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Spectrophotometric Detector Coupling with Flow Injection Analysis unit Using Dithizone Merging Zone Technique for Determination Cadmium (ll)

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Abstract

A simple method using flow injection has been developed for the determination of Cadmium ion (II)), based on the reaction the Cd(II) ion with the Dithizone as reagent in acid medium . A standard or sample solution was injected into the Cadmium(II) stream (flow rate 4.2 ml /min) which was then merged with Dithizone in dilute acid. Under the optimum conditions, a linear calibration graph was obtained over the range of 1-10 µg /ml and the detection limit was 0.0188 µg /ml (s/n = 3). The relative standard deviation of the proposed method calculated from 10 replicate injections of 10 µg /ml Cadmium (II) was 0.160%. The sample throughput was 60 h^{-1}. The method was successfully applied to the determination of cadmium(II) in different samples.

Keywords: Flow injection analysis (FIA) system, Cadmium(II) ion , Dithazone

INTRODUCTION

The injection technique was discovered in 1975 (Ruzicka and Hansen) in Denmark [1] and Stewart and his colleagues in America. [2] This technique is the first generation of FI injection technique, which is characterized by simple, fast, The use of very small amounts of reagent and high symmetry in the process of analysis in an automatic or semi-automatic [3] and high efficiency and speed and distinct and sensitive to chemical analysis [4].

This technology is characterized by the consumption of small quantities of micro-materials and that the optional or selective valve replaces the injection valve, which is a means of selecting models and streams of different flow as well as the flow pipes branching are simple [5], each of these features made SIA technology flexible and easy to adapt to the chemical systems to work [6,7].

Cadmium (Cd) is a silvery white, soft, ductile chemical metal with atomic number 48 and belonging to the group 12 element in d block and period 5. It was discovered by German chemist F.Strohmeyer in 1817 as a constituent of smithsonite ($ZnCO_3$) from zinc ore. Electronic configuration of the cadmium is [Kr] $4d^{10}$ $5S^2$. Cadmium concentration in the earth crust is 0.15ppm and the most common cadmium mineral is greenockite (CdS) [8,9]. Cadmium dissolves in acids and does not dissolve in alkali. Coated cadmium produces toxic yellow fumes[10]. Cadmium can cause serious health problems such as kidney failure and high blood pressure. Cadmium is obtained as a by-product of zinc purification. Cadmium is used in the electroplating of a number of other metals and in the battery industry as it is in the manufacture of nuclear reactors because of its high absorption of neutrons[12]. There are many techniques for determination cadmium ion in differences samples, Stripping Voltammetry Technique was used for determining Cd(II) in tap water[13] and flame atomic absorption spectrometry was used to determine Cadmium in samples of cigarettes ,sediments and food using, dependon the preconcentration system which based on the sorption of cadmium in a minicolumn packed with Amberlite XAD-2 resin functionalized with 3,4-dihydroxybenzoic acid (DHB)[14]. The technique Solid Phase Extraction was used to Preconcentrate Trace Cadmium Using Chemically Modified Nano-Carbon Black with 3- Mercaptopropyltrimethoxysilane [15],and using FAAS determination of Pb and Cd ions in Contaminated Water after Preconcentration by Dithizone-Modified Cellulose Acetate Polymeric Membranes[16]. the preparation and electrochemical application of a chromium(III) oxide modified carbon paste electrode (Cr-CPE) and a screen printed electrode (SPE) was used to determine of Zinc, Cadmium, Lead, Copper and Silver [17]. Determination of Cadmium in Brown Rice Samples by Fluorescence Spectroscopy Using a Fluoroionophore after Purification of Cadmium by Anion Exchange Resin[18].The aim of this paper was to propose an alternative FIA method for spectrophotometric determination of Cd(II). The method is based on Cd-dithizone complex formation in acid medium. As this analytical method was applied in different samples.

