



Centrifugation assisted digestion for simultaneous voltammetric determination of ultra trace metal ions in water and milk samples



Imran Khan*, Umar Jan Pandit, Sneha Wankar, S.N. Limaye

Rare Earth and Electroanalytical Research Laboratory, Department of Chemistry, Dr. HariSingh Gour Vishwavidyalaya (A Central University), Sagar, M.P., India

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ABSTRACT

The present work was aimed to optimize various instrumental and experimental parameters for development of simple and sensitive method for determination of some toxic and essential metal ions in milk and water samples. Differential Pulse Stripping Voltammetric technique was employed for the determination of Pb^{2+} , Cd^{2+} , Zn^{2+} and Co^{2+} at Hanging Mercury Drop Electrode (HMDE) and Hg^{2+} and As^{3+} at Gold-Rotatory Disk electrode (Au-RDE) respectively. The voltammetric analysis was performed after chemical mineralization of the samples by centrifugation assisted digestion. The results obtained were subjected to statistical analysis and concentrations were found above or around the permissible limits. Under the optimized conditions the limit of detection of metal ions was found to be $0.006 \mu g L^{-1}$ (Pb^{2+}), $0.007 \mu g L^{-1}$ (Cd^{2+}), $0.047 \mu g L^{-1}$ (Co^{2+}), $0.013 \mu g L^{-1}$ (Zn^{2+}), $0.001 \mu g L^{-1}$ (Hg^{2+}) and $0.003 \mu g L^{-1}$ (As^{3+}). The developed method produces a simple, rapid, suitable, economical and precise determination of these metal ions with low detection limit and minimum matrix effect.

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1. Introduction

Milk and their products are most diversified natural foodstuffs in terms of composition and also contain more than twenty different trace elements, protein, fat and major minerals. It is a main constituent of daily diet, for infants to old age (Ataro et al., 2008). Toxicity of metal ions is closely related to age, route of exposure, level and frequency of intake, solubility and oxidation state metal ion, absorption rate and mechanism or efficiency of excretion (Patra et al., 2008; Solis et al., 2009). These elements get stored in tissues and cause adverse effects on growing children, including retardation of mental development, kidney dysfunction and also cardiovascular system (Tripathi et al., 1999). The permissible limits of metal ions in milk and water samples as proposed by WHO and FAO are listed in Table S1 (Supplementary).

Milk usually contains low concentration of Pb^{2+} , Cd^{2+} and Hg^{2+} except when dairy animals feed contaminated fodder and water. Pb^{2+} ion contamination also occurs through roadside combustions, combustion of coal and their ashes, lead aided paints and batteries (Tripathi et al., 1997; Rohan et al., 2014). The reduction of Pb^{2+} and Cd^{2+} cannot occur by thermal treatment because Pb and Cd easily bind with casein and also form complex with whey protein

in milk (Shahbazi et al., 2016; Coni et al., 1996). Moreover milk also gets contaminated through metallic Pb^{2+} and Cd^{2+} soldered storage containers (Tokusüogü Lu et al., 2004). Hg^{2+} ion is released in the environment from natural and anthropogenic sources and undergoes biogeochemical transformation processes and can be converted into $MeHg^+$ by microbial activity in aquatic environment (Lehnher et al., 2011). Generally, organic mercury compounds are more toxic than inorganic and elemental mercury, due to their high biomagnifications factor (up to 10^6) in the food chain and their high lipo-solubility (Gao et al., 2012). Whereas Co^{2+} and Zn^{2+} are categorized under essential elements, involve in biological functions *i.e.* components of enzymatic and redox systems (Dugo et al., 2004; Sathawara et al., 2004). Co^{2+} and Zn^{2+} occurred naturally and anthropogenic sources and widely distributed in rocks, soils, water and vegetation. The major source includes coal and residual fuel oil burning and has many strategic industrial uses in cutting tools, surface coatings, cement carbides, ceramics and pigments and in phosphate fertilizers (Gal et al., 2008). These are essential constituent of food for infant nutrition. Zn has been used as Zinc Sulphate in food additives [Food safety and standards regulations, 2011]. It was omitted from the contaminant list of food product by food authority in India. The presence of metal ion and their concentration in various environmental samples and their toxic effects have been reported by various authors. The former study suggested that concentration in food stuff arises due to contamination level in nearby dwelling environment (Solis et al., 2009; Tripathi et al.,

* Corresponding author.

E-mail address: imranchem786@gmail.com (I. Khan).

1999, 1997; Shahbazi et al., 2016; Rohan et al., 2014; Dugo et al. 2004; Sathawara et al., 2004; Singh and Garg, 2006; Sivaperumal et al., 2007; Rath et al., 2009; Sarkara et al., 2004; Kannan et al., 2008; Roychowdhury et al., 2002). The comparative accounts of concentration level of metal ions obtained from different study are shown in Table S2 (Supplementary).

Owing to the high toxicity, mobility, and wide usage, metal ions i.e. Pb^{2+} , Cd^{2+} , Hg^{2+} , As^{3+} , Co^{2+} , Zn^{2+} , Cu^{2+} in different daily used materials, organic chemicals and dyes in agriculture and food processing, have caused serious contamination (Singh et al., 2010). Over the past decades, many analytical techniques have been employed for the determination of heavy metals such as Spectrophotometry (Pillai et al., 2000), Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Ataro et al., 2008), Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) (Carneiro et al., 2015), Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) (Hari Babu et al., 2007), Flame Atomic Absorption Spectrometry (FAAS) (Ghaedi et al., 2009), Atomic Fluorescence Spectrometry (Zeeb et al., 2011), Neutron Activation Analysis (Singh and Garg, 2006), Atomic Absorption Spectroscopy (AAS) (Kannan et al., 2008; Sivaperumal et al., 2007) and Electrothermal AAS (ET-AAS) (Kazi et al., 2009) and has shown satisfactory detection limit upto nano-molar levels in real samples. However, most of these methods are time consuming, manipulative, expensive and require large instrumentation. In comparison to above techniques, Voltammetric stripping techniques are accepted as the most powerful analytical tool for the simultaneous determination of trace elements. It has advantages like extreme sensitivity, selectivity, large concentration range, rapid, precise, economic, ability to metals speciation, as well as easier identification and elimination of interferences (Alghami 2010; Ping et al., 2014; Suturovic et al., 2014).

