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# An Extractive Spectrophotometric Determination of Tin as Sn(II)-6-Chloro-3-hydroxy-7-methyl-2-(4'-methoxyphenyl)-4-oxo-4*H*-1-benzopyran Complex into Dichloromethane

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## Abstract

Tin(II) forms a yellow colored complex with 6-chloro-3-hydroxy-7-methyl-2-(4'-methoxyphenyl)-4-oxo-4*H*-1-benzopyran in hydrochloric acid medium. The complex is extractable into dichloromethane and shows maximum absorbance in the range 424-428 nm. The 1:2 (M: L) complex formed is found to be stable for more than 4 h in dichloromethane. Beer's law is obeyed in the range 0.0 to 1.68 μg Sn(II) $mL^{-1}$ with an optimum range of determination as found from Ringbom plot is 0.23-1.51 μg $mL^{-1}$. The molar absorptivity and Sandell's sensitivity of the complex are $6.29\times10^4$ L $mol^{-1}$ $cm^{-1}$ and 0.0019 μg Sn(II) $cm^{-2}$ at 426 nm, respectively. The method is free from interference of a large number of important anions/complexing agents and cations. The method is quite simple and has been satisfactorily applied to the analysis of tin in various samples including gun metal and tin can.

***Keywords:***

Tin; 6-chloro-3-hydroxy-7-methyl-2-(4'-methoxyphenyl)-4-oxo-4*H*-1-benzopyran; extraction; spectrophotometric determination

## 1. Introduction

Many organic reagents [1-17] have been used as analytical reagents for spectrophotometric determination of tin. However, most of these are not suitable for routine analysis as they lack sensitivity/selectivity or both [4-5, 7-10, 12-16]. A large number of important elements interfere in many of these analytical reagents and in some the complexes formed by them require up to 30 min for full color development [6, 11-12, 14]. Though some sensitive reagents [1-3, 9, 17] are reported, but these tolerate only limited quantities of foreign ions in addition to the requirements of critical pH adjustment and use of the surfactants. In regards to quantitative determination of micro amounts of Sn(II), it appears from the literature that there is still a lot of scope for working out new methods and effecting amendments in the existing ones in view of the restriction generally met with in their applicability especially for reason of their lower sensitivity and selectivity. Keeping in mind the idea of sensitivity and selectivity, a benzopyran derivative 6-chloro-3-hydroxy-7-methyl-2-(4'-methoxyphenyl)-4-oxo-4*H*-1-benzopyran(CHMMPB) was prepared in the laboratory and used for improving the desirable characteristics of the spectrophotometric method for the determination of Sn(II). The reagent CHMMPB was found to give a sensitive reaction with Sn(II). In this work,

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optimization of conditions for the quantitative extraction of Sn(II)-CHMMPB complex were worked out apart from the studies involving stoichiometry and Beer's law determination. Also interference studies for diverse ions were carried out. Using masking agents, the extraction of Sn(II)-CHMMPB complex was made free from interference of large number of metal ions. The extraction of the yellow colored complex of Sn(II)-CHMMPB into dichloromethane forms the basis of the proposed method, which offers the advantages particularly in respect of sensitivity, selectivity and color development time as compared to the existing ones. Different synthetic and technical samples including gun metal and tin can have been analyzed for tin contents.

## 2. Experimental

### 2.1 Apparatus

A UV-Visible spectrophotometer (Model-140-02, Shimadzu) with 10 mm matched cells was used for the routine absorbance measurements. The IR and $^1$H NMR spectra were recorded on Perkin-Elmer 1710 FTIR spectrometer over the range 4000-400 cm$^{-1}$and Bruker 300 MHz respectively. The TGA was carried out using Perkin-Elmer (Pyris Diamond) simultaneous TG- DTA analyzer.