STANDARD SOLUTIONS

Cadmium(II). A standard 1000 µg / ml solution of Cadmium(II) was prepared by dissolving 0.2036 g of of cadmium chloride $CdCl_2.2.5H_2O$ in a 100 ml volumetric flask and diluting to the mark with water. Working solutions were prepared by appropriate dilution of the standard solution.

Dithizone solution. As stock 0.01% solution of Dithizone solution was prepared by dissolving 0.01g of the reagent (Merck) in 25 ml ethanol and made up to 100 ml with ethanol, and stored in an amber bottle.

Buffer solution. A buffer solution papered by mix of 14.75 ml of sodium acetate (CH_3COONa) with a concentration of 0.1N and 35.25 ml of acetic acid (CH_3COOH) was observed at a concentration of 0.1 N .

SDS solution. 0.01% solution was prepared by dissolving0.01g of SDS in 100 ml. water

Trtionx-100 solution 0.01 %. The solution was prepared by dissolved 0.01ml of Trtionx-100 in 100 ml water.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of Cd(II)- Dithizone complex was recorded against the reagent blank. Similarly the absorption spectrum of the reagent Dithizone was recorded against solvent blank. The absorption spectra of both the complexe and reagent were shown in Figure 1. From the absorption spectra it is clear that the Cd(II)- Dithizone wavelength of maximum absorbance measurements was made at 543 nm .

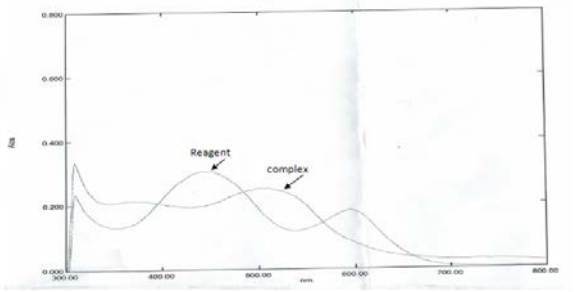

Figure 1. Absorption spectra for the dithizone and Cd(II) – dithizone complex in acid medium .

FIA instrumental

The scheme of manifold of the Flow injection system used is shown in Figure 2. The system consists of a peristaltic pump, reaction coil, and new homemade injection valve its contains two loops in order to loading the Cd(II) solution in buffer solution and Dithizone solution , all these parts combine with integrated flow cell and a A UV–Vis spectrophotometer was used to measure absorbance or peak height of the formed product at 543 nm .

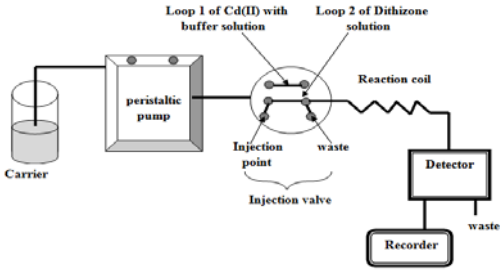

Figure 2. New manifold of the FIA system in the proposed method for the determination of Cd(II)ion

Optimization of flow system

1- Effect of flow rate

The effect of the flow-rate on the peak height was studied in the range of 1.3 - 6.000 ml /min. It was observed that there is an increase in sensitivity with an increase in the flow rate up to 4.2 ml/min and then a decrease for higher flow rates. Thus, a flow rate of 4.2 ml /min was selected due to highest sensitivity and precision and used for subsequent measurements , Figure 3 shown the results. Experiment under the following optimal conditions: Concentration of Cd (II) = 10 µg/ml, length of reaction coil = 20 cm, concentration of Dithizone = 0.01% , Cd (II) ion volume = Dithizone volume =157 µl, pH=4.

