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Spectrophotometric determination of zinc in foods using *N*-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone: Evaluation of a new analytical reagent

K. Janardhan Reddy, J. Rajesh Kumar, C. Ramachandraiah, T. Thriveni, A. Varada Reddy *

Analytical Chemistry Division, Department of Chemistry, Sri Venkateswara University, Tirupati, AP 517 502, India

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Abstract

N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone (ECCT) is proposed as a new sensitive reagent for the extractive spectrophotometric determination of zinc(II). The ECCT forms yellow colored species of zinc(II) at pH range 3.0–5.5 and the complex was extracted into benzene. The Zn(II)–ECCT complex shows maximum absorbance at 420 nm with molar absorptivity and Sandell's sensitivity being 1.55×10^4 lit mol^{-1} cm^{-1} and 4.212×10^{-3} μg cm^{-2}, respectively. The system obeys Beer's law in the range of 0.4–6.0 mg/l, with an excellent linearity in terms of correlation coefficient value of 0.999. Most of the common metal ions generally found associated with zinc do not interfere. The repeatability of the method was checked by finding relative standard deviation (RSD). The developed method has been successfully employed for the determination of zinc(II) in foods. Various certified reference materials (NIST 1573, NBS 1572 and NIST SRM 8435) have been tested for the determination of zinc for the purpose of validation of the present method.

Keywords: *N*-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone; Zinc(II); Extractive spectrophotometry; Foods

1. Introduction

Zinc occurs exclusively in +2 oxidation state. Zinc deposits are not only important commercially for the zinc they contain, but also because of their association with other valuable elements. About one-third of the present zinc production goes into the galvanizing of ferrous metals. Brass alloys consume another one-third of the world zinc production, while the remaining zinc is converted into a number of chemical products (Fisher, 1975; Giroux, Durieux, & Schechter, 1976; William, 1983).

Zinc is an essential element in the nutrition of animals including human beings (Brunborg, Julshamn, Nortvedt, & Frøyland, 2006; Saun, 2005). It acts as a cofactor innumerous of enzymes and plays an important role in protein synthesis and cell division. It exerts a crucial influence on maintenance of cell membrane stability and function of immune system. On the other hand, zinc can be toxic when exposures exceed physiological needs. After single or short-term exposure to concentrations of zinc in water and beverages between 1.0 and 2.5 mg/l, poisoning incidents with symptoms of gastrointestinal distress, nausea and diarrhea are reported (Hernick & Fierke, 2005). Zinc is present in many foods, soil and is also found in a number of pharmaceutical samples, causing environmental pollution. Concentration of zinc greater than 5.0 mg/l affects the potable water nature in alkaline waters. It is clear that zinc is an essential element and has significant importance, both biologically and industrially. When the quantity is more than what is required, zinc produces toxic effects. Hence, separation and determination of zinc(II) from its associated metal ions is indispensable.

Thio- and phenyl thiosemicarbazones are important sulphur and nitrogen containing organic reagents find a wide

* Corresponding author. Tel.: +91 877 2232659/2249666; fax: +91 877 2249611.
E-mail address: ammireddyv@yahoo.co.in (A.V. Reddy).

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range of applications in medicine (Hall et al., 2000) and agriculture, where zinc co-ordinates with these reagents to form stable complexes. The revived (Casas, Garcia-Tasende, & Sordo, 2000; Garg & Jain, 1988; Singh, Garg, & Singh, 1978) literature revealed that only a few thio- and phenyl thiosemicarbazones were employed for extractive determination of zinc(II). The review of literature indicates only a few thiosemicarbazones have been exploited for the spectrophotometric determination of zinc(II). Not much attention has been paid for the extractive spectrophotometric determination of zinc(II) with thiosemicarbazones or other organic chelating reagents (Benamor, Belhamel, & Draa, 2000; Herrador, Jimenez, & Asuero, 1987; Hoshi, Yotsuyanagi, & Aomura, 1977; Leyva, Pavon, & Pino, 1972; Nevado, Leyva, & Ceba, 1976; Sarma, Kumar, Reddy, Kumar, & Reddy, 2002) this has prompted the researchers to make a systematic investigation for utilizing *N*-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone (ECCT) first time for the extractive spectrophotometric determination of zinc(II) in microgram quantities. The title reagent ECCT was proved more stability when complexed with Zn(II) and found that the color of the complex is stable for more than 48 h. ECCT was extracted zinc selectively when associated with following metal ions Mn(II), Mg(II), Mo(VI), W(VI) Ca(II), Cr(III), Fe(II) and Zr(IV), it indicates that ECCT was stable reagent for extractive determination of zinc(II). ECCT is cheap, stable in high temperatures, easier to dispense and store. In our previous studies, we are developed the new analytical methods for determining the transition metals from various samples like environmental, biological and pharmaceutical samples using thio- and phenylthiocarbazones (Sarma et al., 2002, 2003, 2005; Reddy et al., 2004, 2003, 2002). In our ongoing research work, now we reporting the new analytical method for the determination of zinc(II) in foods using ECCT as a complexing reagent.

