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LIQUID-LIQUID EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF Sn(IV) WITH 2,4-DIMETHYl-3H-1,5 BENZODIZEPINE DERIVATIVE AS AN ANALYTICAL REAGENT

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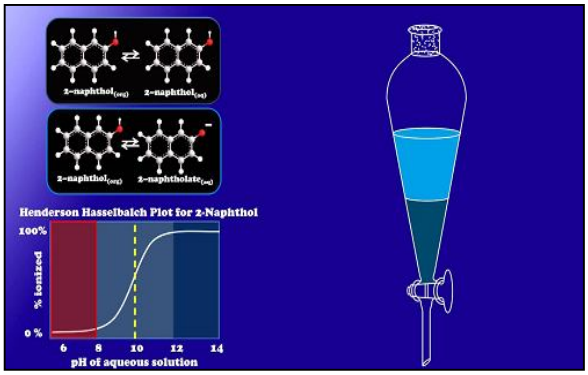
ABSTRACT :

A simple and precise spectrophotometric method is coupled with the solvent extraction technique and used for the determination of Sn (IV) using 2,4-dimethyl-3H-1,5 benzodizepine (DBS) as an analytical reagent. This reagent is synthesized in the laboratory and characterized by NMR (Nuclear Magnetic Resonance), IR (Infrared) and elemental analysis for its purity (Ahluwalia *et al*., 2005; Vogel, 1957). The reagent forms a red-colored stable complex with Tin metal, which can be quantitatively extracted into *n*-butanol at pH 7.6. This Sn (IV)-DBS complex in *n*-butanol exhibits an intense absorption peak at 500 nm. The study of change of color intensity of the Sn (IV)-DBS complex with varying concentrations of the reagent showed that 1 ml of 0.05% of the reagent is sufficient for full color development of 10-ppmTin solution.



Beer's law is obeyed in the range of 1-10 ppm of Tin solution giving a linear and reproducible graph. The stoichiometric ratio of the complex is studied by Job's continuous variation method, the mole ratio method and the slope ratio method. Stoichiometry of the Sn (IV)-DBS complex is 1:1 the molar absorptivity and Sandell's sensitivity is also calculated. Molar absorptivity is 0.4448×10^4 $lmol^{-1}cm^{-1}$ and Sandell's sensitivity is 0.01234 μgcm^{-2}. The newly developed method is then successfully applied to various commercial samples and is observed to be compatible with earlier known methods.

KEYWORDS: *Tin, Spectrophotometric Determination, n-Butanol 2, 4-Dimethyl-3H-1, 5 Benzodizepine*

INTRODUCTION

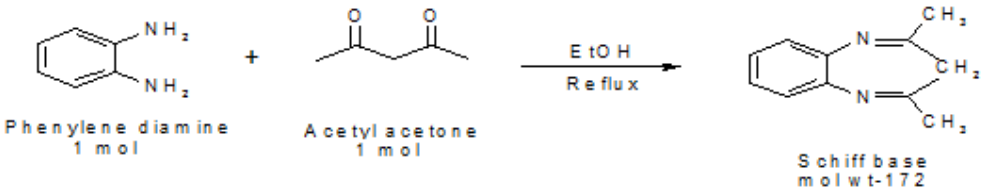
Tin is silvery and soft metal. Pure tin after solidifying keeps a mirror like appearance similar to most metals. But the metal solidifies with dull gray colour. It shows both oxidation states +2 and +4.tin has largest number of stable isotopes in the periodic table. About half of all tin produced was used in solder. The rest was divided between tin plating, tin chemicals, brass and bronze alloys.

Experimental Synthesis of the Reagent 2,4-Dimethyl-3H- 1,5 Benzodizepine (DBS)

Reagent DBS was synthesized by dissolving 1 mole of O-phenylenediamine and 1 mole acetyl acetone in ethanol[1]. The mixture was refluxed for 2 hours. The product obtained was poured in ice-cold water. The solid that appears was then filtered through a Buckner funnel.

The solid thus obtained was recrystallized by ethanol. The purity of the reagent was checked by TLC (Thin Layer Chromatography). Synthesis of the reagent was confirmed by spectroscopic techniques such as NMR, IR, elemental analysis and mass spectrometry[6].

REACTION



Preparation of the Stock Solution

The stock solution of Sn (IV) was prepared by dissolving a weighed amount of Tin Oxide in Small quantity of acidified double-distilled water, and then diluted to the desired volume with double-distilled water and standardized using the EDTA (Ethylene Diamine Tetra Acetic Acid) method[7]. Absorbance and pH measurements were carried out on a Shimadzu UV-Visible 2100 spectrophotometer with 1-cm quartz cells and a digital pH meter with combined glass electrodes, respectively[3].