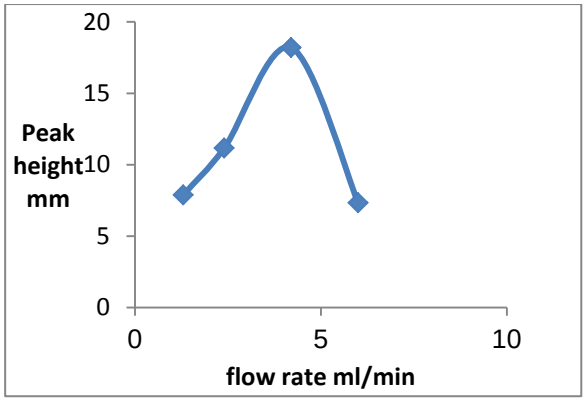

Figure 3: Change of peak height with the flow rate in FIA unit

2-Effect of the reaction coil length

In order to study the effect of the length of the reaction coil at the height of the peak reaction coil lengths of 10-30 cm were tested as Figure 4 . The peaks became higher as the length of coil increased from 10-20cm , but a further increase did not increase peak height and caused peak decreased. The reaction coil length of 20 cm was chosen for further work. The experiment was conducted under the following conditions:

Concentration of Cd (II) = 10 µg/ml, length of reaction coil = 20 cm, concentration of Dithizone = 0.01%, Cd (II) ion volume = Dithizone volume =157 µl, flow rate = 4.2 ml /min , pH=4

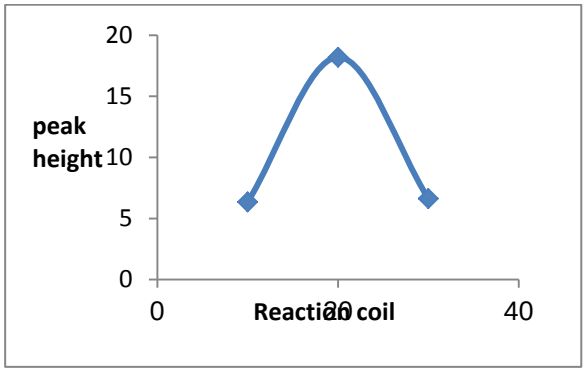

Figure 4:Change of peak height with the reaction coil length in FIA unit

3-Effect of Cd(II) ion volume

The influence of the sample volume on the peak height was investigated by injecting different volumes 78.50-235.50 µl of Cd(II) .The injection volume has a significant effect, yielding increased peak height and reproducibility with increasing of the injection volume 78.50-235.50 µl ,so that 157 µl was chosen for further work as Figure 5. The experiment was conducted under the following conditions: Concentration of Cd (II) = 10 µg/ml, length of reaction coil = 20 cm, concentration of Dithizone = 0.01%, Dithizone volume =157 µl , flow rate = 4.2 ml /min.,pH=4.

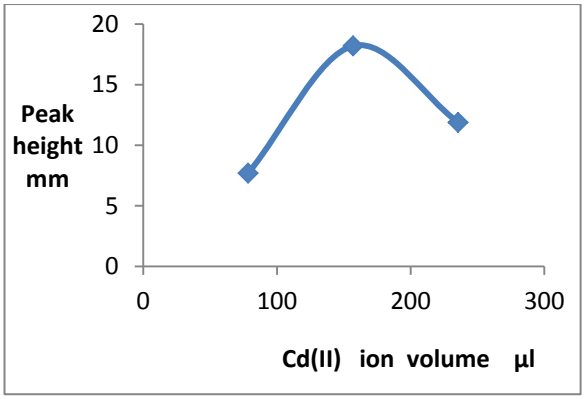

Figure 5:Change of peak height with the sample volume in FIA unit

4-Effect of the reagent volume

The effect of Dithizone volume on the sensitivity was examined by varying it from 78.5 to 235.5 µl by change the loop of the Dithizone length . The absorbance increased sharply with increasing volumes from 78.5 to 157µl, a sample volume of 157µl was employed in this study the result given in Figure 6.The optimized values of the FIA manifold parameters are Concentration of Cd (II) = 10 µg/ml, length of reaction coil = 20 cm, concentration of Dithizone = 0.01%, Cd(II) ion volume =157 µl , flow rate = 4.2 ml /min., pH=4.

