Food Chemistry 221 (2017) 47–53

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Cloud point extraction and diffuse reflectance-Fourier transform infrared spectroscopic determination of chromium(VI): A probe to adulteration in food stuffs

Swapnil Tiwari, Manas Kanti Deb *, Bhupendra K. Sen

School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, Chhattisgarh 492010, India

ARTICLE INFO

Article history:
Received 22 June 2016
Received in revised form 1 October 2016
Accepted 8 October 2016
Available online 11 October 2016

Keywords:
DRS-FTIR technique
Chromium(VI)
Cloud point extraction
Adulteration
Turmeric

ABSTRACT

A new cloud point extraction (CPE) method for the determination of hexavalent chromium i.e. Cr(VI) in food samples is established with subsequent diffuse reflectance-Fourier transform infrared (DRS-FTIR) analysis. The method demonstrates enrichment of Cr(VI) after its complexation with 1,5-diphenylcarbazide. The reddish-violet complex formed showed λ_{max} at 540 nm. Micellar phase separation at cloud point temperature of non-ionic surfactant, Triton X-100 occurred and complex was entrapped in surfactant and analyzed using DRS-FTIR. Under optimized conditions, the limit of detection (LOD) and quantification (LOQ) were 1.22 and 4.02 μg mL^{-1}, respectively. Excellent linearity with correlation coefficient value of 0.94 was found for the concentration range of 1–100 μg mL^{-1}. At 10 μg mL^{-1} the standard deviation for 7 replicate measurements was found to be 0.11 μg mL^{-1}. The method was successfully applied to commercially marketed food stuffs, and good recoveries (81–112%) were obtained by spiking the real samples.

1. Introduction

The importance of chromium has been widely recognized through innumerable researches available on this fascinating element. However, continuous monitoring of chromium is of considerable significance owing to its properties. The properties of metal often depend on its speciation. The commonly existing oxidation states of +3 and +6 displayed by chromium i.e. Cr(III) and Cr(VI) show amazingly contrasting properties (Verma, Verma, & Deb, 2008). The trivalent chromium (i.e. Cr(III)) is biologically essential for its role in sugar and protein metabolism, whereas Cr (VI) is potentially toxic and carcinogenic, and has adverse impact on metabolic processes (Gardner & Comber, 2001). Hence, estimation of Cr(VI) in complex matrices such as food, is of vital importance.

An accurate assessment is required to evaluate the quality of food stuffs since food is one of the basic needs of life. Cr(VI) has been reported as the major component of contaminants used to adulterate the food stuffs (Ellis et al., 2012; Moore, Spink, & Lipp, 2012). Hence the trace level determination of Cr(VI) in food stuffs is of utmost importance. In recent years, the need for more sophisticated and comprehensive methods for detection of Cr(VI) in various matrices has led to the development of novel procedures (Gomez & Callao, 2006; Kotas & Stasicka, 2000). Some of the reported techniques used to determine Cr(VI) include spectrophotometry (Pobozy, Wojasinska, & Trojanowicz, 1996; Rajesh, Jalan, & Hotwany, 2008), flame atomic absorption spectrometry (Kiran et al., 2008; Sun & Liang, 2008), electrothermal atomic absorption spectrometry (Soares, Vieira, & Bastos, 2010; Zhu, Hu, Jiang, & Li, 2005), inductively coupled plasma-mass spectroscopy (Wen, Shan, & Lian, 2002), electrothermal vaporization inductively coupled plasma optical emission spectroscopy (Li, Hu, Jiang, & Wu, 2007), high performance liquid chromatography (Padarauskas, Judzentiene, Naujalis, & Paliulionyte, 1998; Tang, Jiang, Jiang, Wang, & Yan, 2004) and Fourier transform infrared spectroscopic technique (Verma et al., 2008). Gomez and Callao (2006) review about more than 100 analytical methods that have been used to determine chromium concentration in various matrices during 2000–2006.

