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Simultaneous Quantitation of Ascorbic Acid, Lead (II) and Iron (II) in an Industrial Effluent using Differential Pulse Polarography

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Abstract: In the present study, a successful attempt has been made to develop a simple method for the simultaneous determination of ascorbic acid, lead (II) and iron (II) in an industrial effluent using differential pulse polarography (DPP) technique. Quantification of ascorbic acid, lead (II) and iron (II) was done in Sodium acetate buffer of pH 4.5 as a supporting electrolyte. The polarogram recorded for the industrial effluent in sodium acetate buffer (pH 4.5) showed three peaks at +0.137V, -0.345V and -1.238V vs. saturated calomel electrode which were confirmed to be of ascorbic acid, lead (II) and iron (II) respectively by the method of standard addition. The linear dynamic range for ascorbic acid, lead (II) and iron (II) was 3.773µg/mL to 21.62 µg/mL, 1.887µg/mL to11.688µg/mL and 1.887µg/mLto11.688µg/mL respectively. The proposed method was found to be simple, precise, and accurate and can be successfully applied for the analysis and simultaneous determination of ascorbic acid, lead (II) and iron (II) in an industrial effluent.

Keywords: Differential pulse polarography, Industrial effluent, Ascorbic acid, Lead (II), Iron (II), Sodium acetate buffer.

Introduction

Rapid industrialization and abnormal population growth has enhanced water pollution. Monitoring the metal ions and organic compounds in aquatic environment has been a subject of great concern over the last few decades and will continue to be so, as increasing number of metal ions in increasing amounts and a diverse array of organic compounds form a part of an industrial effluent. The heavy metals like Lead, Cadmium, Mercury, Arsenic, Iron, Nickel, Copper and others are used widely in industries. Thus, monitoring of these toxic substances is an integral part of environmental management. Some of these elements may be micronutrients for many living organisms and are required in small amounts for normal healthy growth, but any metal ion in large amount will always cause acute or chronic toxicity.

Lead is such a metal which is used in everything from construction materials to batteries, alloys, textiles, dyes, plumbing, fuel additives, ammunition etc. Lead compounds are considered to be toxic pollutants. It may enter the human body through air, food, water or absorption through skin. With increase in concentration it can cause serious health problems.

Iron is a dietary requirement for most organisms. In small quantities, certain metals are nutritionally essential for a healthy life. These elements are also found in commercially available multivitamin products. Water soluble binary iron compounds such as $FeSO_4$, $FeCl_2$ may cause toxic effects with exceeding concentrations.

Ascorbic acid (Vitamin C) is a water soluble vitamin and is important in forming collagen, a protein that gives structure to bones, muscles and blood vessels. It plays an important role as an antioxidant and free radical scavenger. It has been suggested to be an effective antiviral agent. Vitamin C has been widely used in the pharmaceutical, chemical, cosmetic, food industry as an antioxidant. Thus there is a need to develop an accurate, reliable and easy to implement method for quantification of it in a sample. However there have been difficulties in quantifying Ascorbic acid due to its instability in aqueous solution. This is due to its oxidation to Dehydroascorbic acid which is a reversible reaction.

The present paper deals with simultaneous quantitation of such electroactive species which are commonly associated with effluents from pharmaceutical industries. Determination of Ascorbic acid in tablet dosage forms, juices, fruits and vegetables by different voltammetric methods such as differential pulse voltammetry, cyclic voltammetry has been reported. [1, 2, 3]. Trace determination of lead and its compounds in medicinal plants and biological samples and its voltammetric study has also been carried out[4-5]. Simultaneous determination of trace metals in industrial and domestic effluents by differential pulse anodic stripping voltammetry has also been reported[6]. Metals present in industrial effluents and sludge samples have been separated and concentrated by using other techniques like electrodialysis, coulometry and photocatalysis[9].Simultaneous determination of ferric, ferrous and total iron by extraction differential pulse polarography, application to the speciation of iron in rocks has also been reported[10]. However, less work has been done in the area of environmental chemistry especially on separation and quantitation of electroactive species present in industrial effluents.

