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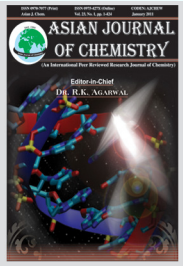

Bis-[2,6-(2'-Hydroxy-4'-Sulpho-1'-Naphthylazo)]pyridine Disodium Salt as a Spectrophotometric Reagent for the Determination of Cadmium in Tobacco and Tobacco Products

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Bis-[2,6-(2'-hydroxy-4'-sulpho-1'-naphthylazo)]pyridine disodium salt (HSNP), a water soluble heterocyclic azo dye has been used for the trace determination of cadmium. *Bis*-[2,6-(2'-hydroxy-4'-sulpho-1'-naphthylazo)]pyridine disodium salt complexes with cadmium(II) to form a purple coloured, water soluble 1:1 complex with molar extinction coefficient (ε) 4.9×10^4 L mol^{-1} cm^{-1} at 575 nm in the pH range 7.1-9.3. Beer's law is obeyed upto 0.00-4.20 ppm of Cd(II). The optimum concentration range for determination of Cd(II) is 0.10-1.42 ppm with Sandell's sensitivity of 0.00229 μg Cd(II) cm^{-2}. The reagent is found to be highly sensitive and can be compared with other reagents for determination of cadmium. Solutions of tobacco have been prepared by dry ashing method and cadmium was determined in these solutions spectrophotometrically by using HSNP in tobacco and tobacco products like cigarettes and bidis of Indian make. Average cadmium level in these tobacco samples are found in the range of 0.542-0.693 μg/2 g of the sample.

Key Words: Spectrophotometry, Cd(II), *Bis*-[2,6-(2'-hydroxy-4'-sulpho-1'-naphthylazo)]pyridine disodium salt, Tobacco, Tobacco products.

INTRODUCTION

Although in nature cadmium occurs in trace amounts and constitutes only 0.00005 % of the crust of the earth. It has been listed by UNEP/WHO as substance dangerous to the environment, because along with such metals as lead, mercury, copper, zinc, chromium, tin and silver it poses a risk of disturbing the balance in ecosystems[1,2]. One characteristic feature of cadmium is its high stability in environment. It is accumulated in soil and living organisms. Cadmium poses a particular risk to the health of humans and animals because it is easily absorbed. It remains in tissues for a relatively long time and is accumulated in vital organs, especially in kidneys and liver. Its biological half-life is 10-30 years. It is not found in the organisms of children, its total amount varies from 30-40 mg in 45-year old people and increases up to the age of 60, when it begins to decrease. A lethal dose of cadmium is 2 mg/1 kg of body weight and is much lower than that of other toxic metals[1]. In the lithosphere cadmium appears mainly in the form of sulphides and its presence is connected with the deposits of zinc and copper. Therefore, emissions of zinc and copper works contribute the highest proportion of industrial cadmium pollution, accounting for 60 % of all anthropogenic sources of pollution with cadmium. The amount of cadmium in the environment may also be increased locally by incineration of solid waste. Inhaling (breathing in) high levels of cadmium can lead to lung damage. Ingesting (swallowing) large amounts of cadmium can cause kidney disease. Occupations that involve handling of cadmium or its compounds carry a higher risk of exposure. Low-level exposure over a long period of time may also cause health problems because cadmium lingers in the body[3-6].

Several reagents for spectrophotometric determination of cadmium(II) has been reported[7,8] of which heterocyclic azo dyes constitute an important class of chromogenic reagents with high photometric sensitivities. In the present method *bis*-[2,6-(2'-hydroxy-4'-sulpho-1'-naphthylazo)]pyridine disodium salt (HSNP), a heterocyclic azo dye has been used for the spectrophotometric determination of cadmium(II) in tobacco and tobacco products. The ligand has been successfully utilized in the spectrophotometric determination of zinc(II) in pharmaceutical samples[9] and in blood samples of diabetic patients[10] and nickel(II) in hydrogenated vegetable oils, chocolates and candies[11].