### 2.2 Preparation and characterization of the Reagent (CHMMPB)

To a solution of 5-chloro-4-methyl-2-hydroxyacetophenone (5.55 g) and 4-methoxybenaldehyde (4.08 g) in methyl alcohol, NaOH (2.40 g) was added at 0-5°C. The reaction mixture was stirred for 3-4 h at room temperature. Thereafter, it was poured on ice and then neutralized with dilute HCl to obtain 1-(5′-chloro-4′-methyl-2′-hydroxyphenyl)-3-(4″-methoxyphenyl)-prop-2-en-1-one. This was then crystallized from ethyl alcohol to give yellow needle shape crystals. A solution containing 1-(5′-chloro-4′-methyl-2′-hydroxyphenyl)-3-(4″-methoxyphenyl)-prop-2-en-1-one (3.0 g) in 30 mL MeOH and aqueous NaOH (20%, 15 mL) was cooled to 0-5°C, a dark red solution was obtained, to this added 10 mL of $H_2O_2$ drop wise with constant stirring for 3 h. The resulting yellow reaction mixture was neutralized with cold dilute HCl. The pale yellow precipitate formed were filtered, washed with water, dried and then recrystallized from EtOH-$CHCl_3$ as yellow needle shaped crystals. The melting point product obtained was found to be 187-191°C (Literature =188-190°C) [18]. The reagent was characterized by elemental analysis, IR and $^1$H NMR. The molecular formula of CHMMPB is $C_{17}H_{13}O_4Cl$and its structure is given below:

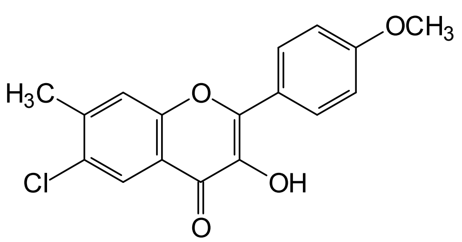

**Fig.1.** The chemical structure of CHMMPB

### 2.3 Reagents and Solutions

All the chemicals used for the development of the method were of analytical grade with high purity. Dichloromethane was distilled and the fraction distilling at 39-41°C was used for Sn(II)-CHMMPB complex extraction.

### 2.4. Tin and other metal ions Standard Solution

The standard stock solution (250 mL) of Sn(II) containing 1 mg mL$^{-1}$ was prepared by dissolving an accurately weighed amount (0.475 g) of $SnCl_2.2H_2O$ (AR. Reidel) in 20 mL of concentrated hydrochloric acid, diluting with deionized water up to the mark and standardized by the $SnO_2$ method gravimetrically [19]. Lower concentration at μg mL$^{-1}$ level was prepared by suitable dilution of this solution containing 0.5 M HCl final acidity. The containers of the tin solution were wrapped with carbon paper and kept in dark place. Stock solutions of other metal ions were prepared at mg mL$^{-1}$ level by dissolving their sodium or potassium salts in deionized water or dilute acid. They were suitably diluted to give μg mL$^{-1}$ level concentration of the metal ions.

### 2.5. CHMMPB Solution

6-Chloro-3-hydroxy-7-methyl-2-(4'-methoxyphenyl)-4-oxo-4*H*-1-benzopyran dissolved in acetone to give 0.1% (w/v) solution.

### 2.6. Dissolution of Alloys Samples

The synthetic samples were prepared by mixing tin solution with solutions of various metal ions in suitable proportions so as to give the composition as shown in Table 1.

**Table - 1 Analysis of various samples by the proposed method**

| Sample composition<br>Matrix* | Sn added, μg | Sn found**, μg |
|---|---|---|
| Cu(0.203), Pb(0.104), Ni(0.00293), Fe(0.00097)$^{a, b}$ | 15.0 | 15.00 |
| Cu(0.103), Sb(0.011)$^{a1}$ | 14.0 | 13.75 |
| Cu(0.170), Co(0.01)$^{a2}$ | 15.0 | 14.87 |
| Al(0.3), Mg(0.005), Cu(0.001), Pb(0.002)$^{a3}$ | 10.0 | 10.13 |
| Cr(0.02), As(1.5), Re(0.2) | 7.0 | 7.00 |
| Cd(2), Ag(0.1), Ti(0.05)$^{c}$ | 12.0 | 11.81 |
| Re(0.04), Ta(0.05), V(0.01)$^{b}$ | 14.0 | 14.13 |
| Sr(1.5), Se(2.5), Th(0.01) | 5.0 | 5.06 |
| Co(2.4), Ba(2.0), Mo(0.002)$^{d}$ | 10.0 | 9.94 |
| Gun metal | 4.9$^{e}$% | 4.65% |
| Tin can | - | 0.16% |

