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Analytical Methods

Evaluation of thiosemicarbazone derivative as chelating agent for the simultaneous removal and trace determination of Cd(II) and Pb(II) in food and water samples

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ABSTRACT

In the present investigation, prepared *N*-ethyl-3-carbazolecarbaxaldehyde-3-thiosemicarbazone (ECCT) and employed for the simultaneous removal and determination of trace amounts of Cd(II) and Pb(II) from food and water samples. Cd(II) and Pb(II) gave yellow and orange colored complexes with ECCT in acetate buffer at pH 6.0 with λ_{max}, 380 and 440 nm, respectively. Both complexes were easily extractable into kerosene at 1:1(M:L) composition. It was in accordance with Beer's law in the range of 0.0–12.0 and 0.0–10.0 $\mu g\ mL^{-1}$ with 0.999 and 0.997 correlation coefficient for Cd(II) and Pb(II) complexes, respectively, indicated a good linearity between the two variables. The molar absorptivity and Sandell's sensitivity were found to be $0.740 \times 10^4\ L\ mol^{-1}\ cm^{-1}$, $1.52 \times 10^{-3}\ \mu g\ cm^{-2}$ for Cd(II) and $1.809 \times 10^4\ L\ mol^{-1}\ cm^{-1}$, $1.15 \times 10^{-3}\ \mu g\ cm^{-2}$ for Pb(II). The precision and accuracy of the method was checked for both metal ions by finding the relative standard deviations ($n = 8$), which were 0.689% and 0.443%, with detection limits of $0.00151\ \mu g\ L^{-1}$ and $0.00264\ \mu g\ L^{-1}$ for Cd(II) and Pb(II), respectively. Further validation using certified reference material, NIST 1568b, resulted in determined concentrations of $0.028 \pm 0.253\ \mu g\ g^{-1}$ for Cd(II) and $0.046 \pm 0.325\ \mu g\ g^{-1}$ for Pb(II). These determined values agree well with the certified values in the reference materials. The interfering effects of various cations and anions were also studied. The proposed method performance was also evaluated in terms of Student '*T*' test and Variance '*F*' test, which indicated the significance of the present method parameters, as an inter comparison of the experimental values using ICP-OES.

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1. Introduction

Heavy metal ions are highly associated with human life from several centuries; however these are toxic even at low concentrations when they enter into human body. These elements are regularly ingested and encountered by humans from various sources such as cosmetics (Shih, Zen, Kumar, Lee, & Huang, 2004; So-Mi, Hye-Jin, & Ih Seop, 2008), pharmaceuticals (Cotte et al., 2006) and chemical industries (Shahryar, Atousa, & Freshteh, 2011; Tasneem et al., 2010). Along with the above heavy metals are natural components of food materials, the simple elemental forms of which cannot be degraded or destroyed (Kong et al., 2010). The major sources of heavy metal ions are water, vegetables, medicinal leaves, milk and vegetable oils and honey (Ang, Lee, & Matsumoto, 2003; La Pera, Saitta, Di Bella, & Dugo, 2003; Nina Bilandzić et al., 2011). Thus, heavy metals ions from food industry have received great attention due to high incidences of contamination through a number of raw agricultural, canned food and seafood products (John, 2011; Moka et al., 2012; Tasneem et al., 2010), as well as their extensive use in industrial applications (Nina Bilandzić et al., 2011). This has caused increased concern over the potential health related impacts from a number of foods throughout the world. Naturally occurring levels of heavy metals below toxic limits are usually not harmful to living organisms, but higher concentration can cause toxic effects, and there is several reported incidences available in the literature (Lu, Toghill, & Compton, 2011; Massadeh et al., 2010; Moka et al., 2012; Tasneem et al., 2010). In this view particular attention has been paid to the presence of heavy metals in food samples.