Objective

The main objective of the study was to provide a simple, rapid, efficient, precise and economical method for the simultaneous determination of Vit C, Pb(II) and Fe(II) from an industrial effluent using differential pulse polarography. The developed method has been validated as per ICH guidelines [7-8]

Abbreviations used: Pb(II) – Lead,Fe(II) - Iron,**Vit C-** Ascorbic acid,**S.C.E-** Saturated calomel electrode,**nA-** nanoamperes.

Materials and Methods (Experimental)

Introduction to the workstation

All the measurements were performed on a fully automated computerized electroanalytical workstation, an electrochemical system PG STAT 30 with 663 VA electrode stand manufactured by Metrohm. It includes 3 electrode system viz. hanging mercury drop electrode as a working electrode, saturated calomel electrode as a reference electrode and platinum electrode as an auxiliary electrode.

Reagents

Merck A.R grade Lead nitrate, L-Ascorbic acid, Ammonium iron (II) sulphate hexahydrate, Sodium acetate trihydrate and Glacial Acetic acid were used.

Preparation of Standard Solution

20 mg of Ascorbic acid and 16 mg of $Pb(NO_3)_2$ and70.2 mg of Ammonium iron(II)sulphate hexahydrate were accurately weighed and dissolved in minimum amount of double distilled water and made up to the mark in three different100 mL volumetric flask. The solutions so prepared contained 200µg/mL of Vit C, 100µg/mL of Pb(II)and 100µg/mL of Fe(II) respectively. All the other standard solutions containing Vit C, Pb(II) and Fe(II) were prepared using this stock solution.

Voltammetric method

20 mL of sodium acetate buffer (pH 4.5) was placed in the dry, clean valtammetric cell. The solution was purged with pure nitrogen gas for 180s. The potential scan between +0.25 V to -2.0 V vs. S.C.E was applied. The operational parameters were as follows: 1] Scan rate- 15 $mVs^{-1.}$ 2] Pulse amplitude- 60mV. After recording a polarogram of the blank, 0.4mL of standard solutions of Ascorbic acid, Pb(II) and Fe(II)were added in succession and polarograms were recorded and peak currents were measured and calibration curves were prepared.

Preparation of sample solution

The sample was an effluent from a pharmaceutical industry. The sample solution was centrifuged and filtered through Whatman paper no. 41. 50 mL of the sample was evaporated to dryness and extracted with water containing 0.2 mL of conc HNO_3 and diluted to 50 mL in a volumetric flask with distilled water. Polarograms for the sample solutions were recorded under the same conditions used for the calibration curve. The amount of Vit C, Pb(II) and Fe(II) were calculated from the measured peak currents and using the equation of the calibration curve. The equation of the calibration curve for Vit C was y=4.2599x-4.9876 and for Pb(II) was y =20.6183x+1.5794 and for Fe(II) was y = 23.0465x-3.9386 where y is the current in nA and x is the concentration in µg/ml

Analytical Method Validation[6-7]

System Suitability

System suitability tests were carried out to ensure reproducibility of the instrument. The system suitability test was carried out by recording polarogram for Vit C, Pb (II) and Fe (II) at one concentration (15.3846µg/ml for Vit C, and 7.6923µg/ml for Pb(II) and Fe(II)) with five replicates and the mean current was used for the calculation. The % RSD in all the cases was found to be less than 2%.

Specificity

The specificity of method was confirmed by comparing the polarograms of the standard solutions containing Vit C, Pb(II) and Fe(II) with the sample solution. The peak potentials recorded for the sample solution were found to be identical to those obtained for the combined standard solution of Vit C, Pb(II) and Fe(II). The addition of the standard solutions of Vit C, Pb(II) and Fe(II) to the sample solution did not change the characteristics of differential pulse polarogram but enhanced the peak current. This confirms the specificity of the method.