*Amount of metal ion shown in parentheses is in mg. * * Average of triplicate analyses; $^{a, a1, a2, a3}$ Correspond to ceco alloy, chinese speculum, argental and magnalium cast Z respectively. $^{b}$ In presence of 50 mg ascorbic acid. $^{c}$ in the presence of 0.1 mg oxalate. $^{d}$ In presence of 0.75 mL (30%, m/v) $H_2O_2$. $^{e}$ Certified value and confirmed by $SnO_2$ method.

### 2.6.1. Gun Metal

A weighed sample of gun metal (0.2 g) was dissolved in 10 mL of concentrated hydrochloric acid and 2-4 mL of concentrated nitric acid by heating and the volume was made up to 100 mL in a volumetric flask. 10 mL of this solution was diluted to 100 mL to get a working solution of low concentration. An aliquot of resulting sample solution was analyzed by the proposed method.

### 2.6.2. Tin can

A weighed sample (0.6 g) of tin can taken in a 100 mL beaker was heated gently with 5 mL of concentrated hydrochloric acid. The sample was dissolved completely by adding 5-10 mL of distilled water and heating until the volume was reduced to 2-5 mL. After cooling, the volume of the solution was made up to 25 mL and suitable portions of the sample solution were analyzed for tin contents.

### 2.7. General Procedure

A sample solution containing up to ≤ 16.8 μg Sn(II) was taken into a short stemmed 125 mL separating funnel with standard joint stopper. To this added 1.5 mL of 6-chloro-3-hydroxy-7-methyl-2-(4′-methoxyphenyl)-4-oxo-4*H*-1-benzopyran (CHMMPB) 0.1% (w/v) in acetone solution, adjusted the final acidity to 0.05 M HCl and made the volume of the aqueous phase up to 10 mL with distilled water. Then 10 mL of dichloromethane was added and the contents were shaken immediately for 40 sec. The two layers were allowed to separate and the lower yellow colored solvent layer was passed through Whatman filter paper (No. 41, 9 cm diameter pretreated with dichloromethane) to remove the water droplets and collected into 10 mL measuring flask. The absorbance of the organic extract was measured at 426 nm against similarly prepared reagent blank. Tin contents in the sample were obtained from a calibration curve plotted under the identical conditions of the method.

#### 2.7.1. Modifications of the method for the V, Fe, Nb, Zr, W, Mo and Ti

In the sample under study Ti(IV) and W(VI) were masked with sodium oxalate, Fe(III) and V(V) with ascorbic acid, Mo(VI) and Nb(V) with $H_2O_2$ and Zr(IV) with sodium phosphate, prior to the addition of reagent and solvent. The respective amounts of the masking agents used are mentioned under the effect of diverse ions.

## 3. Results and Discussion

### 3.1 Spectral Characteristics

The absorption spectrum of the colored Sn(II)-CHMMPB complex against reagent blank in dichloromethane under optimum conditions shows maximum absorbance in the range 424-428 nm (Fig. 1, Curve-A). In this range of the spectrum, the reagent blank against pure solvent dichloromethane shows minimum absorbance (Fig.2, Curve-B). Thus 426 nm was opted as suitable wavelength for the method.

### 3.2 Effect of reagent concentration

The effect of concentration of 6-chloro-3-hydroxy-7-methyl-2-(4'-methoxyphenyl)-4-oxo-4*H*-1-benzopyran (CHMMPB 0.1% in acetone) on the absorbance of the complex has been studied (Table 2; Fig. 3, Curve-A).

