Speciation of Chromium in Organicfruit Samples with Cloud Point Extraction Separation and Preconcentration and Determination by UV-VIS Spectrophotomety

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ABSTRACT

Due to the toxicity of chromium, species depend on their chemical properties and bioavailability, speciation of chromium is very important in environmental samples.A speciation procedure for chromium (III), chromium (VI) and total chromium in environmental samples is presented in this work, based on cloud point extraction (CPE) separation and preconcentration prior to UV-Vis determination of chromium. The method is based on the reduction of Cr (VI) by iodide in acidic media and subsequently formation of I3- anion. Cerium (IV) ammonium sulphate was chosen as an oxidizing reagent for pre-oxidation step of Cr (III) to Cr (VI) species before the addition of iodide to the system, up to chromium in trivalent can be determined by the procedure. The I3- formed can further react with cetyltrimethylammonium bromide (CTAB) and induce its clouding due to formation of an ion-association complex. The formed complex was separated from solution and dissolved in ethanol for spectrophotometric measurement. Experimental parameters for both spectrophotometric reaction and extraction procedure have been optimized. Under optimized conditions Cr (VI) can be determined in the range 0.02-0.9 µgml-1 (R2 = 0.999). Detection limit and relative standard deviation were0.0125 µg mL−1 and8.246×10-4 µg mL−1 (n=3), respectively with 10 mL sample volumes. The proposed method has been successfully applied for determination of chromium (VI) in Organic Fruit: Chino, Lemon, Orange samples with average recoveries of 94, 92 and 95.8 % respectively.

Keywords: Cloud point extraction, preconcentration, Chromium Speciation, Organic Fruit samples

INTRODUCTION

Chromium occurs naturally in the earth crust, but its extensive use in various industrial processes and products has led to widespread chromium contamination in the environment (L. Wang, 2010). In the nature chromium occurs mainly in the oxidation states (III) and (VI) (Hashemi and Daryanavard, 2012). The Cr (III) is essential for plants and animals at trace concentrations, whereas Cr (VI) is considered to be a more toxic from because of its high oxidizing potential(Hashemi and Daryanavard, 2012).

Chromium (III) is vital for almost all living organisms, because a wide variety of metabolic process, including Ribonucleic acid (RNA) synthesis, regulating of insulin, preventing of weight gain and the absorption of proteins use this material. However, existence of chromium in the body's damaged tissue causes to formation of free radicals. Chromium (III) as the most stable form, exist in a considerable amount in nature, while chromium (VI) arises from human activities such as wastewater of textile factories, steel factories and tobacco smoke, and this type of chromium is very toxic and can be fatal.

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Determination of the chromium species is more important than measuring of the total chromium. To determining the oxidation state of chromium species in environmental samples, after preconcentration method, there are different methods such as:coprecipitation (Wang et al., 2002) electrochemical methods (Schick, 1987), ion chromatography (Arab-zavar and Hashemi), solvent extraction and extraction of solid phase (Liang et al., 2000), (Adriá-Cerezo, 2000) capillary electrophoresis (Willard and Young, 1929), ion-exchange separation (Wanget al., 2002), (Menéndez-Alonso et al., 1999), high-performance liquid chromatography (Mittal, 1979), Flame Atomic Absorption Spectrometry (FAAS) (Narin et al., 2008), (Kiran et al., 2008), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Liang et al., 2006), Electrothermal Atomic Absorption Spectrometry (ET-AAS) (Zhu et al., 2005), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Rahman et al., 2005), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Menegarioet al., 2005), (Sawalha et al., 2005), fluorometry (Hosseini and Belador, 2009), (Massumiet al., 2009) and electrochemical (Kubˇ n et al., 2003). To measure the species of the chromium from the preconcentration sample, it requires an optimum simple, safe, inexpensive and short time method.

Cloud point extraction for the isolation of micro-scale organic compounds in environmental samples used in this method is superior to the use of organic solvents is very low. By heating a surfactant micelle solution, above a certain temperature, this solution tarnishes and this means that this is its cloud point temperature (CPT).

Micelle solution where in the concentration of surfactant is less than critical micelle concentration (CMC) can be separated to two distinct phases, one surfactant rich phase that hasa small volume and one watery phase. This phenomenon is due to increase of micelles size and Dehydration of the outer layers of the micelle with increasing of the temperature. This phenomenon is reversible and by decreasing of the temperature, the initial homogeneous solution appears. Cloud temperature depends on surfactant structure and concentration. The ionic strength can change the cloud temperature and makes phase separation by changing of solution density.