Procedure for the Extraction

Overall, 1 ml of aqueous solution of Tin metal and 1 ml of the reagent were mixed in a 50-ml beaker. The pH of the solution was adjusted to 7.6. It must be noted that the total volume should not exceed 10 ml. The solution was transferred to a 100-ml separating funnel. The beaker was washed twice with *n*-butanol and transferred to the same funnel. The two phases were shaken for 2 minutes and allowed to separate. The organic phase was collected in a 10-ml measuring flask and made up to the mark with an organic solvent if required. Sn (IV) in the organic phase is determined spectrophotometrically.

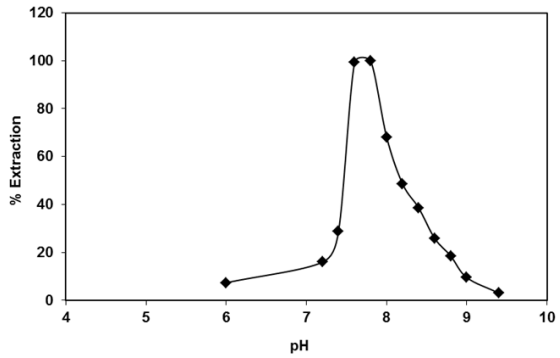
RESULTS AND DISCUSSION

The reagent DBS formed a red-colored complex with Sn (IV), which was extracted into the organic phase. Extraction of the Sn (IV)-DBS complex from an aqueous phase by *n*-butanol was studied over a wide range of experimental conditions. The results of various studies are discussed below.

Extraction as a Function of pH

Extraction of tin with DBS has been studied over the pH range 1-10 and presented in Fig.1. Fig.1 indicates that percentage extraction of Tin was maximum from pH range 7.4 to 8.4. Hence, further study was carried out at pH 7.6

Fig. 1: The Effect of pH on the Extraction of tin with DBS in *n*-Butanol



Absorption Spectrum

The absorption spectrum of Sn (IV): DBS in n-butanol showed maximum absorption at 500 nm. Absorption due to the reagent at this wavelength was nearly negligible. Hence, absorption measurements were carried out at 500 nm[2].

Influence of Diluents

The suitability of the solvent presented in Table 1, was investigated using organic solvents such as chloroform, ethyl acetate, xylene, hexane, diethyl ether, toluene, *n*-butanol, carbon tetrachloride, nitrobenzene, cyclohexanone, etc. The extraction of Sn (IV): DBS was maximum in *n*-butanol. Hence, *n*-butanol was used for further extraction studies as it gave a better and quicker phase separation.

Table 1: Observation Table for Effects of Various Solvents on the Sn(IV)-DBS Complex

S No.	Solvent	Percentage Extraction
1	Nitro benzene	20.91
2	Cyclohexanone	8.23
3	Iso-amyl alcohol	48.94
4	Hexane	2.32
5	Ethyl acetate	3.78
6	*n*-butanol	99.99
7	Chloroform	5.60
8	Diethyl ether	1.5
9	Tolune	1.5
10	CCl4	1.5
11	Xylene	2.73

Effect of Salting-Out Agents

The presence of 0.1-M salts of various alkali and alkaline metals does not show any effect over the absorbance value of the Sn (IV)-DBS complex extract. Therefore, no salting-out agent was required during the extraction.

Effect of Reagent Concentration

The minimum amount of the reagent required for color development of the metal Sn(IV) in 10 ml of aqueous solution at pH 7.6 was found by varying the reagent concentration from 0.1 ml to2.0 ml of 0.05% DBS in methanol keeping the other factors constant. The absorbance remained nearly constant when the volume of the reagent solution used was more than 1 ml. Therefore, 1 ml of 0.05% reagent was chosen for quantitative determination of the metal.

