

# Spectrophotometric Determination of Tin (IV) in Solder and Brass Using 6-[(*E*)-(1,5-Dimethyl-3-Oxo-2-Phenyl-2,3-Dihydro-1*h*-Pyrazol-4-Yl)Diazenyl]-1*h*-Indole-2,3-Dione

Chinyere, Evans Eledalachi, Okenwa, Jude Chukwudi, Ukoha, Pius Oziri

Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Enugu State, Nigeria

**Abstract:** *In the present paper, a new method is proposed for the spectrophotometric determination of tin (IV) in solder and brass. The ligand, 6-[(E)-(1, 5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)diazenyl]-1H-indole-2,3-dione was synthesized by coupling diazotized 1-phenyl-2,3-dimethyl-4-aminopyrazole-5-one and 1H-indole-2,3-dione. It formed coloured complex with Sn(IV). The ligand and complex were characterized via UV, IR and NMR spectroscopy. The analytical data show that Sn(IV) formed complex, with 2:1 metal-ligand stoichiometry when reacted with the ligand respectively. Sn(IV) was determined spectrophotometrically by measuring the absorbance at 421.4 nm. Beer's law was valid between 0.34-2.81 ppm, with calibration and analytical sensitivities of 0.068 and 67.00 ppm respectively. Very few elements were found to interfere in the method. The method is quite simple and useful; its applicability has been tested by the analysis of solder and brass.*

**Keywords:** 4-aminoantipyrine; isatin; spectrophotometry; tin(IV); alloys.

## 1. Introduction

Tin is a heavy metal and has serious accumulative effect. The health scares concerning the element have been many as most of the toxic contamination in humans and animals is from foods and drinks <sup>1</sup>. Organotin compounds used in stabilizing polyvinylchloride during container-forming operations can migrate into food stuff package in such containers <sup>2</sup>. To check pollution and high risk of disturbing the chemical balance in the ecosystem, there is a lot of existing regulations to monitor the accumulation of tin and other toxic metals in the environment.

There is the "clean air act", first enacted in 1970 in the United States, to mandate levels of air pollution, including tin and other metals <sup>3</sup>. Likewise, the environmental protection agency of the United States of America (EPA) has set water quality criteria for levels of metals in both fresh and salt water systems. The American food and drugs administration regulations, permit the presence in certain food stuffs, as a result of migration (during container forming), of two organotin compounds, namely; dioctyltinSS-bis(iso-octylmercaptoacetate) and dioctyltinmaleate polymer. The concentration of either, or any combination of both may not exceed 1ppm, which represents 0.158 or 0.259 ppm of tin (as organotin), respectively in food stuff. It is necessary to achieve safe concentration levels for tin, because getting rid of it when high levels are found in the environment is however another problem <sup>3</sup>.

Many methods have been devised for the spectrophotometric determination of tin<sup>4-17, 18-20</sup>. These methods are based on the interaction of tin with organic reagents, which display redox properties. Under such conditions tetravalent tin has a greater tendency to form complexes. Most of the spectrophotometric methods possess low selectivity and are sometimes not sensitive enough.

Consequently, a search for more sensitive and selective reagents is on the rise. Reagents which form stable coloured complexes with tin on reacting in acid solutions are of particular interest.

In the work described here, we examined 6-[(*E*)-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl) diazenyl-1*H*-indole-2,3-dione, herein referred to as 'DPDD' as analytical reagent for tetravalent tin (Sn(IV)) determination. The choice of DPDD is prompted by the growing importance of the 4-aminoantipyrine based reagent and their metal complexes in coordination and analytical chemistry <sup>21-26</sup>. The reagent has an ion-discriminating ability and forms a very stable complex with tin (IV) <sup>27-30</sup>. DPDD has been synthesized and used for the antimicrobial studies of some complexes <sup>31-33</sup>, but reports in the literature concerning the analytical application to the determination of Sn(IV) was not found.

We therefore report the viability of DPDD in the spectrophotometric determination of tin(IV) in solder and brass without any extraction procedure. The optimum and fundamental conditions of Sn(IV)-DPDD complex formation have been established, as precursor to the application in samples. Although atomic absorption or emission spectroscopic methods are good for the determination involving no separation, the proposed method is useful when it is necessary to obtain quantitative information about Sn(IV) by a suitable method other than AAS.

## 2. Experimental

### 2.1 Apparatus and reagents

A UV visible spectrophotometer (model: Jenway 6305) with a quartz cuvette of 1.0 cm path length was used. Analytical grade reagents were used without further purification. A

stock solution of tin(IV) was prepared by dissolving 0.063 g of tin(IV) chloride ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) in distilled water and made up to mark in a 50  $\text{cm}^3$  volumetric flask. It was found to contain 0.0360 M tin (IV).

