chem. 2018;42(18):14901–14908. https://doi.org/10.1039/C8NJ00782A.
38. Shishov A, Gerasimov A, Nechaeva D, Volodina N, Bessonova E, Bulatov A. An effervescence-assisted dispersive liquid-liquid microextraction based on deep eutectic solvent decomposition: determination of ketoprofen and diclofenac in liver. Microchem J. 2020;156:104837. https://doi.org/10.1016/j.microc.2020.104837.
39. Hu L, Qian H, Yang X, Li S, Zhang S, Lu R, Zhou W, Gao H. Effervescence-assisted dispersive liquid-liquid microextraction based on the solidification of a floating ionic liquid with a special collection method for the rapid determination of benzoylurea insecticides in water samples. RSC Advances. 2016;6(97):95283–95291. https://doi.org/10.1039/C6RA17889H.
40. Sorouraddin SM, Farajzadeh MA, Qarajeh HN. Effervescence-assisted dispersive liquid-liquid microextraction for trace analysis of Co(II) and Ni(II) from aqueous sample based on phthalic acid as a complexing agent. Anal. Bioanal. Chem. Res. 2019;6(2):365–380.
41. Hadgu T, Amare M. Assessment of the level of chromium species in the discharged effluents of Haik and Debre Berhan tanneries in the Amhara Region using ICP-OES and UV-VIS spectrometry. Ethiop. J. Sci. & Technol. 2016;9(2):123–138. https://doi.org/10.4314/ejst.v9i2.5.
42. Sajid M, Kabeer M, Falath W. Development of membrane-based inverted liquid–liquid extraction for the simultaneous extraction of eight metals in seawater before ICP-OES analysis. Molecules. 2020;25(15):3395. https://doi.org/10.3390/molecules25153395.
43. Lasarte-Aragonés G, Lucena R, Cárdenas S. Effervescence-assisted microextraction-one decade of developments. Molecules. 2020;25(24):6053. https://doi.org/10.3390/molecules25246053.

44. Shigematsu T, Gohda S, Yamazaki H, Nishikawa Y. Spectrophotometric determination of chromium (III) and chromium (VI) in sea water. Bull. Inst. Chem. Res. 1977;55(5):429–440.

45. Sahoo CK, Sudhakar M, Sahoo NK, Rao SRM, Panigrahy UP () Validation of Analytical Methods: A Review. Int J Chromatogr Sep Tech: IJCST-112. 2018. https://doi.org/ 10.29011/IJCST-112.000012.

46. Saminathan J, Sankar ASK, Anandakumar K, Vetrichelvan T. Simple UV spectrophotometric method for the determination of fluvastatin sodium in bulk and pharmaceutical formulations. E-J Chem. 2009;6(4):1233–1239. https://doi.org/10.1155/2009/530206.

47. Dadfarnia S, Shabani AMH, Shishebor MR, Cisakht KH. Separation, preconcentration and speciation of chromium by solid phase extraction on immobilised Ferron. Int J Environ Anal Chem. 2011;91(13):1320–1328. https://doi.org/10.1080/03067319.2010.496039.

48. Alves VN, Coelho NMM. Selective extraction and preconcentration of chromium using Moringa oleifera husks as biosorbent and flame atomic absorption spectrometry. Microchem J. 2013;109:16–22. https://doi.org/10.1016/j.microc.2012.05.030.

49. dos Santos Azevedo Leite V, de Jesus BGL, de Oliveira Duarte VG, Constantino VRL, Izumi CMS, Tronto J, Pinto FG. Determination of chromium (VI) by dispersive solid-phase extraction using dissolvable Zn-Al layered double hydroxide intercalated with L-Alanine as adsorbent. Microchem J. 2019;146:650–657. https://doi.org/10.1016/j.microc.2019.01.063.