The challenge to determine ultra-trace analytes at low concentration has been solved to a great extent employing separation techniques as a mandatory step prior to analysis (Paleologos, Giokas, & Karayannis, 2005). Various extraction techniques have been developed for determination of Cr(VI). Some of them are liquid-liquid extraction (Beni, Karosi, & Posta, 2007; Wang, Song, Ma, & Liang, 2000) single drop micro-extraction (Verma et al., 2008), solid phase extraction (Rajesh et al., 2008), co precipitation

* Corresponding author.
E-mail address: debmanas@yahoo.com (M.K. Deb).

http://dx.doi.org/10.1016/j.foodchem.2016.10.034
0308-8146/

(Gopikrishna, Gladis, Rambabu, Rao, & Naidu, 2004), ion chromatographic speciation (Gurleyuk & Wallschlager, 2001), and electrothermal and photometric speciation methods (Boussemart, Van den Berg, & Ghaddaf, 1992; Komarek & Holy, 1999). The above mentioned techniques are comparable in terms of sensitivity and selectivity, but some of them are associated with disadvantages of consumption of large amount of solvents and poor reproducibility. Cloud point extraction (CPE) exceeds the aforementioned techniques in being very simple, and economically effective. Further, this method does not require the use of toxic solvents (Castor et al., 2016). The potential of CPE can be stated as it has been extensively used for preconcentrating variety of metals and also biomolecules like chlorophylls (Hassanien, Hassan, Mortada, & El-Asmy, 2011; Paleologos et al., 2005; Sun, Liu, & Zhao, 2014). CPE is based on a simple phenomenon that, when nonionic surfactants are heated to a particular temperature, known as cloud point, they become turbid forming cloud like appearance. Above this temperature the micellar phase separation takes place and two distinct phases: a surfactant rich phase and bulk aqueous phase are formed (Altunay & Gurkan, 2015). During the phase separation process, the hydrophobic complex so formed gets entrapped in the surfactant rich phase and thus gets separated. This depends upon the equilibrium constant of micellar medium (Kiran et al., 2008; Paleologos et al., 2005). The use of CPE as a speciation process for Cr(VI) has also been reported (Kiran et al., 2008; Lu, Tian, Wu, & Zhao, 2009; Shemirani, Abkenar, Mirroshandel, Niasari, & Kozania, 2003; Zhu et al., 2005). In this paper we report a simple and environmentally benign method for determination of Cr(VI) employing CPE coupled with diffuse reflectance-Fourier transform infrared (DRS-FTIR) technique. The Cr(VI) is complexed with diphenylcarbazide (DPC) resulting in reddish-violet colored complex and is extracted using triton X-100 as nonionic surfactant. Cr(VI) has also been determined by FTIR (Verma et al., 2008), but use of CPE as preconcentration process and subsequent FTIR analysis in food samples has not been done before.

2. Materials and methods

2.1. Instrumentation

Fourier transform infrared spectral scans were performed in the region of 4000–400 cm^{-1} using an FTIR (Nicolet iS10 model, Thermo Fisher Scientific Instrument, Madison WI USA), equipped with deuterated, L-alanine doped triglycine sulfate (DLaTGS) detector. DRS-accessory (Nicolet iS10 model, Thermo Fisher Scientific Instrument, Madison WI USA), was employed for diffuse reflectance measurements. In diffuse-reflectance the light leaves the analyte surface from many different angles. The accessory was operated by sliding into the sample slide mount in the FTIR compartment. For characterization of Cr(VI)-DPC complex, a double beam UV–Visible spectrophotometer (Evolution 300 model, Thermo Fisher Scientific Pvt. Ltd.) was employed. An electronic balance of 10 μg precision (CP225D model, Sartorius, AG Gottingen Germany), was used for weight measurements. Variable volume (10–100 μL) micropipettes (Galaxo Smith Kline Pharmaceuticals) were used for handling liquid volumes.