Robustness

The robustness of the method was examined by observing the consistency of the peak height and the peak shape with the deliberately made small changes in the experimental parameters. It is a measure of the capacity of the method to remain unaffected by small, but deliberate variations in method parameters and provides an indication of its reliability during normal usage. To determine the robustness of the proposed method, the following variations were made in the analytical parameters. The Scan rate was changed by ± 0.5 $mVs^{-1}$and the Pulse amplitude ± 1.0 mV These parameters were deliberately changed one at a time and the effect of these changes on the peak shape and peak currents were studied. The proposed method was found to be robust.

Linearity and Dynamic range

The linearity for Vit C, Pb(II) and Fe(II) in a solution containing the three was determined. In the concentration range 3.773µg/mL to 21.62 µg/mL for Vit C, 1.887µg/mLto11.688µg/mL for Pb(II) and ,1.887µg/mLto11.688µg/mL for Fe(II) a good linearity was obtained. The equation of the calibration curves is presented in **(Table1).**

Limit of Detection and Limit of Quantitation

The limit of detection (LOD) and the limit of quantification (LOQ) for Vit C, Pb(II) and Fe(II) were fixed at signal to noise ratio of 3:1 and 10:1

respectively. Twenty replicates of the blank solution were recorded and the mean current value at the peak potential of Vit C (i.e. at +0.137V) and Pb(II) (i.e. at -0.345 V) and Fe(II) (i.e. at -1.238V) were calculated. The concentration at which the peak current was found three times of mean blank current was taken as the limit of detection and the concentration at which peak current was found to be ten times the mean blank current was selected as the limit of quantification. The LOD and LOQ of Vit C, Pb(II) and Fe(II) were 3.7735µg/mL and 7.143µg/mL, 0.971µg/mL and 1.887µg/mL and1.887µg/mL and 3.571µg/mL respectively.

Intra-day and Inter-day Precision

The variability of the method was tested with the intra-day and inter-day precision. It was checked by recording the polarograms of standard solutions of Vit C, Pb(II) and Fe(II) in the concentration ranges 7.143µg/mL to 19.718µg/mL for Vit C and 3.571µg/mL to 9.859µg/mL for Pb(II) and Fe(II). Intra-day precision was tested by recording the polarograms at an interval of four hours and inter-day precision twice a day with a gap of three days. The mean % RSD for intra-day and inter-day precision for Vit C was found to be 0.57% and 0.73% and for Pb(II) 0.46% and 1.01% and for Fe(II) 0.52% and 0.91% respectively.

Quantitation / Determination

The validated method was used for the determination of Vit C, Pb(II) and Fe(II). Polarograms were recorded under the optimum experimental conditions for the sample solution. Resulting peak currents for Vit C, Pb(II) and Fe(II) were measured and the amount of Vit C, Pb(II) and Fe(II) was calculated using calibration curve equations. The results are presented in (Table 2).

Accuracy (Recovery)

The recovery technique was used to evaluate the accuracy of the method. The method of standard addition was employed for the purpose. A fixed volume of the standard Vit C, Pb(II) and Fe(II) solution was added to the sample solutions and the mixed solutions so obtained were analyzed by the proposed method. The percentage recovery was determined at different percentage levels i.e. the added amounts ranging from 20% to 75% of the amount present in the sample. The results of the recovery analysis for Vit C, Pb(II) and Fe(II) are presented in (Table 3).

Table 1: METHOD VALIDATION PARAMETERS FOR ASCORBIC ACID, LEAD (II) AND IRON (II)