EXPERIMENTAL

The ligand, *bis*-[2,6-(2'-hydroxy-4'-sulpho-1'-naphthylazo)]-pyridine disodium salt (HSNP) has been synthesized by the method of Barman *et al.*[11]. A stock solution of 1×10^{-3} M has been prepared in double distilled water and dilute solutions of required strengths have been prepared as when necessary.

Stock solution of cadmium was prepared by dissolving appropriate amount of cadmium(II) chloride (BDH) and was standardized by the standard method. A 1×10^{-3} M solution was prepared[12] in double distilled water by diluting the stock solution.

Dilute solutions of hydrochloric acid and sodium hydroxide were used for pH adjustment. A borate buffer of pH 8.8 was prepared.

The absorbance was measured by UV-1700 Pharmaspec UV-visible spectrophotometer (Shimadzu) and UV-visible spetrophotometer 108 (Systronics) with matched quartz cell of 10 mm path length. The pH measurements were carried out with an Elico LI 120 digital pH meter. Pre-calibrated pipettes, burettes and measuring flask (Borosil make) were employed for volume measurements.

RESULTS AND DISCUSSION

Spectral characteristics of the complex and effect of pH: A series of solutions containing known amount of cadmium(II) (1.0 mL of 1.0×10^{-4} M) and a solution of HSNP (1.0 mL of 1.0×10^{-3} M) were prepared and pH were adjusted at different levels in a total volume of 10.0 mL. The spectra of the solutions were recorded against the corresponding reagent blanks. It has been observed that only one complex is formed at all pH values (Fig. 1). Plot of pH *versus* absorbance at λ_{max} (575 nm) shows that constant and maximum absorbance is exhibited in the pH range 7.1-9.3.

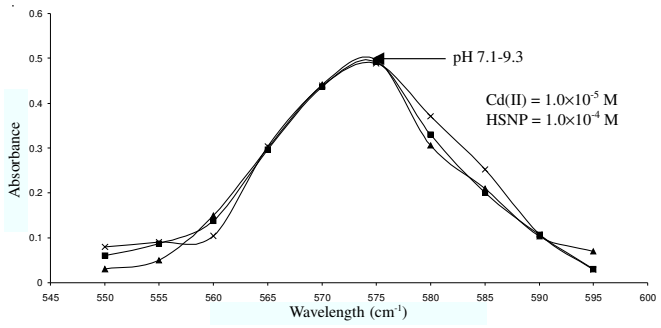

Fig. 1. Absorption spectra for Cd(II)-HSNP complex at different pH

Beer's law validity and optimum concentration range: Linearity between the absorbance of the complex and Cd(II) concentration was examined by varying the concentration of Cd(II) in the solutions containing a fixed amount of the ligand solution at pH 8.8 and measuring the absorbance at 575 nm against the corresponding reagent blank. Beer's law is obeyed from 0.00-4.20 ppm of Cd(II). The result obtained for the validity of the Beer's law optimum range of concentration for accurate determination as calculated from Ringbom's plot is 0.10-1.42 ppm of Cd(II).

Effect of reagent concentration: Study of the effect of reagent concentration on complexation reaction showed that for maximum complexation six times reagent is required. In subsequent studies, however, 10 times molar excess of the reagent was used.

Molar composition of the complex: The stoichiometry of the complex was ascertained by making use of Job's method of continous variations. The curve obtained by plotting absorbance *versus* mole fraction of the metal ions at 575 nm and pH 8.8 shows that the metal to ligand ratio in the complex is 1:1.The physico-chemical characteristics of the Cd-HSNP complex is summarized in the Table-1.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF THE Cd(II)-HSNP COMPLEX

λ_{max}	575 nm
Beer's law validity	0.00-4.2 ppm Cd(II)
Optimum concentration range	0.1-1.42 ppm Cd(II)
Sandell's sensitivity	0.00229 μg Cd(II) cm^{-2}
Molar extinction coefficient (ε)	4.9×10^4 L mol^{-1} cm^{-1}

Recommended procedure for determination of cadmium: To a suitable aliquot containing 1.0-14.2 μg cadmium(II), add 1 mL of 1×10^{-3} M HSNP solution, followed by 1 mL borate buffer of pH 8.8. Dilute to 10 mL and measure the absorbance at 575 nm against the corresponding reagent blank. The concentration of cadmium(II) is determined from the calibration curve recorded under the identical conditions.

