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SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM IN VARIOUS SAMPLES USING SALYCILIDIN-0-AMINOPHENOL (SAPH)

Annotation: *A simple, rapid and sensitive spectrophotometric method was developed for the determination of Cd (II) using Hydroxy)]-2-hydroxy-phenyl (methylin) amino benzene (SAPH) The name is common salycilidin-0- aminophenol (SAPH) as an analytical reagent. The metal ion in aqueous and methanol medium forms yellow colored complex with SAPH showing maximum absorbance at 434 nm. Since SAPH method is more sensitive, it was applied for the determination of cadmium in samples.*

Keywords: *Cadmium determination, spectrophotometry, react.*

Аннотация: *Простой, быстрый и чувствительный спектрофотометрический метод был разработан для определения Cd (II) с использованием гидрокси)] - 2-гидроксифенил (метилин) аминобензола (SAPH). В качестве обычного салицилидин-0-аминофенола (SAPH) аналитический реагент. Ион металла в водной и метанольной среде образует комплекс желтого цвета с SAPH, показывающим максимальную абсорбцию при 434 нм. Поскольку метод SAPH является более чувствительным, он был применен для определения кадмия в образцах.*

Ключевые слова: *Определение кадмия, спектрофотометрии, реагировать.*

1. Introduction:

Spectrophotometric methods is one of the most important ways, which is used in analytical chemistry, because it wide used in researches field, and has sensitivity, accuracy, simplify and low cost, The diversity UV-Vis. analysis (direct, extraction, kinetic…etc) by using organic reagents make it possible to determine a lot of elements in many analytical samples.

Cadmium in trace amounts is important industrially [1,c.1563], as a toxicant [2,c. 428] and biological nonessential [3,c.22], as an environmental pollutant [3,c.22] , The accurate determination of cadmium in agroindustrial, environmental, biological, soil and food samples is of importance because of the toxicity of this heavy metal and related compounds which are extremely toxic and responsible for a number of deaths [5,c.548], .Symptoms of cadmium poisoning include instantaneous hypertension, shortening of life-span, kidney damage, bronchitis, retardation of growth, gross abnormalities of the vital organs, alopecia(loss of hair), diabetes, diarrhea, nausea, liver injury, anemia, renal cancer in human and the risk of prostatic cancer [5,c.548]. All these findings cause great concern regarding public health, demanding accurate determination of this metal ion at trace and ultra trace levels. Many sensitive techniques such as X-ray fluorescence [6,c.266], Neutron Activation Analysis (NAA) [7,c.193], Grafite furnace atomic absorption spectroscopy (GF-AAS) [8,c.7], Inductively coupled plasma-mass spectrometry (ICP-MS) [9,c.85], Inductively coupled plasma-optical emission spectroscopy (ICP-OES) [10,c.276], High Performance Liquid Chromatography (HPLC), Spectrofluorimetry [11,c.89] and Pulse polarography [12,c.9] have been widely applied to the determination of cadmium. These methods are disadvantageous in terms of cost and the instruments used in routine analysis.

In the present study, we are reporting rapid, simple, sensitive and selective methods for the determination of traces of cadmium (II) with SAPH, anew reagent.

This paper describes synthesis, characterization and analytical properties of new reagent (SAPH). Since the reagent is more sensitive, it is used for the determination of cadmium in various samples.

2. EXPERIMENTAL:

2.1. Apparatus

A Jasco V–530 UV–VIS spectrophotometer (Japan) with 1 cm quartz cells was used for all absorbance measurements under the following operating conditions: scan speed medium (400 nm/min), scan range 200–1100 nm and slit width 2 nm. Spectra were automatically obtained by Jasco system software. pH measurements were made with ORION 250A (USA) with combined glass pH electrode.

the results of the suggested method were coincidental with the analysis data of the same samples with the -Atomic Absorption technique as a comparative method.

2.2. Reagents and materials

All chemicals used were of analytical-reagent grade of the highest purity available procured from Merck. Doubly distilled de-ionized water was used throughout the experiment.

2.3. SAPH solution

A 1×10^{-2}M solution was prepared by dissolving 0.213 g of SAPH in 100 ml of water. And methanol, The reagent solution is stable for at least 48 h. (Figure 1). Structure of salycilidin-0- aminophenol (SAPH).

2.4. Cadmium standard solution

A 100 mL amount of stock solution (1 mg mL^{-1}) of cadmium was prepared by dissolving 228.2 mg of purified-grade (Merck, proanalysis grade) hydrated cadmium sulfate $3CdSO_4.8H_2O$ in doubly distilled water. More dilute standard solutions were prepared by appropriate dilution of aliquots from the stock solution with deionized water as and when required.

