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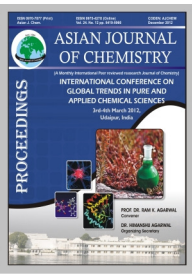

Spectrophotometric Determination of Trace Cadmium in Tobacco with *Tris*-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, Trisodium Salt†

PRATAP SINGH KADYAN, DEVENDER SINGH and ISHWAR SINGH*

Department of Chemistry, Maharshi Dayanand University, Rohtak-124 001, India

*Corresponding author: E-mail: ishsingh@rediffmail.com

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A simple, sensitive and selective spectrophotometric method is developed for the determination of cadmium in aqueous solution. The metal ion forms a dark brown coloured complex with *tris*-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt in the pH range 5.5-7.0. The complex shows maximum absorbance at 510 nm. Beer's law is obeyed in the range 0.0-2.4 ppm of Cd(II). The molar absorptivity and Sandell's sensitivity are 5×10^4 L mol^{-1} cm^{-1} and 0.0021 µg cm^{-2} respectively. The composition of the complex is 1:2. The effect of interfering ions has been studied and the method has been applied to determine Cd(II) in tobacco.

Key Words: Trace analysis, Cadmium(II), *Tris*-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-*s*-triazine, trisodium salt, Spectrophotometry.

INTRODUCTION

With ecological and health problems attracting high attention, it is important that trace metals such as Cd(II), Hg(II), Cu(II) *etc*. be determined in environmental and biological samples. Cadmium is a non-essential element for plants and could be taken and accumulated by plant tissues. Cadmium is very harmful to humans if enters in the food chain[1-5]. Determination of cadmium in tobacco and vegetables has an increasing importance. Many methods have been used for the determination of cadmium, such as atomic absorption spectrometry[6], inductively coupled plasma atomic emission spectrometry[7], mass spectrometry[8], X-ray fluorescence spectrometry[9], neutron activation analysis[10], differential pulse anodic stripping voltametry[11]. Still spectrophotometry is an important analytical technique for the determination of cadmium due to its simplicity and low cost.

Triazine dyes are well suited for spectrophotometric determination of cadmium. Each reagent has its advantages and disadvantage with respect to sensitivity, selectivity, colour reaction and linear range. Some of the available spectrophotometric methods for the cadmium(II) are listed in Table-1.

This paper reports, a water soluble *tris*-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, tri sodium salt (THT) as an analytical reagent for the micro determination of cadmium(II), whereas, a limited number of heterocyclic azo dyes find their use for the determination of cadmium, comparatively this reagent has been found to have fair sensitivity and high selectivity for cadmium(II). Thus the reagent was utilized to determine cadmium in tobacco.

EXPERIMENTAL

A Bausch and Lomb spectronic 2000 spectrophotometer with 10 mm matched glass cells was used for recording spectra and a Beckman pH meter was used for pH measurements.

***Tris*-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt (THT) solution:** THT as synthesized earlier[12,13] was used as a 1×10^{-3} M solution prepared by dissolving 0.90 g in 1 L of double distilled water. Solutions more than a week old were discarded.

Cadmium(II) solution: A stock solution of cadmium(II) was prepared by dissolving reagent grade cadmium acetate dihydrate in double distilled water and it was standardized volumetrically with EDTA[14]. Subsequent dilution were made, as desired, from the stock solution.

Phosphate buffer, pH 6.4: A phosphate buffer[14] was prepared by diluting 250 mL of 0.2 M potassium dihydrogen phosphate and 63 mL of 0.2 M sodium hydroxide to 1 L with double distilled water.

All chemicals used were of analytical reagent grade.

Determination of cadmium(II): To a suitable aliquot containing 6.25-42.5 µg of cadmium(II) ion, add 1 mL of 2.5×10^{-3} M THT solution followed by 2 mL of phosphate buffer and make up the volume to 25 mL with double distilled water.