Of all the heavy metals, Pb(II) and Cd(II) are important to consider in terms of food chain contamination because of their toxicity (Efendioglu, Yagan Asci, & Bati, 2010; Moka et al., 2012; Skrzydlewska, Balccrzak, & Vanhacckc, 2003; Tasneem et al., 2010; Tufekci et al., 2013). Pb(II) and Cd(II) ions causes both acute and chronic poisoning, exhibits adverse effects on the kidney, liver, heart,

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vascular and immune system. Moreover Pb(II) and Cd(II) exposure causes chromosome aberration, skin allergy, cancer and birth defects (Houlbrèque et al., 2011; Shahryar, Atousa, & Freshteh, 2011; Shahryar, Kobra, & Freshteh, 2011; Shih et al., 2004; So-Mi et al., 2008). The main anthropogenic sources of these elements are the combustion of fuel, industrial emissions, varnishes and chemical colorants (Vereda Alonso, Siles Cordero, García de Torres, & Cano Pavón, 2006). These are absorbed by water and vegetables, especially, leafy vegetables absorbs higher amount of Pb(II) and Cd(II) through their leaves (Demirezen & Aksoy, 2006). Hence, there is a great need to develop a simple, sensitive, selective and inexpensive method for the determination and continuous monitoring of these heavy metal levels in food and water samples.

In this perspective a number of methods have been developed for the simultaneous determination of Cd(II) and Pb(II) in real matrices using several analytical techniques: AAS (Correia, Oliveira, & Oliveira, 2000; Efendioglu et al., 2010; Ezoddin, Shemirani, Abdi, Saghezchi, & Jamali, 2010; Tufekci et al., 2013), ICP-AES (Kumar, Ramana, Harinath, Seshaiah, & Wang, 2011), ICP-OES (Massadeh et al., 2010; Zhu & Chiba, 2012), ICP-MS (Skrzydlewska et al., 2003; Zhang, Li, Du, Li, & Chang, 2012), neutron activation analysis (Furuta, Nakahara, Hatsukawa, Matsue, & Sakane, 2008), electro chemical methods (Bui, Li, Han, Pham, & Seong, 2012; Lu et al., 2011; Nagles, Aranciba, & Rios, 2012), voltammetry (Lezi, Economou, Dimovasilis, Trikalitis, & Prodromidis, 2012; Mahesar et al., 2010; Tarley, Santos, Baeta, Pereira, & Kubota, 2009) and other techniques (Vereda Alonso, Siles Cordero, García de Torres, & Cano Pavón, 2006). Usually, such techniques involve amendment steps and, increasing expense, as well as often low selectivity and sensitivity (Kong et al., 2010; Shahryar, Atousa, & Freshteh, 2011). Often, spectrophotometric methods are preferred, as they are cost effective, easy to handle, with a comparable sensitivity and accuracy, with good precision. Thus spectrophotometric method is one of the most commonly used techniques for routine analysis of metals, and also for the simultaneously determination of multiple elements (Hashem, 2002).

Although there are many spectrophotometric organic complexing reagents (Agnihotri, Ratnani, Singh, & Singh, 2004; Arain, Laghari, & Khuhawar, 2003), which can be used for the spectrophotometric determination of Cd(II) and Pb(II), they suffer from disadvantages, such as low sensitivity, incomplete extraction, and interference from a large number of foreign ions. Among these reagents, thio- and phenylthiosemicarbazones play a unique role. These are frequently used as complexing agents in the spectrophotometric and extractive spectrophotometric determination of various metal ions (Ahmed, 2008; Reddy, Lee, Seshaiah, & Babu, 2013; Reddy, Seshaiah, & Reddy, 2011; Salinas, SBnchez, & Diaz, 1986), due to their metal chelates finding a wide range of applications in medicine and in agriculture (Nabid et al., 2012; Narayana, Reddy, Reddy, Sung Ok Baek, & Reddy, 2012). However, literature survey reveals that only a few thiosemicarbazones are employed for the direct and extractive spectrophotometric determination of Cd(II) and Pb(II) (Arain et al., 2003; Reddy et al., 2008; Reddy, Reddy, & Reddy, 2010), but not for their simultaneous spectrophotometric determination. A few other reagents are used for simultaneous spectrophotometric determinations of Cd(II) and Pb(II) (Agnihotri et al., 2004; Hashem, 2002; So-Mi et al., 2008). Even though, they suffer from interference with one other. Hence, ECCT chosen as a complexing agent for the simultaneous removal and extractive spectrophotometric determination of Cd(II) and Pb(II), without interference. Recently, it has been used for the extractive spectrophotometric determination of Ni(II), Cu(II), Co(II) and Zn(II) in foods and environmental samples (Ramachandraiah, Kumar, Reddy, Narayana, & Reddy, 2008; Reddy et al., 2007; Reddy, Kumar, Ramachandraiah, Reddy, & Reddy, 2008; Reddy, Kumar, Ramachandraiah, Thriveni, & Reddy, 2007).

