

Determination of Zn, Cd, Pb and Cu metals in ground water of District Hapur, Uttar Pradesh (India) by anodic stripping voltammetric technique

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Abstract

In the present communication determination of Zn, Cd, Pb and Cu metals has been carried out from ground water of Hapur District, Uttar Pradesh (India) using differential pulse anodic stripping voltammetry (DPASV) at Hanging Mercury Dropping Electrode (HMDE). Determination of Zn, Cd, Pb and Cu was carried out by using acetate solution as buffer (pH 4.6) with a sweep rate of 0.06 V/sec and pulse amplitude 0.05 V by HMDE by standard addition method. The minimum level of Zn, Cd, Pb and Cu should also be near to zero and the concentration found in the ground water sample of Hapur (India) as analyzed 2.1834, 0.0509, 0.0116 and 0.0331mg/L⁻¹ respectively.

Keywords: Anode stripping voltammetry, hanging mercury dropping electrode, heavy metals, ground water, district Hapur

Introduction

Heavy metal contamination of groundwater more often than not goes unnoticed and remains hidden from the public view. Presently, it has raised wide spread concerns in different parts of the world and results reported by various agencies have been alarming (Borah et al; 2009). The indiscriminate use of chemicals, fertilizers, pesticides and industrial effluents throwing in the ground water has become a non-tolerable environmental and public health problem (Mohan et al. 2013). Heavy metals poisoning has become a major health problem, especially, since the industrial revolution (Sehgal, et al, 2012). The toxic metal ions present in the ground water are a serious concern now a day in India and around the globe. There is also evidence of prevailing heavy metal contamination of groundwater in many areas of India (Manjappa, et al; 2005, Singh, et al. 2010; Puthiyasekar et al 2010; Rawat, et al 2003). The estimation of these toxic metals in ground water will be very much helpful in under understanding the pollutional load

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¹Department of Chemistry, Gurukula Kangri University, Haridwar (UK), India ²Project Directorates for Farming Systems Research, in ground water (Kaushik, et al, 2009). As heavy metals have categorized for environmental toxins which are present in the ground water used for drinking, irrigation and cooking. The metals entering our food chain or body have tendency to accumulate in some parts and may result in chronic damage to those parts of our body. Although, the natural concentration of metal varies in the fresh water depending upon the metal ion concentration in the soil. It is highly recommended to develop trace element analysis techniques that may separate different elemental species prior to trace elemental analysis. Each day, contaminated drinking water contributes to the death of millions of the poorest people of India and around globe too. In addition, nearly one third of all household consumables are unsafe due to from unprotected sources. Heavy metal toxicity has grown up as a serious concern all over the world, as these heavy metals pose adverse effects on all forms of living organisms in the biosphere. These heavy metals are not readily degradable in the environment and accumulate in the animal and human bodies to a very high toxic levels leading to undesirable effects (Kaur and Mehra, 2012). Uttar Pradesh government has a target of providing safe water and sanitation to its entire citizen by 2020. However, the country has still a long way to go as many rural areas have

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insufficient water to meet the most basic drinking and household needs. Lack of access to safe water and sanitation has significant health impacts as water borne diseases are very acute. The technique Differential Pulse Anodic Stripping Voltammetry (DPASV) has proved to be a powerful method of analysis for trace metal ion in the contaminated ground water. As it can detect the level up to ppb in the contaminated sample. DPASV technique has the advantage for employing in these studies as it also works in the presence of high salt concentration. The metal speciation and differentiation between free and complex metal ion is also possible. In the present communication it has been taken into account to determine to determine metals such as zinc, cadmium, lead and copper in the ground of district Hapur, (U.P.), India.

Materials and methods

Reagents/Chemicals

All chemicals used in experiment are AR grade like nitric acid, potassium chloride, sodium hydroxide, glacial acetic acid, lead nitrate, copper nitrate, cadmium nitrate, zinc nitrate and Sulphuric Acid (Rankem), double distilled water was obtained from double distillation unit. Glassware was cleaned thoroughly, rinsed several times with distilled water and then dried prior to use.