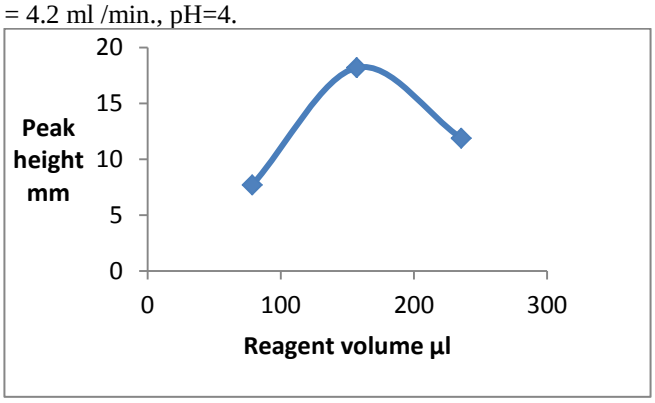

Figure 6:Change of peak height with the Dithizone volume in FIA unit.

5-Effect of pH medium

The effect of pH on the peak height of Cd(II) at different pH value of Cd(II) ion in the solution was changed over 4.0-6.0 pH as Figure 7, and the peak heights were measured for each pH level of Cd(II) solution . At all pH levels of Cd(II), maximum peak heights were found at pH 5. Therefore, a pH 5 for the acetate buffer system was chosen throughout the study. This buffer solution papered by mix of 14.75 ml of sodium acetate (CH_3COONa) with a concentration of 0.1N and 35.25 ml of acetic acid (CH_3COOH) was observed at a concentration of 0.1 N . The optimized values of the FIA manifold parameters are Concentration of Cd (II) = 10 µg/ml, length of reaction coil = 20 cm, concentration of Dithizone = 0.01%, Cd(II) ion volume =, Dithizone volume =157µl , flow rate = 4.2 ml /min.

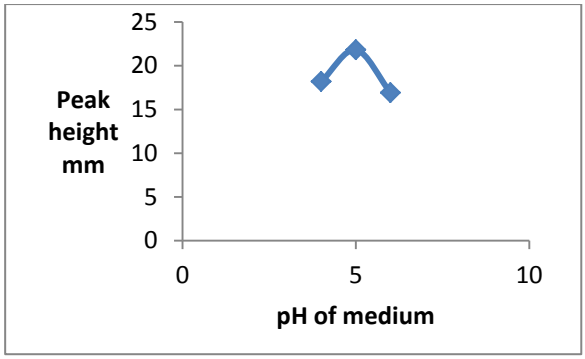

Figure 7:Change of peak height with pH of Cd(II) ion solution in FIA unit.

6-Effect of Dithizone concentration

Effect of Dithizone solution on peak height was studied at different concentrations from 0.005-0.03 %, Figure 8 shows that ,the concentration effect on the peak height of Cd(II) ion was obtained with 0.01% . So 0.01% was chosen for the further work. The optimized values of the FIA manifold parameters are Concentration of Cd (II) = 10 µg/ml, length of reaction coil = 20 cm, concentration of Dithizone = 0.01%, Dithizone volume = Cd(II) ion volume =157µl , flow rate = 4.2 ml /min., pH= 5.

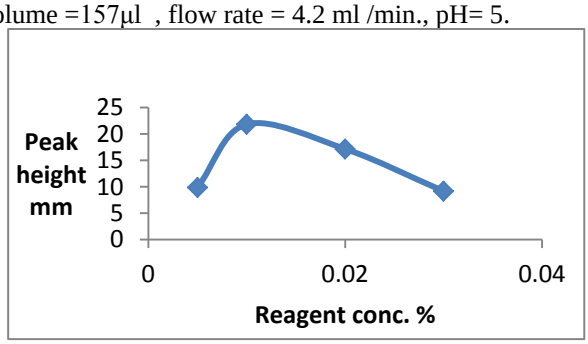

Figure 8:Change of peak height with reagent concentration in FIA unit.