It was found to be nil in the absence of the reagent and increased with the corresponding increase in reagent concentration. For 1.0-3.2 mL, the absorbance was maximum thereafter, it starts declining. Therefore, 1.5 mL of the reagent was considered sufficient for the system.

### 3.3 Effect of Acidity

The absorbance of the Sn(II)-CHMMPB complex was found maximum in HCl medium, where as it was observed to be low in $H_2SO_4$, $CH_3COOH$ and $HClO_4$. At 0.032 M HCl the absorbance of the complex was 0.390, which increases when acid concentration was raised to 0.04 mol $L^{-1}$. From 0.040-0.066 mol $L^{-1}$ HCl, the absorbance of the complex was maximum and remains constant, thereafter, it shows a downward trend (Table 2; Fig. 3, Curve-B). Hence, for achieving maximum absorbance, 0.05 mol $L^{-1}$ HCl was chosen for the method.

### 3.4 Effect of equilibration time

There was no change in the absorbance of the Sn-CHMMPB complex if the aqueous solution containing ions was equilibrated with the solvent for 30 to 300 sec (Table 2). Thus in order to save time, 40 sec was kept as the contact time.

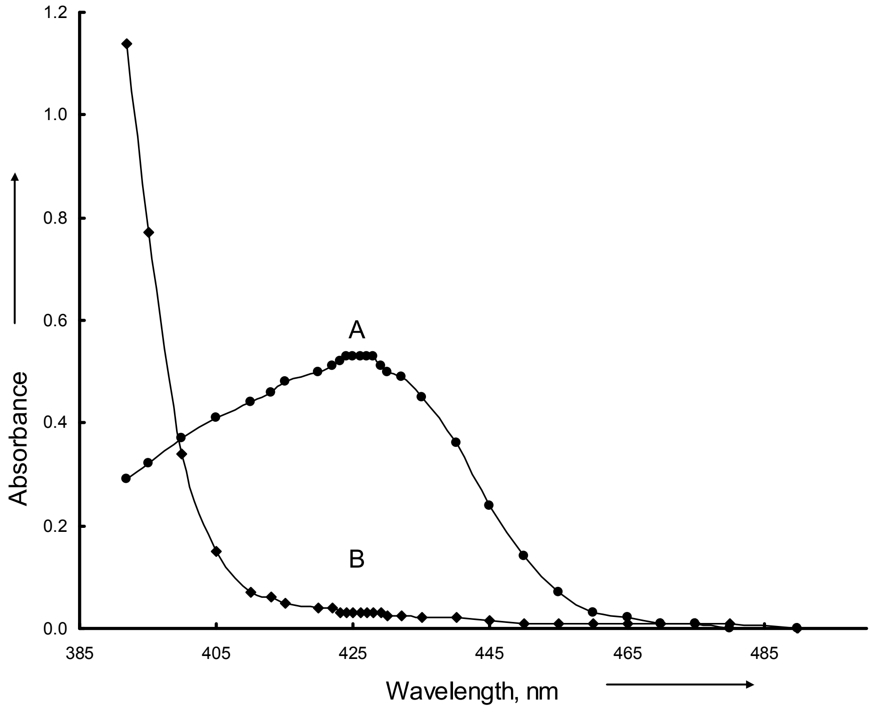

**Fig. 2.** Absorption spectrum of Sn(II)-CHMMPB complex into dichloromethane. Curve-A - 1.0 μg Sn(II) $mL^{-1}$ measured against reagent blank, Curve-B - reagent blank measured against dichloromethane.