The desired metal trapped in surfactant that has mophilic properties and finally forms two phases that separate easily from each other. The first use of the CPE technigue for preconcentration of metalswas pioneered by watanabe et al. (Goto et al., 1977), who studied the extraction of manganese with 1-(2-pyridylazo)-2-naphthol (PAN) as acomplexing agent. Extracting ligands such as 1-(2-thiazolylazo)-2-naphthol (TAN) (Saitoh et al., 1989) 8-hydroxyquinoline (8-HQ) (Paleologos et al., 2001) and lately, dibromophenyl fluorine (BR-PF) (Zhuet al., 2005) have been used for cloud point extraction in several procedures.

With reduction of carbon chain length and ethylene oxide sections, the cloud point increases. The whole process is similar to liquid-liquid extraction only with this difference that theorganic phase makes dispersed suspensions by conversion of initial homogeneous solution to a heterogeneous solution.

In this paper, we confront with an acidic reaction environment via reduction of chromium (VI) by iodide. By using of hydrochloride acid, the environment of the spectrophotometer that can't separate the ion species of chromium (III) and (VI) becomes completely acidic. The ultrasonic waves' energy is used to accelerate the reaction between Cr and I. In this study, after CPE pre concentration, cloud point measured with UV-visible device by cationic CTAB surfactant that is diluted with ethanol.

EXPERIMENTAL

Instrument

Spectrophotometer UV-Vis (Varirn) Model EL-181728 with a quartz cell was used. PH meter Model GP - 353, with a glass electrode was used. A pars nahand ultrasonic bath (model parsonic mini 40 KHZ) was used as the wave energy device. Centrifuge Model H - 11nKokuan was used to separate the aqueous and organic phases.

Chemical reagents

All of the utensil used for analysis were soaked in 10% nitric acid for at least 12 hours and then washed in pure water at least three times. Standard solution of Chromium with concentration of 1000µgmL-1 prepared from a mixture of $K_2Cr_2O_7$ and $Cr(NO_3)_3.9H_2O$ salts and Double water. CTAB surfactant, potassium iodide salt, Buffer (glycine – hydrochloric acid), amberlit resin column, Cerium (IV) ammonium sulphate; all of this chemical component except surfactant solution were kept in a refrigerator for one month. All of this was obtained from Merck except absolute ethanol 99.7% that was prepared in our company for medicine uses.

Samples and Sample Pretreatments

Organic samples of lemon and chino prepared from Iran - Shiraz – Jahrom and organic samples of orange were prepared from Iran – Sari. At first, organic samples of fruits were taken in double water for 15 minutes and then washed for 3 minutes. Skins of organic fruits were separated and dried in an oven with temperature of 60˚C for 4 hours and after that placed in room temperature for 2 hours to entirely drying. After that, samples were rubbed in porcelain mortar until became completely powder and passed through the filter net to separation of large particles from other, 1.5 g of dried skin of organic fruits was weighted by analytical balance with an accuracy of 0.0001 and put into a container and next under the hood (by considering of all safety precautions), 5 ml from nitric acid was added to container, and its lid was slowly closed to appear brown fumes. Next that, 5 ml from hydrochloride acid was poured into the container, and its lid was closed and then placed on a heater with temperature of 120-130˚C for 6 hours and so that very bright and clear yellow solution was obtained.

Column Dimensions and Effect of Packing Material

A column with 10cm in length and 1cm in diameter was used. Bottom of the column was closed with glass wool and 3g resin (strong acid) were added in 25 ml double water to form slurry and poured into the column. While the precipitation of resin was occurred, the column was stricken until the resin goes to the state of most impact sediment. To activate the resin, 1 molar hydrochloride acid was prepared and resin was washed with this solution by rate of 0.5 ml min-1. In addition, before the starting of the experiment, the column was washed with double water by the same rate.

Procedure

24 hours before the beginning of the test, all equipment were washed carefully with HNO_3 10% and double water. In a 10 ml volumetric flask, prepared a solution with the same concentrations of $K_2Cr_2O_7$ and $CrCl_3.6H_2O$ salts. 1 ml of this solution with the concentration of 0.1ppm was taken into a 10ml volumetric flask and then 1 ml Cerium (IV) ammonium sulphate was added to this flask. After that, this solution was added to the prepared column by rate of 0.5 mlmin-1. From the burette that was placed below the column, 1 ml was taken and then 1 ml of glycine -hydrochloric acid buffer (pH=1), 2 ml of potassium iodide solution (8×10-4 molar) and 3 ml of surfactant solution (4×10-4 molar) alsoadded and then the

volume of obtained solution was completed with double water. The contents of the flask were transferred to a graded test tube and its cap was closed and then was placed in an ultrasonic bath for 20 minutes. After centrifuging for 15 minutes with the speed of 2000 rpm, was placed in an ice bath until the phase of surfactant rich (bottom phase) to be viscose. Then, the aqueous phase was removed by a Pasteur pipette and the phase of surfactant rich was solved in 1 ml of absolute ethanol, and the absorption of obtained solution was measured by a spectrophotometer device in 360 nm wave length.