Parameters	Values		
	Ascorbic acid	**Pb(II)**	**Fe(II)**
System suitability (n=5) %RSD	0.49%	0.71%	0.456%
Linearity range (µg/ml)	7.143to19.718µg/ml	3.571 to 9.859µg/ml	3.571 to 9.859µg/ml
Slope (m) a)	4.2599	20.6183	23.0465
Intercept(c) a)	-4.9876	1.5794	-3.9386
Correlation coefficient (R^2)	0.9992	0.9998	0.9992
LOD (µg/ml)	3.7735 µg/ml	0.971 µg/ml	1.887 µg/ml
LOQ (µg/ml)	7.143 µg/ml	1.887 µg/ml	3.571 µg/ml
Intraday precision (n=5)	0.57%	0.46%	0.52%
Interday precision (n=5)	0.73%	1.01 %	0.91%
Recovery	98% to 102%	98% to 102%	98% to 102%

a) Of the equation y = mx + c, where y is peak current, m is the slope, x is the concentration and c is the intercept

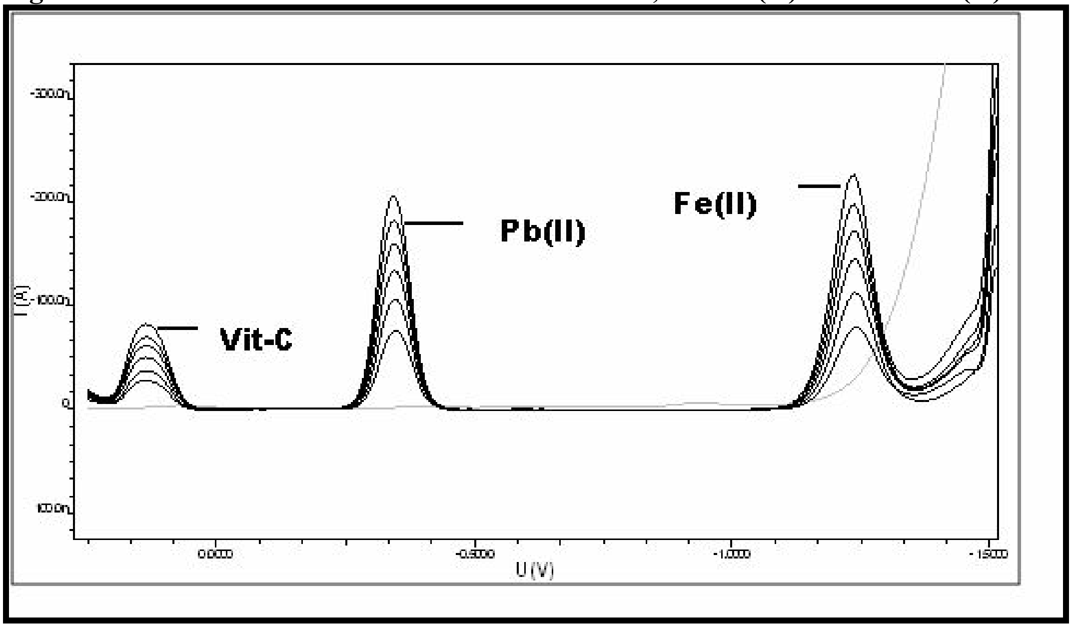
Table 2: RESULTS OF QUANTITATION STUDIES FOR ASCORBIC ACID, LEAD (II) AND IRON (II)

	Ascorbic acid	**Pb (II)**	**Fe (II)**
Conc in µg/ml	916.41	434.54	687.41
% RSD (n=5)	1.14	1.25	0.90

Table 3: RESULTS OF RECOVERY STUDIES FOR ASCORBIC ACID, LEAD (II) AND IRON (II)

Standard	Level	Conc. of std [µg/ml]	Conc. of std Found [µg/ml]	RSD (%) (n = 3)	Recovery (%)
Ascorbic acid	30%	2.82	2.79	0.9	98.94%
	50 %	4.57	4.53	1.17	99.12%
	70%	6.22	6.31	1.03	101.45%
				Mean	99.84%
Lead (II)	35 %	1.41	1.40	1.09	99.29%
	55%	2.28	2.30	1.1	100.87%
	75%	3.11	3.17	0.79	101.92%
				Mean	100.69%
Iron (II)	20%	1.41	1.42	1.08	100.71%
	35%	2.28	2.25	1.33	98.68%
	50%	3.11	3.05	0.83	98.07%
				Mean	99.15%