**Table 2.** Effect of various parameters on the absorbance of Sn(II)-CHMMPB complex

| HCl[a](M) | 0.032 | 0.036 | 0.038 | 0.04-0.066 | 0.07 |
|---|---|---|---|---|---|
| Absorbance | 0.390 | 0.430 | 0.490 | 0.530 | 0.470 |
| CHMMPB [b](mL) | 0.4 | 0.6 | 0.8 | 1.0-3.2 | 3.4 |
| Absorbance | 0.120 | 0.230 | 0.380 | 0.530 | 0.500 |
| Equilibration time[c] (sec) | 0.0 | 10 | 20 | 25 | 30-300 |
| Absorbance | 0.030 | 0.250 | 0.450 | 0.490 | 0.530 |

Conditions: [a]- HCl = variable, Sn(II) = 10 μg, CHMMPB (0.1% (m/v) in acetone) = 1.5 mL; aqueous volume = solvent volume = 10 mL, solvent = dichloromethane, equilibration time = 40sec, $\lambda_{max.}$ = 426 nm, at room temperature;

[b]- CHMMPB concentration variable, HCl = 0.05 M, other conditions being the same as in (a)

[c]- Variation in equilibration time, CHMMPB (0.1% (m/v) in acetone = 1.5 mL; other conditions being the same as in (b).

### 3.5 Effect of various organic solvents

Tin(II) forms a yellow complex with CHMMPB in HCl medium which was extracted by various organic solvents namely dichloromethane, carbon tetrachloride, 1,2-dichloroethane, chloroform, isobutyl methyl ketone, benzene, toluene, ethyl acetate, isoamylacetate, n-butanol and isoamyl alcohol in the decreasing order of the absorbance. Hence, dichloromethane showing maximum and stable absorbance was used as extractant for the metal complex. A single equilibration of the aqueous phase with equal volume (10 mL) of dichloromethane under optimum conditions gives quantitative (100 %) recovery of Sn(II)–CHMMPB complex.

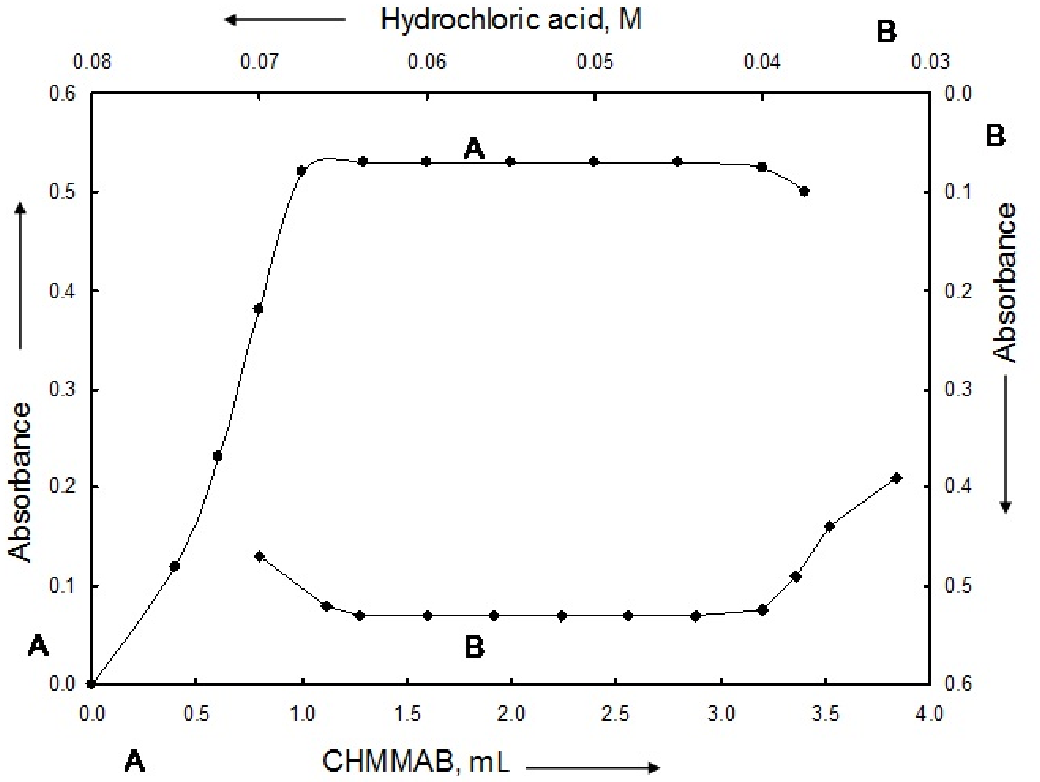

**Fig. 3.** Effect of concentration: (A) CHMMPB; (B) Hydrochloric acid concentration on the absorbance of Sn(II)-CHMMPB complex at 426 nm.