RESULTS AND DISCUSSION

In this study, typology of chromium based on reduction of Cr^{6+} to Cr^{3+}in acidic media with low PH was occurred.

$$2HCrO^{4-} + 6I^{-} + 14H^{+} \longrightarrow 2Cr^{3+} + 3I_2 + 8H_2O$$

Iodide ion was used as a reducing agent to react with chromium (VI) and produce I3- and chromium (III) ions. Due to low concentration of chromium in the sample, cloud point method was used for preconcentration to I- will react with CTAB and forms a negatively charged complex. Ammonium cerium sulfate (IV) $[Ce(NH_4)4(SO_4)_4]$ are used to oxidization of all chromium (III) to chromium (VI) and following reaction occurred:

$$3\ Ce^{+4} + Cr^{+3} \longrightarrow Cr^{+6} + Ce^{+3}$$

Cr^{6+} sample was passed through the column that coated with strong acidic resin and samples from itsbottom collected and then preconcentration and extraction with UV-Vis device carried out and finally, absorption of chromium (VI) occurred.

Effect of pH

Sample solution pH plays an important role in the formation of metal complexes and preconcentration, so to ensure the synthesis; the complex is carrying out in the best pH. Wide range of pH from 1 to 9 was investigated. The results of tests showed that when the pH of reaction increases, due to formation of chromium hydroxide sludge, efficiency of extraction is reduced and thus the absorption decreases. When the quantity of H+ increases in the environment, the reaction between [I3-] and [CTAB] was increased and thus the absorption increases. On the other hand, when the pH of environment increases, reveres reaction was occurred and as a result, Cr^{3+} converts to Cr^{6+}. Thus, pH=1 was selected as the optimum pH for future tests.

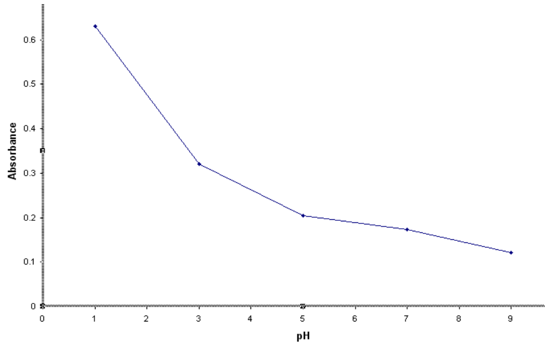

Figure1. effect of pH on CPE.Other conditions:3ml CTAB 4×10 -4, 2ml KI 8×10-4, ultrasonic time 20min, Centrifuges time15min, 0.1ppmChromium(VI), pH=1

Effect of CTAB concentration

To improve the preconcentration factor, the effect of surfactant concentration within the range of 4×10-3 to 4×10-5 molar was investigated. CTAB concentration has a great influence in the extraction process such that with increasing of the amount of surfactant, viscosity of the rich phase increases and whatever the viscosity of the surfactant becomes further than a certain amount, the sensitivity is reduced. Accordingly, the concentration of 4×10-4 molar has been reported as an optimum concentration.

Effect of potassium iodide concentration

To study the effect of the potassium iodide salt amount as an effective agent to form a complex with metallic chromium ion, it's necessary in the experimental conditions that the ratio of salt to metal for preparation of complex became optimum, because in researches use from this salt to further reaction between [I3-] and [CTAB] and as a result can separate more Cr (VI).

The effect of potassium iodide on the absorption of potassium dichromate solution by the method of extraction when the concentration of KI is in the lower range, due to incomplete reaction between [I-], [I3-] and [CTAB], decreased and when the concentration of KI increases, again the absorption is decreased due to precipitation of salt at the bottom of the sample container. Accordingly, the concentration of 8×10-4 molar has been reported as an optimum concentration.