A thermostated water bath maintained at different temperatures was employed for temperature experiments. An ultracentrifuge, 3599 g, (R-8C model, Remi Laboratories, India) was used to accelerate phase separation. A digital pH meter (335 model, Systronics) was employed for pH measurements. All glasswares were washed properly with mild detergent using Ultrasonic Bath, (3.5L100H/DIC model, PCI Analytics, Pvt. Ltd., India) to ensure sensitivity and rinsed with ultrapure water. Ultra-pure water system with conductivity value 18.2 Ω (Barnstead Smart2pure model, Thermo Fisher) was used to obtain ultra-pure water.

2.2. Standard solutions and reagents

All reagents and materials used were of analytical grade. Special care was taken during the handling of all glasswares to avoid any possible contamination and to maintain the sensitivity of the method. A stock solution containing 1000 μg mL^{-1} Cr(VI) was prepared by dissolving appropriate amount of potassium chromate (Merck KGaA Darmstadt, Germany, 99.9%) in ultra-pure water and diluted to 1 L. Appropriately diluted solution of the above standard chromate(VI) solution were used for further work. Triton X-100 was obtained from Sigma was used as a surfactant for CPE process and was prepared at 2% (v/v) concentration. A 0.1% (w/v) solution of DPC was prepared by dissolving appropriate amount of 1,5-diphenylcarbazide in 100 ml of ethanol. Potassium bromide used in the analysis was of infrared spectrometric grade, Merck KGaA 64271 Darmstadt, Germany.

3. Experimental design

The determination of Cr(VI) is based on formation of Cr(VI)-DPC complex followed by enrichment of complex by CPE technique. For CPE, triton X-100 was used as nonionic surfactant. The extract was then analyzed by DRS-FTIR. The procedure for CPE of Cr(VI) and its DRS-FTIR analysis has been elaborated in the Section 3.1 and 3.2.

3.1. CPE of Cr(VI)

For CPE, 10 μL aliquots each of solutions containing the analyte (10 μg mL^{-1}), DPC (0.1%, w/v) and triton X-100 (2%, v/v) in a final 5 mL aqueous phase in a 10-mL glass vial. The pH of the mixture was maintained acidic by using 0.1 mL 0.1 N HCl and the mixture was kept in a thermostated water bath maintained at 85 °C for 30 min. The mixture was transferred to a centrifuge tube (10-mL) and centrifuged at 1600*g* for 5 min to ensure the complete phase separation. The surfactant rich phase gets settled at the bottom of the tube. The supernatant phase was removed and the surfactant rich phase was taken for DRS-FTIR analysis.

3.2. DRS-FTIR analysis of extracted analyte

The extracted analyte mixture containing Cr(VI)-DPC complex along with surfactant triton X-100 was delivered over 0.1 g preweighed finely ground IR grade KBr for DRS-FTIR scan. The KBr was dried around 100 °C, for 5–10 min, prior to spectral scan to remove water aberration. The FTIR was purged for 30 min with >99.99% analytical grade nitrogen gas using external purge kit (iS10 iZ10 model, Thermo Fisher Scientific), to minimize atmospheric interferences. The dried KBr was then filled over the sample cup and analyte was carefully delivered over it. Diffuse reflectance accessory with XT/KBr beam splitter and Deuterated, L-alanine doped triglycinesulphate (DLaTGS) detector was employed in the present work. The software OMNIC 9.1, automatically performs the spectral scaling and the resultant absorptions are then analyzed for quantification. All spectral scans were measured in the absorbance mode with resolution of 4 cm^{-1}. Number of scans per sample was set to 32. Omnic 9 software was used for spectral analysis. Seven replicate measurements were conducted for 10 μg mL^{-1} of analyte with all required precautions.

4. Results and discussion

4.1. Complexation of Cr(VI) with DPC

Diphenylcarbazide is one of the most widely used chromophoric reagent employed for determination of Cr(VI). The reason for this is the selectivity and sensitivity of DPC towards Cr