2.5. Procedure for Preparation of water samples

Different water samples were collected from various places. The samples (150 ml) were stored at 5oC in metal free polyethylene bottles. Water samples were filtered through whatman filter paper no. 41 and collected into 250 ml beakers. All the filtered environmental water samples were evaporated nearly to dryness with a mixture of 10 ml con HNO_3 and 5ml of con H_2SO_4 and then cooled to room temperature. The sample was digested in the presence of an excess potassium permanganate solution. The residues were then heated with 10 ml of deionized water in order to dissolve the salts. The solutions were cooled and neutralized with dilute NH_4OH. The digest was transferred into a 25 ml calibrated flask and diluted up to the mark with deionized water.

2.6. Preparation of the calibration graph

An aliquot of the stock solution containing 0.1-10 µg/mL of cadmium (II) was transferred into a 25 mL volumetric flask. Buffer solution (5mL) and SAPH (2.5 mL of 10^{-3} mM) were added. The solution was diluted up to the mark with distilled water and mixed well. The absorbance of the solution was measured after about 30 minutes at 434 nm against a reagent blank. The amount of cadmium in the sample solution was then deduced from the calibration graph.

3. RESULTS AND DISCUSSION

Cadmium reacts with (SAPH) in buffer solution and gives yellow colored complex. The complex has a maximum absorbance at 434 nm. The optimum reaction conditions for the quantitative determination of the metal-ligand complex was established through a number of preliminary studies, such as the effect of acidic medium, reagent concentration, interference of foreign ions, in order to develop a rapid, selective and sensitive spectrophotometric method for the determination of cadmium (II) at microgram levels.

3.1. Absorption spectra of the reagent and Cd (II)-SAPH complex

Absorption spectra of Cd (II)-SAPH complex and reagent show maximum absorbance at 434 nm and 325,252 nm, respectively (Figure 2). The reagent showed

minimum absorbance at the wavelength of maximum absorbance of the complex. Hence, all the spectral measurements of the complex were therefore carried out at 434 nm.

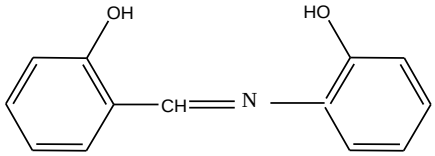

Figure 1.,Structure of salycilidin-0- aminophenol (SAPH)

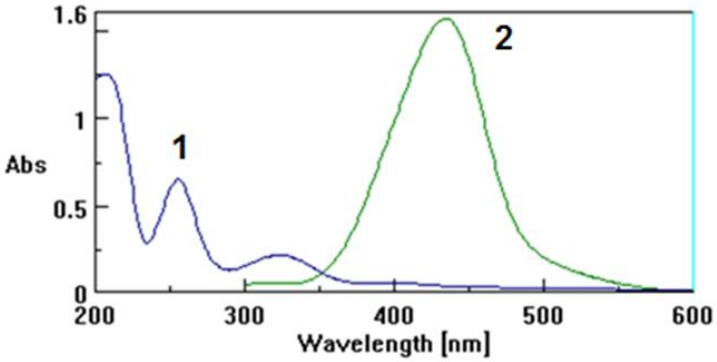

Figure 2., (1) Absorption spectra of reagent

(2) Absorption spectra of Cd-SAPH complex

3.2. Optimization of reaction conditions

The spectrophotometric properties of the colored product as well as the different experimental parameters affecting the color development and its stability were studied and optimized by changing each variable in turn, while keeping all others constants. In all experiments.

3.2.1 Effect of.. pH

The effect of pH on the peak height of Cadmium(II) at different concentrations was investigated with a fixed reagent concentration in the pH range of 3.0 – 10 and the peak height was measured for each concentration level of Cadmium(II) At all concentration levels of Cadmium(II) maximum peak heights were found pH 9.0 Therefore, a pH 9.0 was selected for further studies.achieved. Therefore, 5 ml of borates buffer was used for the better results (Figure 3).

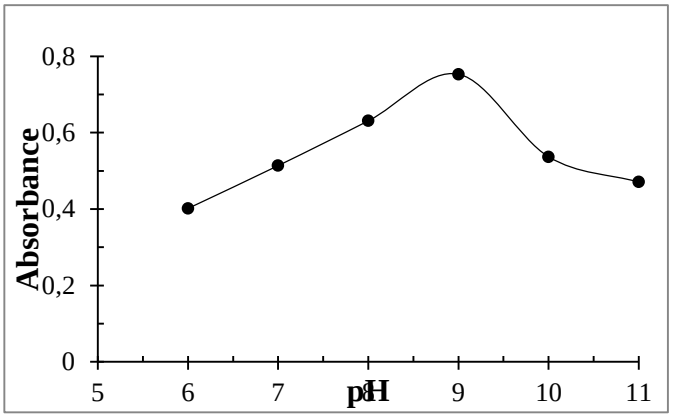

Figure 3.,the varing pH effect on the absorbance of the formed complex Cd(II)-SAPH

3.2.2 Effect of Solvent

Because SAPH is insoluble in water, an organic solvent was used for the system. Of the various solvents (benzene, chloroform, acetone, carbon tetrachloride, nitrobenzene, ethanol and 1, 4-dioxane) studied, ethanol was found to be the best solvent for the system. No absorbance was observed in the organic phase. In 50% (v/v) ethanolic medium, maximum absorbance was observed a 50% ethanolic solution was used in the determination procedure.