Sample collection and preparation

Ground water samples were collected in 1 L polyethylene tubes from the different areas of Hapur district in the month of August 2013 to October 2013 for the determination of Zn, Cd, Pb

and Cu and analyzed within a week. Nitric acid digestion of all the samples was done using AR Grade HNO₃ for diminishing the interference by organic matter prior to estimation of the heavy metals. Acid digestion for water is carried out in the following way: 20 mL of water sample +2 mL of conc. HNO₃. Then sample is heated on hot plate at 80° C upto 1-2 hrs. Some amount of double distilled water is added and filtered through Whatman paper 42. Final volume is made 50 mL with double distilled water.

Preparation of supporting electrolyte (Acetate buffer) and standard

55.9 g AR grade potassium chloride (KCl) was taken in a 500 mL volumetric flask. To this about 100 mL of double distil water was added. 25 mL 30% w/v NaOH and 14.2 mL glacial acetic acid (CH₃COOH) was filled up to 500 mL with double distilled water. The pH of the buffer should be 4.6.1 mg L⁻¹ mixed standard of zinc, cadmium, lead and copper was prepared for the Voltammetric analysis from stock solution of 1000 mg L⁻¹. 2.5, 5, 10, 20, 50 ppm standard solutions of Pb(NO₃)₂, Cd(NO₃)₂ , Cu(NO₃)₂ and Zn(NO₃)₂ were prepared individually with double distilled water.

Instrumentation operating conditions

Voltammetric determination of Zn, Cd, Pb and Cu were performed with 663VA stand Metrohm with three electrode system consisting Hanging Mercury Drop Electrode (HMDE) as working electrode, Platinum (Pt) as auxiliary electrode and Ag/AgCl/KCl (3mol/L) as reference electrode. The operating parameters are given in Table 1.

 Table1: Operating parameters for the determination of Zn,Cd, Pb and Cu by DPASV

Parameters	Description			
Initial Purge Time	30 sec			
Deposition Potential	-1.20 V			
Deposition Time	60 sec			
Equilibration Time	10 sec			
Pulse Amplitude	0.05 V			
Start Potential	-1.20 V			
End Potential	0.10 V			
Voltage step	0.006 V			
Voltage Step time	0.1 sec			
Scan rate	0.01 V/sec			
Sweep rate	0.06 V/sec			
Modulation Amplitude	0.025			
Modulation Time	0.05 sec			



Anodic stripping voltammetric measurements

buffer (pH 4.6) was taken in polarographic cell and then the measurement was started under the given parameters of Table 1, voltammograms of the blank was recorded. 5 mL of water sample was added polarographic to vessel and then voltammograms of the sample solutions was recorded under the same conditions. After the sample voltammogram was recorded, 0.1 mL of 1 mg L^{-1} mixed standard (Zn, Cu, Cd and Pb) was added twice and then voltammogram of standard was recorded (Fig.1, 2). ASV is the two step

20 mL double distilled water and 2 mL of acetate measurement. In the first step the metal ions like Zinc, Cadmium, Lead, and Copper present in the test solution gets deposited on the mercury electrode surface (amalgamation) at deposition potential of -1150 mV. In the second step all the deposited ions are anodically stripped by scanning the potential range from -1150 to +100 mV. All the measurements are done by standard addition technique in which first the sample was taken into polarographic vessel and the current was measured after the addition of 100µL of standard solution. The procedure was repeated three times and the current was measured.



Fig 1 :Standard addition method recorded at the HMDE in acetate buffer soloution (pH 4.6) scan rate .01 V s-1



Fig 2:Differntial pulse voltatagrams recorded at the HMDE in acetate buffer soloution (pH 4.6) scan rate .01 V s-1



Result and Discussion

A comparison of heavy metal concentration among all the sites using different standards (table 2) shows that there is moderate contamination of heavy metals in groundwater of Hapur district. High concentration of most of these heavy metals arising from industrial areas has been indicating

that these industries could be the primary source of heavy metals. The sources of Zn into the water bodies could be effluents of electroplating industries, sewage effluents have mentioned that the Zn concentration probably increased in the groundwater due to the immersed idols painted with multicolour. Zn was found in the range of 0.1225 -6.4723 ppm and the mean 2.1834ppm was found.