Figure-1. POLAROGRAMS OF ASCORBIC ACID, LEAD (II) AND IRON (II)

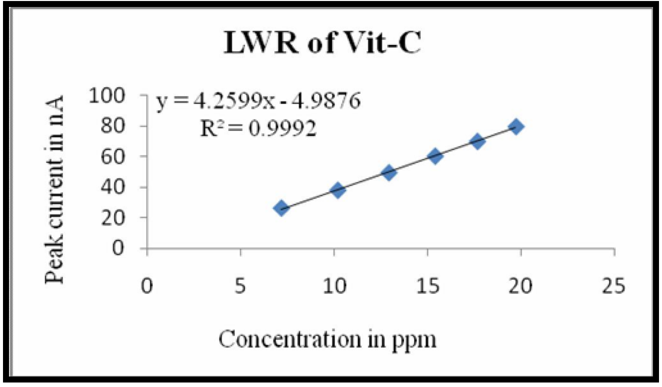


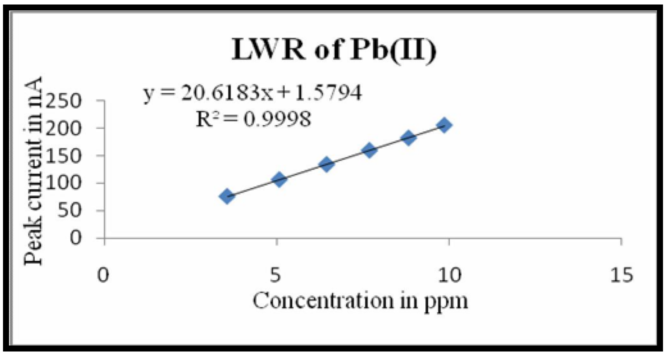
Results and Discussion

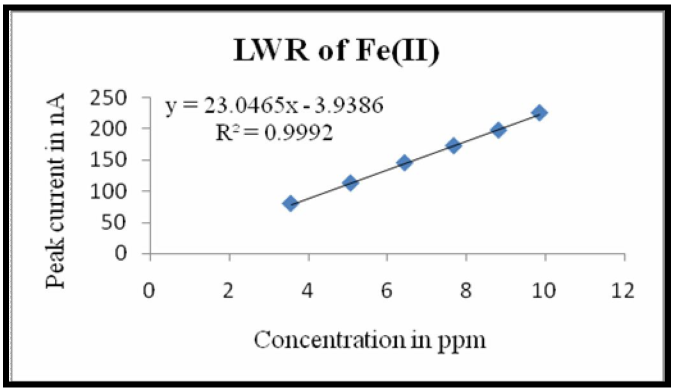
The present study provides determination of Vit C, Pb(II) and Fe(II) from the industrial effluents using the technique of differential pulse polarography. The method was validated as per the ICH guidelines (Table 1-3). Before validation, optimization of the conditions i.e. pH, supporting electrolyte, scan rate and pulse amplitude were optimized. The polarographic response of the sample for Vit C, Pb(II) and Fe(II) in different supporting electrolytes has been studied. With KCl as the supporting electrolyte the sample showed only one broad peak for Vit C and Fe(II). However, separate peaks were produced with Sodium acetate buffer pH 4.5 as the supporting electrolyte.

Pulse amplitude of 60mV was chosen as the optimum as there is loss of resolution at high pulse amplitude and with low pulse amplitude the current obtained was low. The Differential Pulse Polarogram of Vit C, Pb(II) and Fe(II) were recorded at various scan rates. At scan rates higher than 15mVs^{-1} the width of peak increases, its height decreases and peak shape was distorted. At lower scan rates than 15mVs^{-1} peak current was lower. So a scan rate of 15mVs^{-1} was chosen as a best for the analysis.

Figure-2. LINEARITY GRAPHES FOR ASCORBIC ACID, LEAD (II) AND IRON (II)







LWR: Linear working range
ppm: µg/ml

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