3.2.3 Effect of reagent concentration

Different volume of molar excess of SAPH was added to fixed Cd(II)concentration and the a**b**sorbance's were measured adopting the standard procedure. It was observed that 100 fold molar excess of reagent with respect to metal ion is necessary to get maximum absorbance. Hence, a 100 fold molar excess of reagent was used for further experimental studies. The absorbance of the solution was measured at different time intervals to ascertain the time stability of the color complex.

3.2.4 Time, Temperature and Color Stability

Under the optimized conditions, although the color developed instantaneously, 30 min were allowed to obtain the maximum and constant absorbance in the method. The yellow colored product was stable for one week. The absorbance varied by not more than 1% over a period of two days for the method and color development was independent of temperature in the range of 25 ^{o}C – 45 ^{o}C.

3.3. Analytical method validation

3.3.1. Calibration, graph reproducibility and detection limit

Using the optimized composition and conditions described above. The effect of the Cd concentration was studied over 1.00-10.0 µg/mL for convenience of the measurement. The calibration curves gave an excellent linear for (0.2-6.0µg/mL), as shown in (Figure 4) at 434nm, The molar absorption coefficient and the Shandell's sensitivity were found to be 0.5 x 10^4 L mol^{-1} cm^{-1} and 0.031 µg cm^{-2} of Cd respectively. The selected analytical parameters obtained are summarized in Table 1.

3.3.2. Precision and accuracy

The precision and accuracy of the method was studied by analyzing solutions containing known amounts of Cd(II)within the Beer's law limit. Percentage relative standard deviation (RSD %) as precision and percentage recovery as accuracy of the suggested method

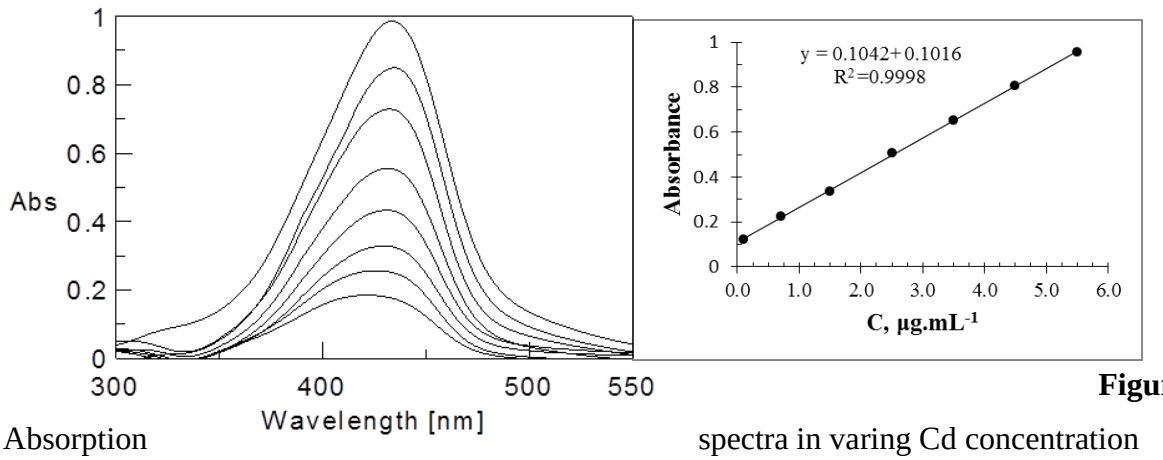

Figure (4). - Absorption spectra in varing Cd concentration

The linear range between absorbance formed complex and Cd concentration

Table.1. Analytical characteristics of method

Parameters	
Wavelength / λ_{max} (nm), complex	434
Wavelength / λ_{max} (nm), reagent	325,252
Solvent	Water + methanol
pH	9
Time / min	30
Temperature /^{o}C	25±40^{o}C
Mole of reagent required mole of metal ion for full color developed	100 Fold
Composition of complex as obtained in Job's and molar ratio methods (M:L)	2 : 1
Molar absorption Coefficient/ L mol $^{-1}$cm^{-}	0.5×10^{4}
Linear range/µg mL^{-1}	0.2-6.0
Detection limit /µg mL^{-1}	0.05
Sandell's Sensitivity /µgcm^{-2}	0.031
Relative Standard Deviation	0.27--3.78
Regression Co-efficient	0.9998
Slope	0.1042

were calculated and showed in Table 2. The values of relative standard deviations for different concentrations of Cd determined from the calibration curves. These results of accuracy and precision show that the proposed method have good repeatability and reproducibility. The lower values of relative standard deviation (%) and percentages of error indicated the high accuracy of the method.