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TABLE-1
COMPARISON OF SENSITIVITIES OF VARIOUS SPECTROPHOTOMETRIC REAGENTS FOR CADMIUM(II)

Reagent	λ_{max} (nm)	Molar absorptivity (L $mol^{-1}cm^{-1}$)	References
2-Hydroxy-4-*n*-butoxy-5-bromophenone thiosemicarbazone	440	4.0×10^3	15
Cinnamaldehyde-4-hydroxybenzoylhydrazone	383	5.6×10^4	16
p,p'-Dinitro-sym-diphenylcarbazide	630-640	2.05×10^4	17
3-Methylthiophene-2-carbaxaldehyde thiosemicarbazone	360	4.0×10^4	18
1,2-Dihydroxy anthraquinone-3-sulphonic acid, sodium salt (Alizarin red S)	422	2.24×10^3	19
2,4-Dimethoxybenzaldehyde-4-hydroxy benzoylhydrazone	387	3.68×10^4	20
2-Acetylpyridine-4-methyl-3-thiosemicarbazone	360	3.7×10^4	21
5,7-Dibromo-8-hydroxyquinoline	396	5.3×10^3	22
4-Hydroxy-3,5-dimethoxybenzaldehyde-4- hydroxybenzoylhydrazone.	400	4.81×10^4	23
Tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, tri sodium salt	510	5×10^4	This work

Measure the absorbance at 510 nm against a reagent blank prepared under similar conditions.

RESULTS AND DISCUSSION

Tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt (THT) is a multi-dentate water-soluble heterocyclic azo dyes (Fig. 1) and is very sensitive towards cadmium(II) ions. The metal ion forms a dark brown coloured complex with maximum absorbance at 510 nm (Fig. 2). The colour development is maximum and constant at pH 5.5-7.0 (phosphate buffer). The complex had maximum colour development when 2-molar excess of THT was used. However, in further studies, at least-5-fold molar excess of THT was maintained. The composition of the complex as determined by Job's method of continuous variation was 1:2 (M: L). Optimum conditions and other optical constants determined for both the Cd(II)-complex are shown in Table-2.

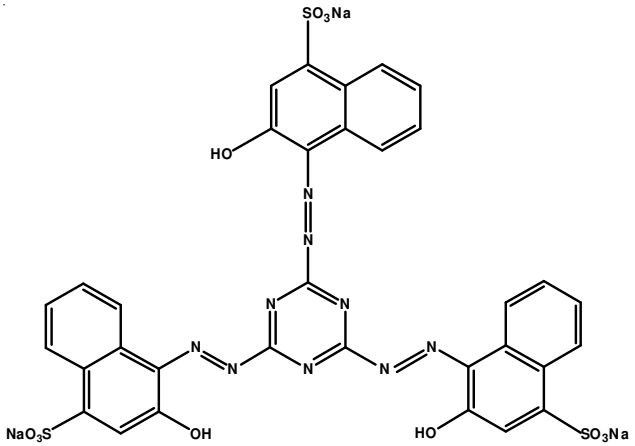

Fig. 1. Chemical structure of *tris*-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt (THT)

TABLE-2
PHYSICO-CHEMICAL CHARACTERISTICS
OF Cd (II)-THT COMPLEX

Characteristics	Cd(II)-THT complex
λ_{max} (nm)	510
pH Range	5.5-7.0
Reagent required for full complexation (mol)	2.0
Beer's law range (ppm)	0.0-2.4
Optimum concentration range (ppm)	0.25-1.7
Sandell's sensitivity (μg cm^{-2})	0.0021
Molar absorptivity (ε) (L $mol^{-1}cm^{-1}$)	5×10^4
Composition (M : L) by Job's method	1 : 2