The aim of this work was to prepare a reagent, ECCT, with an objective to develop a sensitive and selective extractive spectrophotometric method for the simultaneous removal and determination of Cd(II) and Pb(II) in food and water samples, and it was found to be relatively more sensitive and selective than some of previously reported methods (Table 1).

2. Materials and methods

2.1. Apparatus

A Shimadzu 2450 UV–Vis spectrophotometer with a 1.0 cm quartz cell was used to measure absorbance of solutions. pH adjustment was carried out by An Elico LI-120 digital pH meter. A Perkin–Elmer Optima 2100 DV inductively coupled plasma optical emission spectroscopy, USA, was used for the inter comparison of results. A Nicolet FT-IR 560 Magna spectrometer using KBr (neat) was used to obtain the infrared spectra of the compound (ECCT). A Bruker 300 MHz NMR spectrometer was used to obtain the ^{1}H NMR spectra of the ligand.

2.2. Reagents

All the reagents used were of AR grade, unless otherwise stated here. Prepared *N*-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone (ECCT) as per the procedure reported elsewhere (Reddy et al., 2007). As prepared ligand structure was confirmed with the help of spectroscopic studies, such as FT-IR, ^{1}H NMR and their data are provided here.

The molecular formula and molecular weight of ECCT are $C_{16}H_{16}N_4S$ and 296 g, respectively. ^{1}H NMR data ($CDCl_3$/DMSO) are as follows: δ 1.43 (t, 3H, $-CH_2-CH_3$); 4.41 (q, 2H, $-CH_2-CH_3$); 7.18–8.48 (m, 9H, Ar–H and $-NH_2$); 9.16 (s, 1H, $-CH{=}N$); 11.62 (s, 1H, NH). FT-IR data of ECCT (using KBr pallet): The stretching frequency was observed at 1678 cm^{-1} indicates ECC carbonyl group ($>C{=}O$). When ECC reacts with thiosemicarbazide, the corresponding Schiff base ECCT is formed, and its IR spectrum shows a new stretching frequency at 3241 and 3142 cm^{-1} which is assigned to $-NH_2$ and –NH groups of thiosemicarbazones, respectively. The absorption spectrum at 1626 cm^{-1} is attributed to $>C{=}N-$. A new absorption peak at 1236 cm^{-1} was observed for the thio-carbonyl group. This peak indicates the condensation of the carbonyl group of ECC and the NH_2 group of the 3-thiosemicarbazide occurred leading to the formation of ECCT.

2.3. Preparation of working standard solutions and buffer solutions

The stock solutions were prepared by dissolving 0.270 g $Cd(CH_3COO)_2\cdot 2H_2O$ and 0.380 g $Pb(CH_3COO)_2\cdot 3H_2O$ in 1.0 L double distilled water. The solution was made up to the mark and standardized using standard methods (Vogel, 1961). Lower concentrations of Cd(II) and Pb(II) solutions were prepared by diluting the stock solution with double distilled water. 1.0 mol L^{-1} sodium acetate and acetic acid solutions were prepared in double distilled water and suitable portions of these solutions were mixed to obtain the desired pH.

2.4. Preparation of water and certified reference material samples for the determination of Cd(II) and Pb(II)

Different water samples were collected from Gyeongju, Republic of Korea. The collected water samples were filtered using filter paper (Whatman No. 41) and then each filtered water sample was evaporated nearly to dryness with a mixture of 4.0 mL of concentrated H_2SO_4 and 8.0 mL of concentrated HNO_3 in a fume cupboard,

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