Table 2. Accuracy and precision for the determination of Se in pure soluation

[Cd^{+2}], µg/mL			RSD %	Recovery %
Taken	Found[a]	SD		
0.40	0.395	0.0153	3.78	98.75
0.60	0.591	0.0140	2.36	98.50
2.00	1.983	0.0112	1.24	99.15
4.00	4.021	0.0110	0.273	100.25

[a]Five independent analyses**.**

3.3.3. Effect of diverse ions

The extent of interference by diverse ions was determined by measuring the absorbance of solutions containing 5 μg/mL of Cd(II)and various amounts of diverse ions. The criterion for an interference was an absorbance value varying by more than ±2% from the expected value of cadmium (II) alone. The results presented in Table 3 show that a large excess of cations and anions which are usually associated in the determination of Cd (II), do not interfere.

Table 3. Tolerance limits of diverse ions in the determination of 5 μg/mL of cadmium (II).

Ion Added	Tolerance limit μg/mL	Ion Added	Tolerance limit μg/mL
Fe(II)	125	Co (II)	65
Fe(III)	75	Ag (I)	225
Hg(II)	160	V (V)	310
Ni(II)	300	Tartrate	485
Zn(II)	420	Iodate	302
Mn(II)	285	Urea	288
Cr(III)	300	Citrate	386
Ca(II)	400	Bicarbonate	423
Ba(II)	380	Sulphate	368
Cu(II)	600	Oxalate	257
NI(II)	740	Nitrate	320
Pb (II)	8.3	Acetate	189

3.3.4. Composition and stability constant of the complex

Job's method of continuous variation and molar-ration methods were applied to ascertain the stoichiometric composition of the complex. It was found that SAPH forms 2:1 complex with Cd(II)as shown in the (Fig.5).

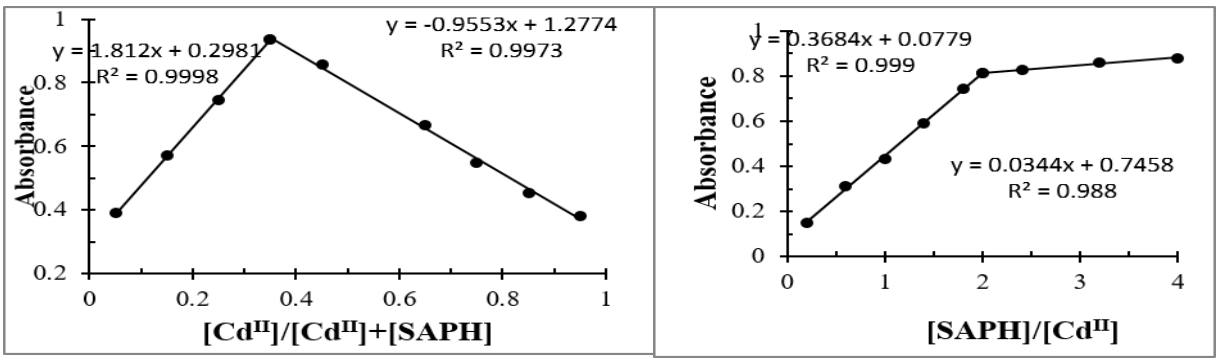

Figure.5. continuous variation and molar-ration methods

3.3.5. Application

The proposed spectrophotometric method is applied for the determination of Cd(II)in in various samples. A known aliquot of the above sample solutions were taken and the cadmium content was determined as described is given in the general procedure, and the results of the suggested method were coincidental with the analysis data of the same samples with the Atomic Absorption technique as a comparative method. Table (4).

Table 4. Determination of cadmium in some environmental water samples

n = 5 , α = 0.95

Samples	[Cd], μg/mL	SD, μg/mL	RSD%
Tap water	0.298	0.01	3.35
Well water	0.912	0.013	1.42
Waste water	6.32	0.011	0.17

4. CONCLUSION

The author has introduced a new sensitive reagent SAPH for the direct spectrophotometric determination of trace amounts of Cd (II). The proposed spectrophotometric method is simple, highly sensitive and selective for the determination of Cd(II)in water. when compared with other spectrophotometric methods. The proposed method is simple, rapid and common metal ions such as Fe^{3+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+},Mn^{2+}, Cr^{3+} do not interfere. It also offers advantages like reliability and reproducibility in addition to its simplicity instant color development and less interference effect. The method has been successfully applied for the determination of cadmium in various samples.

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