Effect of diverse ions and their tolerance limits: Effect of diverse ions has been studied by preparing synthetic solutions containing 1.142 μg/mL of cadmium(II) and varying amounts of diverse ions. Cadmium content in these solutions was determined by following the recommended procedure. The amounts of ions which did not cause deviation of ± 2 % in absorbance are given below:

Nitrate, nitrite, sulphate, acetate, fluride, bromide, sulphite (1000 fold each); chloride, thiocyanate, citrate (200 fold each); tartarate, oxalate (50 fold each); magnesium(II), calcium(II), barium(II) (500 fold each); strontium(II) (40 fold); aluminium(III), manganese(II), antimony(III) (500 fold each); lead(II), molybdenum(VI), zirconium(IV), vanadium(V) (20 fold each); iron(III) (10 fold); copper(II), silver(I), zinc(II), mercury(II) (5 fold each).

However, EDTA, cyanide, sulphide, iodide, thiourea, thiosulphate, nickel(II), cobalt(II), interfere seriously in the determination of the metal ion.

Determination of cadmium in tobacco and its products: Dry ashing method is used in determining the cadmium contents of tobacco and its products. Heat 5 g of sample in a silica crucible in a low Bunsen flame to burn. Now, heat the content strongly to 450-500 ºC. Cool and add 2.0 mL of concentrated nitric acid. Evaporate to dryness and ignite again at 450-500 ºC for ≈ 1 h. Take utmost care to avoid loss by sputtering. Dissolve the resulting white ash in the minimum volume of dilute nitric acid. Neutralize the acid by adding NH_3 solution and remove the excess ammonia by heating. Make up the volume to 25.0 mL in a standard flask. Pipette 2.5 mL of the solution and determine cadmium by the recommended procedure.

Recovery of cadmium from tobacoo and its products: The present method using HSNP as a spectrophotometric reagent for cadmium is found to be a sensitive one. The method has been successfully used to determine cadmium contents in tobacco and its products. The recovery of cadmium has also been checked by standard addition procedure and confirms the accuracy and suitability of the method. The results are summarized in the Table-2.

TABLE-2
RECOVERY DATA OF CADMIUM(II) FROM TOBACCO AND TOBACCO PRODUCTS

Tobacco samples	Cd(II) present in 2 g of the sample solution (average of five readings) (μg)	Cd(II) added (μg)	Cd(II) present (μg)	Cd(II) found (μg)	Recovery of Cd(II) (%)
Raw tobacco leaves	0.693	0.562	1.255	1.238	98.6
Cigarettes (filter tipped)	0.542	0.562	1.104	1.124	101.8
Cigarettes (non-filtered)	0.564	0.562	1.126	1.146	102
Bidi	0.634	0.562	1.196	1.183	98.9
Processed tobacco leaves	0.642	0.562	1.204	1.215	100.9

Conclusion

The present method utilizes *bis*-[2,6-(2'-hydroxy-4'-sulpho-1'-naphthylazo)]pyridine disodium salt (HSNP) for the spectrophotometric determination of cadmium(II). The ligand HSNP is highly water soluble and its aqueous solutions are found to be highly stable. Determination of cadmium in raw tobacco and tobacco products by the proposed method is quite simple, reproducible and has high degree of accuracy. The recovery data close to 100 % indicates the accuracy and precision of the proposed method. The proposed method is found to be simple, rapid and a highly sensitive one.

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