### 3.6 Beer's law obedience, stability and other statistical parameters

The calibration curve was constructed at 426 nm according to the general procedure. The metal complex obeys Beer's law up to 1.68 µg Sn(II)/mL (Fig. 4). The optimum concentration range of tin which can be measured accurately, as obtained from Ringbom plot [20] is found to be 0.23-1.51 ppm. The molar absorptivity and Sandell's sensitivity of the complex are $6.29\times10^4$ L $mol^{-1}$ $cm^{-1}$ and 0.0019 µg Sn(II) $cm^{-2}$ respectively under the optimum conditions of the procedure. In dichloromethane Sn(II)-CHMMPB complex was found to stable for more than 4 h. Ten replicate determinations containing 1 µg Sn/mL gives a mean absorbance value of 0.533 with a relative standard deviation of 0.27%.

### 3.7 Stoichiometry of the complex

The ratio of tin(II)-CHMMPB in the extracted species was determined using their equimolar solution ($8.425\times10^{-4}$ M) at three different wavelengths 410, 426, 445 nm by Job's method of continuous variations as modified by Vosburgh and Cooper for a two-phase system [21-22]. The sharp break in the curves indicates a metal-to-ligand ratio is 1:2 in the extracted species (Fig. 5). This was further supported by the mole ratio method [23] by taking the concentration of Sn(II) as $4.218\times10^{-4}$ mol $L^{-1}$ and measuring the absorbance again at three wavelengths 410, 426, 445 nm under the optimum conditions of the procedure.