2. Experimental

2.1. Reagents and solutions

All Chemicals and reagents used were of analytical grade (Merck, India). Deionised water was used for the preparation of all solutions. All glassware were initially washed with detergent and deionised water. In voltammetric cell, contaminated mercury after using in HMDE was cleaned by using conc. HNO_3 and water.

2.2. Standard and Buffer Solutions

The standard solutions of 0.01 M of each Pb^{2+} , Cd^{2+} , As^{3+} , Zn^{2+} , Hg^{2+} and Co^{2+} were prepared by dissolving $Pb(NO_3)_2$, $CdCl_2$, $NaAsO_2$, $ZnCl_2$, $HgCl_2$ and $Co(NO_3)_2$ respectively in deionised water. All solutions were stored in polypropylene bottles. 0.02 M acetate buffer of pH 4.5 was prepared from both Sodium Acetate and Acetic Acid.

2.3. Apparatus

The electrochemical measurements were performed on a software controllable Ω 797 VA Computrace (Ion Analyzer Swiss made) equipped with conventional three electrode system consisting of a Ag/AgCl (saturated KCl) as reference electrode, Platinum wire as auxiliary electrode and HMDE and Au-RDE as the working electrode for voltammetric measurements. The pH measurements were performed with Systronics μ -pH 361 Digital Analyzer. Centrifugation was carried out on Remi 8C Laboratory Centrifuge. Agilent 7700x ICP-MS was used for the ICP-MS analysis.

2.4. Sampling

Milk samples were collected randomly in morning and evening time from the local dairies in the proximity of polluted sites of Sagar city (Latitude- $23^{\circ}83'N$, Longitude- $78^{\circ}71'E$ and 1758 feet above sea level), M.P. India. Samples were categorized accordingly as Raw milk-1 (morning time), Raw milk- 2 (evening time) and third category includes Adulterated Milk samples by adulterating with 40% water (catchment area's water) in milk sample. Milk samples were collected from lactating cattles of around 3 years old, in clean, acid-washed 250 mL polyethylene bottles directly from the teats and immediately placed in cooler box. On arrival in laboratory, about 40 g milk was placed in 250 mL volumetric flask and stored in freezer (-15 to $-20^{\circ}C$) till further analysis. The water samples were also collected from same sites and added with 2.5 mL 8 M HNO_3 to avoid microbial activities. A total of 360 milk samples were collected during Pre-Monsoon season (April–June), Monsoon (July–September), Post Monsoon (October–December) and in Autumn (January–March) from the six different selected sites.

2.5. Sample preparation

2.5.1. Water samples

For the analysis of metal ions, water samples were filtered through whatman No.40 filter paper and transferred to round bottom flask fitted with cap and evaporated to 1/4th of its original volume. The pH was adjusted to 4.0 by adding concentrated HCl and kept in refrigerator for further analysis. Due to volatile nature of Hg^{2+} , filtered samples were treated in closed system using kjeldahl flask. The filtered solutions were added with 5% $KMnO_4$, 4% $K_2S_2O_8$, concentrated HNO_3 and H_2SO_4 . The mixture was heated to $<60^{\circ}C$ for 20–30 min, allowed to cool and immediately added with $NH_2OH-HCl$ to reduce excess oxidant activity. For the analysis of As^{3+} , filtered samples were transfer to kjeldahl flask, added with concentrated HNO_3 and H_2SO_4 . The pH was adjusted to 4.0 by adding 0.1 M NaOH. Blanks were prepared with same procedure.

2.5.2. Centrifugation assisted extraction of milk samples

Prior to the extraction processes the milk samples were brought to room temperature followed by centrifugation for 10 min at 5000 rpm. The upper phase including lipids and fats was discarded and lower phase including minerals was transferred to another tube and added with concentrated $HClO_4$, glacial acetic acid and H_2O_2 and again centrifuged for 20 min. The supernatant containing metal ions was collected and filtered at pore size of $0.20 \mu m$. The pH was adjusted to 4.0 by adding 0.1 M NaOH. For the Hg^{2+} analysis, after the separation of upper lipid phase, lower phase was transferred to another tube closed with cap, added with 5% $KMnO_4$, 4% $K_2S_2O_8$, concentrated HNO_3 and H_2SO_4 and centrifuged for 20 min and immediately $NH_2OH-HCl$ was added to reduce excess oxidant activity and filtered. For the analysis of As^{3+} , lower phase was treated separately with concentrated HNO_3 , HCl and 5% KI in closed tube and centrifuged for 20 min. KI was added for reduction of As^{5+} to As^{3+} . Blanks were prepared with same procedure and all the digestions were prepared in triplicate.

2.5.3. Conventional wet digestion method

To evaluate the efficiency of centrifugation process of extraction, the result obtained were compared with Conventional wet digestion method. The duplicate milk samples were prepared in similar manner as described in Centrifugation Assisted extraction method upto centrifugation and chemical treatment. The mixtures were then heated up to $60-90^{\circ}C$ for 15 min. For Hg^{2+} and As^{3+} , samples were heated $<60^{\circ}C$ in separate closed vessels. The extract was filtered through whatman No.40 filter paper. The pH was adjusted

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