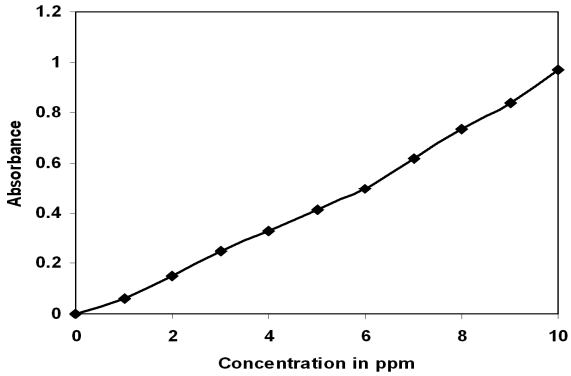
Effect of Equilibration Time and Stability of the Complex

The study of change in absorbance with variation in equilibrium time for extraction of the complex into an organic solvent shows that equilibration time of 1 minute is sufficient for quantitative extraction of tin. The study of stability of color of the Sn(IV)-DBS complex with respect to time shows that absorbance due to extracted species is stable up to 34 hours, after which a slight decrease in absorbance is observed. Throughout the experimental work, for practical convenience, measurements were carried out within 1 hour of extraction of tin.

Calibration Plot

A calibration plot of absorbance against varying tin concentration and fixed DBS concentration gives a linear and reproducible graph in the concentration range 1-10 ppm of Sn (IV) (Figure 2). This shows that Beer's law is obeyed in this range. Both molar absorptivity and Sandell's sensitivity were calculated to be 4448 $lmol^{-1}cm^{-1}$ and 0.01234 µg cm^{-2}, respectively.

Fig. 2: Calibration plot of Sn (IV)-DBS complex



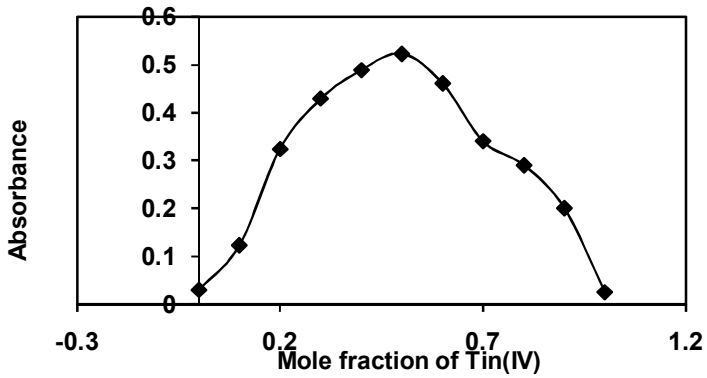
Effect of Foreign Ions

The effect of other ions presents in various amounts indicated no interference in the spectrophotometric determination of 10 ppm of tin. Ions that showed interference in the spectrophotometric determination of tin were overcome using appropriate masking agents.

Nature Of Extracted Species

The composition of the extracted Sn (II)-DBS complex was determined by Job's continuous variation method[4], the slope ratio method (Figure 3) and the mole ratio method[4]. It shows that the composition of the Sn (IV)-DBS complex is 1:1.

Fig. 3: Job's Continuous Variation Curve



Precision and Accuracy

The precision and accuracy of the developed spectrophotometric method were studied by analyzing ten solutions each containing 10 µg of tin in the aqueous phase. The average of ten determinations was 9.90 and variation from mean at 95% confidence limit was ±0.1250.

Effect of Foreign Ions

The tolerance limit of different metal ions was studied by carrying out determinations of 10 µg of Sn (IV) in the presence of a large number of foreign ions. It shows no interference with most of the foreign ions on the extraction of tin. Interference of some metal ions is masked using appropriate masking agents (Table 2).

Table 2: Masking Agents Used

S No.	Interfering Ions	Masking Agents
1	Co (II)	Sodium fluoride
2	Fe(III)	Sodium fluoride
3	Pb (II)	Sodium thiosulphate
4	Mn (II)	Sodium fluoride
5	EDTA	Boiled with concentrated HNO3
6	CN-	Boiled with concentrated HNO3 and formaldehyde

Applications

The proposed method was successfully applied for the determination of tin from various alloys, ores and pharmaceutical samples. The results were found to be in good agreement with those obtained by the standard known method[5] (Table 3).

Table 3: Observation Table for Determination of Sn(IV) using DBS from Different Samples

S No.	Sample	Standard Method	Present Method
A	**Alloys**		
1	Bronze alloy	12%	12.2%
B	**Synthetic Mixtures**		
1	Sn(55)+ pb(45)	55 ppm	54.55 ppm
2	Sn(100)+Fe(100)+Ni(100)	100 ppm	99.40 ppm

CONCLUSION

The proposed method is more highly sensitive and selective than the reported methods for the extractive spectrophotometric determination of microgram amounts of tin. It offers advantages like reliability and reproducibility in addition to its simplicity, instant color development and suffers from less interference. It has been successfully applied to the determination of tin at the trace level in synthetic mixtures and alloys.

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