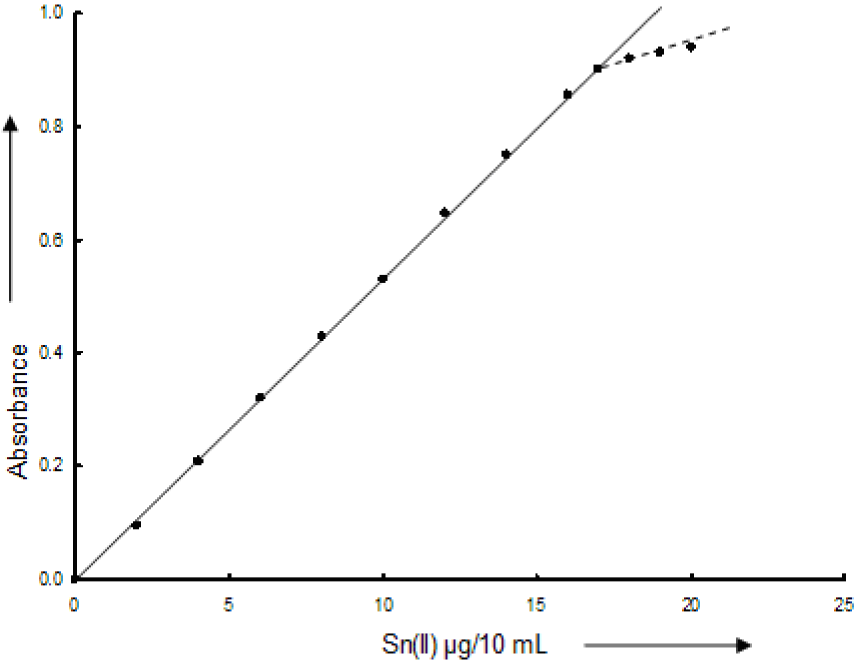

**Fig. 4.** Beer's law obedience of Sn(II)-CHMMPB complex into dichloromethane at 426 nm.

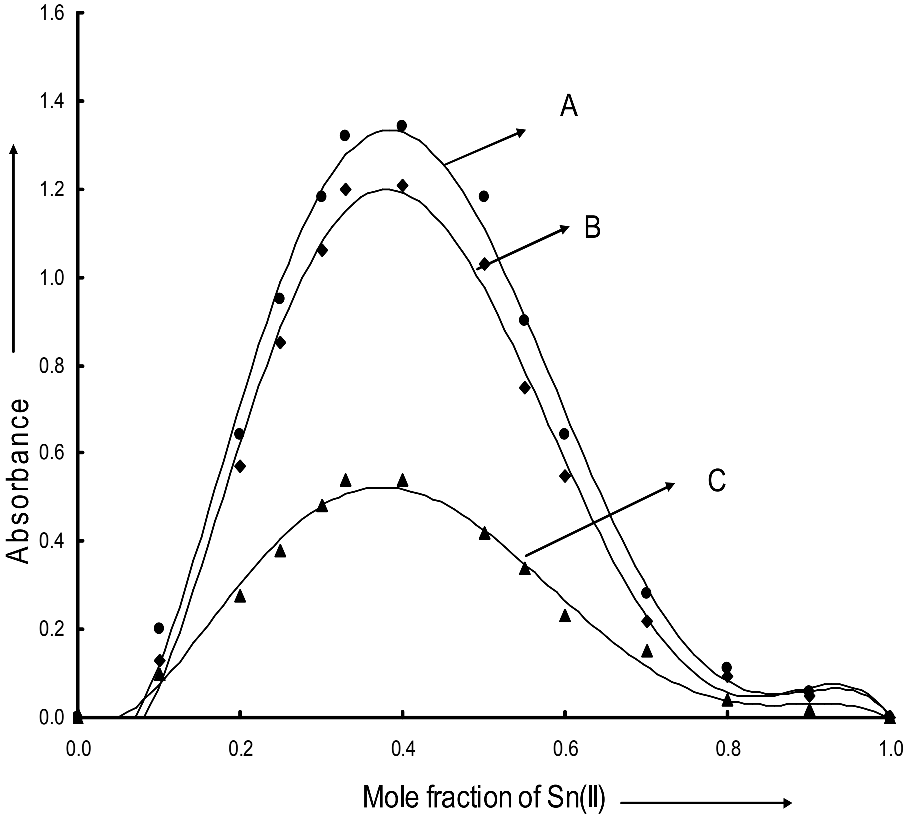

**Fig. 5.** Job's method of continuous variations of Sn(II) and CHMMPB: (A) 426 nm, (B) 410 nm and (C) 445 nm

In order to get further insight about the stoichiometry and structure of the complex, the complex has been synthesized by the reaction of $SnCl_2$ and CHMMPB in 1:2 molar ratios according to the following equation:

$$SnCl_2 + 2C_{17}H_{12}O_4ClH \xrightarrow[CH_3COCH_3]{HCl} [Sn(C_{17}H_{12}O_4Cl)_2] + 2HCl$$

$SnCl_2.2H_2O$ (AR. Reidel) 0.113 g was dissolved in minimum amounts of hydrochloric acid and CHMMPB 0.316 g in acetone separately. Two solutions were mixed and stirred for 4-5 min a yellow solid product separated out. The product was filtered on a Buckner funnel and was washed with water. The yellow precipitates were then dissolved in warm dichloromethane, filtered and kept on a water bath to remove the solvent. The last traces of the solvent were removed under reduced pressure resulting in fine yellow product.

The complex $[Sn(C_{17}H_{13}O_4Cl)_2]$ is yellow in colour, soluble in common organic solvents such as $C_6H_6$, $CHCl_3$, $ClCH_2CH_2Cl$, $CH_2Cl_2$ etc., however, insoluble in acetone, ethers etc. The complex is highly stable to moisture and oxidation. The Sn complex has been found to decompose above ~ 360 ºC.