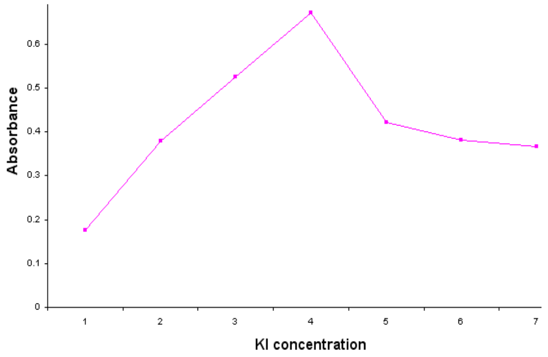

Figure 2. effect of KI concentration on CPE.Other conditions:3ml CTAB 4×10 -4, 2ml KI 8×10-4, ultrasonic time 20min, Centrifuges time15min, 0.1ppmChromium(VI), pH=1

Effect of ultrasonic time

When a sample is placed in an ultrasonic bath, due to conversion of energy, the temperature of the bath water increases that this phenomenon increases the micelle concentration and capacity of solubility of micelle solution, in the other words, dehydration of the polar head of poly-oxy ethylene is increased, and the growth of the micelle accumulations is increased and because of this, the efficiency of extraction increases. By placing the sample in the ultrasonic bath, the mixing of sample become well, Furthermore, the oxidation of [I-] to chromium (VI) that is relatively slow, with the assistance of ultrasonic waves energy, can increase the absorption intensity of the reaction. Accordingly, the ultrasonic time 20 min has been reported as an optimum time.

Interferences

The effect of external ions on the signal intensity of chromium (VI) was investigated by measuring of absorption from solutions containing 10 µgmL-1 of each metal ion in presence of a different amount of other ions. The tolerance limit is defined as the concentration of added ion that caused less than 5% relative error in the determination of Cr. In addition, due to use of amberlite, most of the cations retain at resin column and by this treatment, it was found that common coexisting ions didn't have significant effect on the separation and determination of Cr (VI). The maximum tolerances of investigated cations and anions are given in Table 1. Cr recoveries were nearly quantitative in the presence of other ions.

Table 1. Tolerance ratios of diverse ions on the determination of 10 μgmL-1 of Chromium (VI)

Ion	*Tolerance limit (W/W)*
Mn^{+2}	15
Cu^{+2}	100
Mg^{+2}	100
Cd^{+2}	50
Ca^{+2}	50
Na^{+1}	50
K^{+1}	100
Zn^{+2}	50
Fe^{+3}	50
F^{-}	100
No_2^{-}	15
Cl^{-}	100

Analytical Features

Analytical characteristic's data of Cr (III) and Cr (VI) were summarized in Table 2. Under the optimum experimental conditions, the relative standard deviation (RSD) for three replicate measurements of 10 μg ml-1 of chromium (VI) were 8.246×10 -4 respectively. The amount of chromium in 10 ml of sample solution is measured after preconcentration by CPE in final volume of 0.5 ml absolute ethanol.

Table 2. Analytical characteristics of the method (N:3)

Parameters	*Cr*
Regression equation	Y=0.0197X+0.0916
Liner range (μg ml^{-1})	0.02-0.9
Limit of detection ($3S_B$/m blank, μg ml^{-1})	0.0125

Determination of Cr (III) and (VI) in Real Samples

The reported method was applied to determination of Cr(III) and Cr(VI) species in organic samples of chino, lemon and orange. This method successfully applied for the preconcentration and specification of the low amounts of Chromium species in organic fruits chino, lemon and orange. These samples were subjected to preconcentration and metal ions determination using the reported procedure. Obtained results were shown in Table 3.

Table 3. Analytical results for speciation of Cr(III)and Cr(VI) in organic fruits samples

Sample	*Concentration (µg ml^{-1})*		*Recovery (%)*	
	3	*Cr(VI)*	*Cr(III)*	*Cr(VI)*
Chino	1.307	0.071	98	94
Lemon	1.097	0.059	91.3	92
Orange	1.561	0.063	97.2	95.8

CONCLUSION

In this study, trace amount of chromium (III) and (VI) species were extracted with applying the method of cloud point extraction and CTAB surfactant and preparation of amberlite resin column, and satisfactory results were obtained. One of the goals of this project has been the optimization of cloud point extraction method to measurement of trace amount of chromium species in the skin of organic fruits (chino, lemon, orange). Method of cloud point extraction is a strong analytical method for improving of the detection limit in analysis of metals; furthermore, it's a fast, simple, safe, non-polluted and low cost method that has high efficiency for determining of trace concentrations of chromium in foods.

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