Zinc levels have been found to be significantly high at CHSE Hapur in water samples. The source for Zn might be the electroplating industries and colour based work in these area. Lead levels have been found to be significantly higher at pilkhuwa for water. The Pb concentration varied from 0.0063 -0.0270 ppm, with a mean of 0.0116 ppm during analysis. The high concentration of Pb in the water

can be related to the lead-based battery making industrial units across the Hapur industrial areas and also through vehicular emissions. In some cases, Pb is used to stabilize the land pipes/plastic pipes that results in Pb contamination of the drinking water (Pillai, 1983). The concentration of lead may be due to lead battery-based units spread across the industrial areas or vehicular use in these industrial zones. A previous study by Rawat et al. (2003) has reported high concentrations of Cr in the effluents from these industrial areas. The average value of Zn and Cu levels in water was higher than WHO and EPA quality criteria for groundwater. Comparison with WHO water quality criteria 2005 for ground water also shows that Zn, and Pb exceed the stipulated limit at most sites. Besides these industries, hosiery dyeing industries of Pilkhuwa and near Delhi industries can also be contributing the heavy metal load. Examination of to correlations between metal levels in groundwater showed high statistically significant correlation between Cu - Zn and Cd - Pb(Table 3).

Table 2: Statistical analysis of the water samp	les
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Heavy metals	Min	Max	Mean	Median	S.D.	Std err	95% conf.
Zn	0.1225	6.4723	2.1834	1.6481	2.0079	0.6350	1.4364
Cd	ND	0.0509	0.0509	0.0509	Indefinite	0.0000	
Pb	0.0063	0.0270	0.0116	0.0096	0.0066	0.0023	0.0055
Cu	0.0052	0.0995	0.0331	0.0068	0.0426	0.0174	0.0447

Metal	Zn	Cu	Pb	Cd
Zn	1.00000			
Cu	0.01738	1.00000		
Pb	-0.44601	-0.24626	1.00000	
Cd	-0.36062	-0.19366	0.82279	1.00000

This suggests possibility of similar sources of these heavy metals. Similar correlation was not seen between other metals, thereby suggestive of different sources of contamination. Heavy metal levels in this segment of the river indicate pronounced anthropogenic activity being carried out in Delhi and urban centers in its vicinity. Comparisons with standards of various heavy metals show that the levels are higher than desirable, and pose a growing threat to aquatic life and groundwater. Rawat, M. *et al* 2003; reported that concentration of Zn, Cd, Pb, Cu in tap water of



Delhi (India) were found to be 0.174 mg/L, 0.001 mg/L, 0.002 mg/L, 0.011 mg/L respectively. Cd is a poisonous metal and can cause serious health problems even if ingested in small concentration. It has the tendency to get accumulated in the body tissues that results in lung problems and kidney damage. Effluents from industries like battery making, dye making, pigment making, alloy making are the major sources of Cd into the water bodies (Kaushik et al; 2009). Cd concentration varied from ND - 0.0509 ppm, mean of 0.0509 ppm (table 2). Cu is an essential nutrient. At lower concentrations, Cu ions cause headache, nausea, vomiting and diarrhea and at high concentrations, it causes anaemia, gastrointestinal disorder and also leads to liver and kidney malfunctioning in extreme cases. The concentrations for Cu ranged from 0.0052 - 0.0995 ppm and the mean values were 0.0331 ppm (table 2). Heavy Metal Contamination of Groundwater in the Assam is found to be within thepermissible limit of WHO (1997) with an average of 0.038 ppm Borah et al.(2009). Assessment of heavy metals in River Yamuna segment flowing through Delhi, Cu ranged from 1.011-3.087 ppb and 0.871 to 2.85 ppb during summer and winter season, respectively, and the mean values were 1.898 ppb and 1.759 ppb for summers and winters respectively (Kaur and Mehra, 2012).

Conclusion

In this work, the most appropriate conditions were fixed to determine DAPSAV using single method on hanging mercury drop electrode (HMDE). Direct determination of Zn, Cd, Pb and Cu in the tap water sample is possible by DAPSAV. Under working conditions the amount of Zn, Cd, Pb and Cu in tap water sample has been successfully determined. It can be very useful for human health concern. This method is rapid, sensitive and less costly as compared to other analytical methods. A possible reason for this could be the industrial effluents, as the industrial areas of Hapur contain various metal and other industries. The increased levels of heavy metals in the water lead to accumulation of heavy metals in the agricultural soils and plants grown on these contaminated soils which affect the health of humans and animals. Hence, it is obligatory to rectify the various heavy

metals resources which lead to addition of these. In addition, water should be tested regularly to keep an eye on the heavy metal pollutant into the water.

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