In IR spectrum of CHMMPB a band appears at ~1625 $cm^{-1}$ due to ν(C=O) stretching vibration. However, the spectrum of the complex shows a band at ~ 1615 $cm^{-1}$ due to stretching vibration of carbonyl ν(C=O) group coordinated to tin. This small decrease in value of carbonyl stretching vibration indicates the coordination of carbonyl oxygen of CHMMPB to tin.

A band observed at ~3480 $cm^{-1}$ due to ν(O-H) in the CHMMPB [8] is absent in the IR spectrum of the complex indicating its deprotonation. The appearance of new band at about 600 $cm^{-1}$ is the assigned to ν(Sn-O) stretching in the complex [24]. The IR spectrum of the tin complex suggests monobasic bidentate nature of CHMMPB. The $^1H$ NMR of the complex shows a number peaks in the region δ 8.50 to 6.88 ppm due to different types of phenyl protons as observed in CHMMPB.

The thermal gravimetric analysis of the complex shows weight loss between 345ºC to about 660ºC due to the decomposition of organic moiety i.e $(C_{17}H_{12}O_4Cl)_2$. The end result is the formation of $SnO_2$ [24] by TGA Curve. On the basis of the spectrophotometric and the above mentioned results, the most probable structure of the Sn(II)-CHMMPB complex is 1:2.

### 3.8 Effect of diverse ions

Under optimum conditions of the procedure, the effects of different anions/complexing agents have been studied on the basis of the absorbance of the complex. Thiourea, sulfite, nitrate, carbonate, sulfate, sulfosalicylic acid, chloride, iodide and bromide (100 mg each); thiocyanate (60 mg); ascorbic acid (50 mg); acetate (40 mg); tartrate (25 mg); phosphate (15 mg); citrate (10 mg ); EDTA disodium salt (5 mg); oxalate (0.1 mg); fluoride and dithionite (0.05 mg each); glycerol (1 mL) and $H_2O_2$ (30%, w/v) (0.75 mL) did not influence the absorbance of the tin complex. The figures in parenthesis indicate the amount of sodium and potassium salts of the anions in mg.

Among the cations of Zn(II), Pb(II), Ba(II), Mg(II), Ni(II), Cd(II), Hg(II) and Al(III) (10 mg each); Ca(II) (9 mg); Co(II) and Mn(II) (8 mg each); As(III) and Sr(II) (7 mg each); Ce(IV) and Se(IV) (5 mg each); Be(II) (4 mg); U(VI) (3 mg); Ag(I) and Ir(III) (2.5 mg each); Os(VIII) and Re(VIII) (2 mg each); Cu(II) (1.5 mg); Cr(VI) (1 mg); Ta(V), Ru(III) and Pd(II) (0.2 mg each), Pt(IV) (0.15 mg); Bi(III), Au(III) and Th(IV) (0.1 mg each) and Sb(III) (0.030 mg ) are tolerated as these cause < 1% error. Fe(III), Zr(IV), Nb(V), V(V), Mo(VI), W(VI) and Ti(IV) did not interfere in the presence of respective masking agents i.e. for 1 mg of

Fe(III) and V(V), 100 mg ascorbic acid ; 1 mg of Nb(V), 4 mg sodium oxalate; 0.1 mg of Mo(VI), 5 mg of sodium dithionite; 1.5 mg Zr(IV), 1 mg of W(VI) and 0.3 mg of Ti(IV), 7 mg sodium phosphate were added prior to the addition of CHMMPB in 10 mL aqueous volume under optimum conditions of the procedure.

## 4. Conclusions

For the determination of micro-amounts of tin, the proposed method is simple, rapid, sensitive and selective; it is also free from the interference of a large number of metal ions. Therefore, the procedure assumes in view of the scarcity of better methods for determining tin. The wide applicability of the method is tested by the analysis correspond to ceco alloy, chinese speculum, argental, magnalium cast Z (Table 1). The method is also applicable for the determination of tin in gun metal and tin can samples with satisfactory results. The high reproducibility of the method is tested by performing several sets of experiments while keeping the same amount of tin metal ions in each set; the relative standard deviation of the method is 0.27%.

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