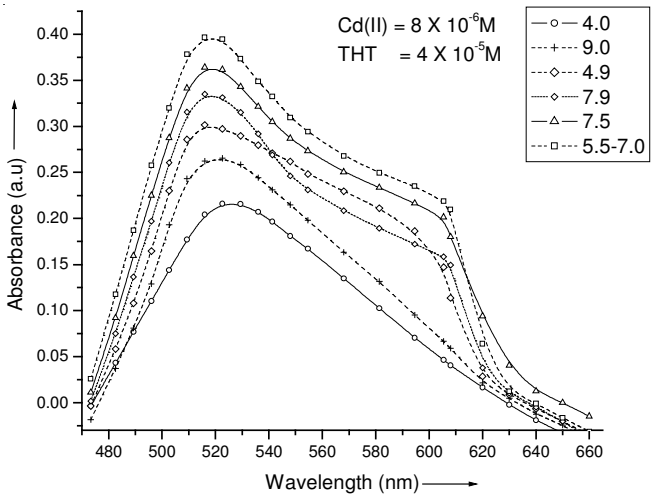

Fig. 2. Absorption spectra of Cd(II)-THT complex at different pH levels

Effect of diverse ions: In the determination of cadmium(II) at 1.0 μg/mL level, fluoride, chloride, bromide, nitrite, nitrate, sulphate, sulphite, thiosulphate, tartrate, borate, oxalate, thiourea, thiosemicarbazide, cyanide, thiocynate, phosphate, alkaline earths, lanthanides, aluminum(III), chromium(III), vanadium(V), molybdenum(VI), tungsten(VI), gold(III) and platinum metals did not interfere at all. However, iodide and EDTA were found to interfere seriously. Complexing anions like fluoride, cyanide, thiosulphate, thiourea, thiocyanate, tartrate, arsenate and phosphate do not interfere and these have been used in masking some of the interfering cations. Cadmium(II) can therefore be determined selectively in presence of many base metal as well as noble metals.

Table-3 represents the tolerance limits in ppm of various ions in solution that caused a deviation smaller than ± 2 % in absorbance for the determination of cadmium (II).

Application for determining cadmium(II) in tobacco: In the present study, different tobacco products like cigaretts, biri, chewing tobacco and snuff were collected from the local market at Rohtak. Tobacco contents were taken out from samples of each brand by removing white papers/wrappers in case of cigarettes and cigars; leaf in case of biris; chewing tobacco from packets snuff were taken directly. All samples were ground to nearly 200 mesh size using agate mortar and pestle and homogenized. One gram of each sample was weighed and taken in Teflon crucible. 10 mL of HNO_3, 1 mL of $HClO_4$ and 5 mL of HF were added and heated on a hot plate for nearly 6 h, small washing of 2 N HNO_3 was added

and dried to dryness on hot plate. The above process was repeated again. Lastly 10 mL of HNO_3 was added to remove any traces of $HClO_4$/HF and evaporated to dryness. The digested sample were dissolved in water containing few drops of HNO_3 and finally diluted to 25 mL. Cadmium contents were determined using the recommend procedure. The amounts of cadmium present in different tobacco products are shown in Table-4.

TABLE-3
TOLERANCE LIMITS OF DIVERSE IONS IN THE DETERMINATION OF 1.0 µg/mL OF CADMIUM(II)

Foreign ions	Tolerance limits (ppm)	Masking agents
S^{2-}	400	-
Zn(II)	2.5	IO_3^-
Hg(II)	10	$S_2O_3^{2-}$ or T.U.
Mn(II)	8	AsO_4^{3-}
Fe(II)	20	CN^-
Co(II)	20	CN^-
Ni(II)	20	CN^-
Cu(II)	12	$S_2O_3^{2-}$
Ag(I)	25	CN^-
Pb(II)	25	PO_4^{3-} or $S_2O_3^{2-}$
In(III)	40	S^{2-}
Bi(III)	40	S^{2-}
Sb(III)	40	S^2
Th(IV)	50	PO_4^{3-}or F^-
UO_2(II)	15	$(NH_4)_3AsO_4$

TABLE-4
MEAN CONCENTRATION OF CADMIUM ALONG WITH THEIR STANDARD DEVIATION (SD)

Brand		Cadmium found (µg/g) Mean of 5 readings	S.D.
Cigarettes	Four square	0.48	0.05
	Gold flake	0.39	0.06
	Panama	0.28	0.05
	Classic	0.42	0.04
Cigars	Kings Adward	0.75	0.07
	Impirial	0.58	0.07
Biri	Shiv	0.67	0.06
	Biri No. 22	0.38	0.06
	Kisan	0.44	0.06
Chewing Tobacco	Rajdarbar	0.21	0.05
	Golden	0.49	0.08
	Swagat	0.36	0.11
Snuff	Desi	0.41	0.10
	Manjul	0.42	0.07

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