The analysis of zinc from various foods was recently studied by (Reddy, Kumar, Sarma, & Reddy, 2002) and (Sarma et al., 2006) using benzildithiosemicarbazone (BDTSC) and pyridioxal-4-phenyl-3-thiosemicarbazone (PPT) as chelating reagents by spectrophotometrically and other researchers reported on zinc recovery from food staffs by various analytical techniques (Martínez, Rincón, & Ibáñez, 2006; Ruz et al., 2006; Santelli, Bezerra, SantAna, Cassella, & Ferreira, 2005).

2. Materials and methods

2.1. Apparatus

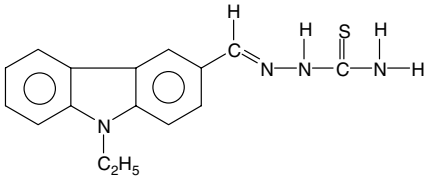
Shimadzu 240 UV–Vis spectrophotometer with 1.0 cm quartz cell was used for absorbance studies. An Elico LI-120 digital pH meter was used for pH adjustment. A Perkin–Elmer 2380 atomic absorption spectrometer was used for the comparison of results.

2.2. Reagents

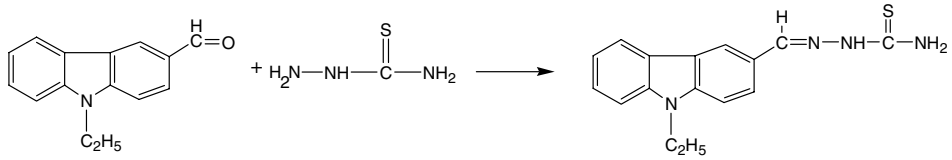
A 0.5 g *N*-ethylcarbazolecarboxaldehyde (ECC) was dissolved in 25.0 mL ethanol and mixed in a flask containing 1.5 g thiosemicarbazone dissolved in 25.0 mL of 1:1 ethanol–water mixture. The resulting reaction mixture was refluxed on water bath for 2 h. It was allowed to stand at room temperature until pale yellow crystals were formed (Cristofol, Rojas, & Pavon, 1991). These were separated and recrystallized from ethanol (Scheme 1).

Molecular formula and molecular weight of ECCT are $C_{16}H_{16}N_4S$, 296, respectively. ^1H NMR data ($CDCl_3$/DMSO): 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). IR Data (KBr): The ECC stretching frequency was observed at 1678 cm^{-1}. After reacting ECC with thiosemicarbazide corresponding Shieff base ECCT is formed and its IR spectrum indicated new stretching frequency at 3241 and 3142 cm^{-1}. These two absorptions are assigned to $-NH_2$ and –NH groups of thiosemicarbazone, respectively. Another new absorption at 1626 cm^{-1} is attributed to >C=N—. A new absorption at 1236 cm^{-1} was observed for the thiocarbonyl group. These spectra therefore suggest that the condensation between the carbonyl group of ECC and NH_2 group of the 3-thiosemicarbazide has taken place leading to the formation of ECCT.

Hence, the structural formula of the reagent ECCT may be given as follows:



N-Ethyl-3-carbazole carboxaldehyde-3-thiosemicarbazone (ECCT)



N-Ethylcarbazolecar -boxaldehyde | Thiosemicarbazone | ECCT

Scheme 1.