Linearity and Calibration graph

The linearity of the proposed method was investigated by recording the detector responses in the range 1-10 µg/ml . Typical peaks obtained with Cd(II) concentration are illustrated in Figure. 9 and Table 11.The equation of the line (y = 1.952x + 1.320) was used for the determination of Cd(II). correlation coefficient R^2 = 0.985) . Using a signal of three times the noise ratio, as the limiting requirement, the experimental detection limit was found to be 0.0188 µg /ml.

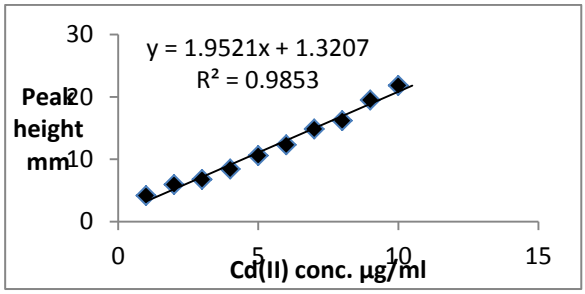

Figure 9 : Calibration graph of Cd(II) ion at optimum conditions and λmax = 543nm using homemade FIA unit.

Table11: Effect of the concentration of Cd(II) ion on the peak height

Cd(II) conc. µg/ml	Peak height (mm)			Peak height mean mm	SD	RSD%
1	4.14	4.14	4.19	4.16	0.032	0.769
2	6.33	6.02	5.51	5.95	0.149	2.665
3	6.78	6.77	6.72	6.76	0.032	0.473
4	8.72	8.58	8.00	8.43	0.381	4.519
5	10.71	10.70	10.37	10.59	0.193	1.822
6	12.03	12.22	12.64	12.30	0.312	2.536
7	14.76	14.82	14.97	14.85	0.108	0.727
8	16.21	16.21	16.15	16.19	0.045	0.278
9	19.48	19.52	19.50	19.50	0.020	0.103
10	21.83	21.84	21.84	21.84	0.007	0.032

Table2: Repeatability for 10 µg/ml of the Cd(II) ion using FIA unit .

No.	1	2	3	4	5	6	7	8	9	10	Mean	S.D	RSD%
Peak height mm	21.83	21.80	21.83	21.83	21.84	21.82	21.81	21.80	21.84	21.80	21.82	0.035	0.160

Table3: Determination of Cd(II) ion in differences samples using FIA unit .

Sample	taken value µg/ml	found value µg/ml	Recovery%
Fish sardines , Iraq	5.266	4.25	95.54%
Fava Beans, Foul Medammes, Iraq	5.182	4.81	95.74%
Fish Tuna ,Iraq	5.30	4.46	95.54%
Fish Nawras, Syria	5.183	4.49	99.86%
Corn, Syria	5.164	4.316	95.67%

Repeatability

This study was conducted to find out the extent of the results and the efficiency of the system at concentration of Cd(II) ion 10 µg/ml ,the results shown that , the designed system is highly tuned and efficient ,as in Table 2.

Effect of interfering ions

The effects of interferences ions such as some actions (Cd^{2+}, Ca^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}) and anions (Cl^-, SO_4^{2-}, $CH3COO^-$, CO_3^{2-}, F^-) in determination of Cd (II) ion it was 5 and 50 µg/ml for each ions in the determination of Cd(II) ion by the proposed system

were studied., the results indicate the general freedom from interferences.

Applications

The Cadmium contents of differences samples were analyzed by the proposed method, and the results are summarized in Table 3. In all cases, the results were compared with the atomic absorption measurements and the of the proposed method and using standard method Therefore, the results was indicating that the developed method is as accurate and precise.

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