## 2.2 Synthesis and spectral characteristics of DPDD

DPDD was synthesized according to reported methods<sup>32-40</sup>. 0.1218 g of 4-aminoantipyrine (0.0006 M) was dissolved in 1.0  $\text{cm}^3$  of conc. HCl (37 %) in 5.0  $\text{cm}^3$  of distilled water, and was diazotized with  $\text{NaNO}_3$  solution (0.0600 g) in 20  $\text{cm}^3$  of distilled water below 5.0 °C. The resulting diazotized 4-aminoantipyrine was immediately poured into a mixture of 0.0882 g of isatin (0.0006 M) and 2.5000 g of sodium acetate (0.3050 M) in 30.0  $\text{cm}^3$  distilled water, using mechanical stirring at ice temperature. Full detail of the syntheses and spectral characteristics of DPDD and its Sn(IV) complex is available elsewhere<sup>41</sup>.

## 2.3 Preparation of the alloys (solder and brass)

1.0g of a given alloy was taken to which 25-30  $\text{cm}^3$  of aqua regia was added, and the mixture heated gently till the alloy decomposed completely. Then conc HCl was added in installments of 4.0  $\text{cm}^3$ . The solution was evaporated to dryness. The residue was dissolved in 10 M HCl (20  $\text{cm}^3$ ) and diluted to 1.0  $\text{dm}^3$  for 1000 ppm of the alloy. Lower concentrations of the solution were obtained by serial dilution. Tin concentration was determined in the solutions of the alloys using flame AAS method.

## 2.4 General procedure

An aliquot of a standard solution of tin(IV) was transferred into a 20  $\text{cm}^3$  test tube. The pH was adjusted to 1.0 with hydrogen phthalate/sodium hydroxide buffer. Distilled water was added, followed by the addition of the appropriate amount of DPDD to react under a given concentration in a total volume of 5.0  $\text{cm}^3$  for 45 minutes at 40 °C. The absorbance measurement was taken at 421.4 nm in a 1.0 cm quartz cuvette, using a mixture of the buffer and distilled water as blank.

## 3. Results and Discussion

### 3.1 Composition of Sn (IV)-DPDD complex

As reported elsewhere<sup>40</sup>, the absorption spectrum of the Sn(IV)-DPDD complex against reagent blank in ethanol, under optimum conditions showed maximum absorption at 421.4 nm for the complex. Thus all measurements were made at this wavelength. The stoichiometry of the Sn (IV)-DPDD complex was investigated by the slope-ratio method.  $7.20 \times 10^{-4}$  M solution of Sn(IV) was fixed (excess) in a reaction with varying amounts of the ligand, ranging from  $7.20 \times 10^{-5}$  to  $5.04 \times 10^{-4}$  M concentration of the ligand reacted with varying amounts of Sn(IV). The ratio of the slopes of the absorbance (at 421.4 nm) values plotted against the corresponding concentrations for the two sets of observations show that Sn(IV) to ligand (DPDD) mole ratio obtained is 2:1. The plots are shown in Figures 1 and 2 respectively.

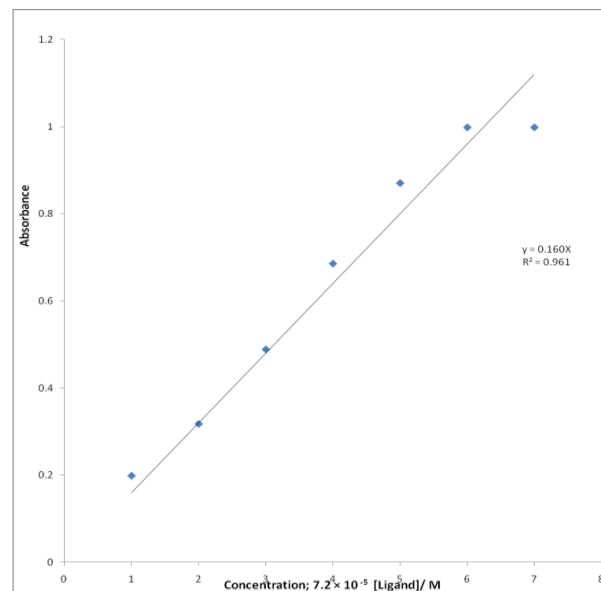


Figure 1: Slope-Ratio plot for Sn(IV) complex at Fixed metal concentration ( $7.20 \times 10^{-4}$  M)

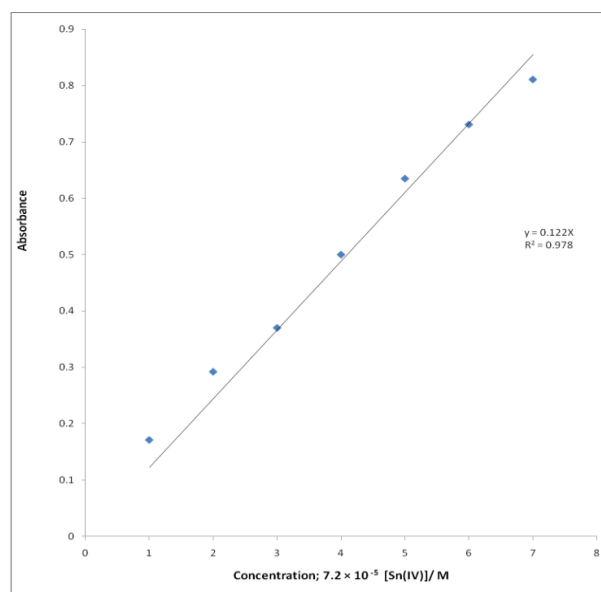
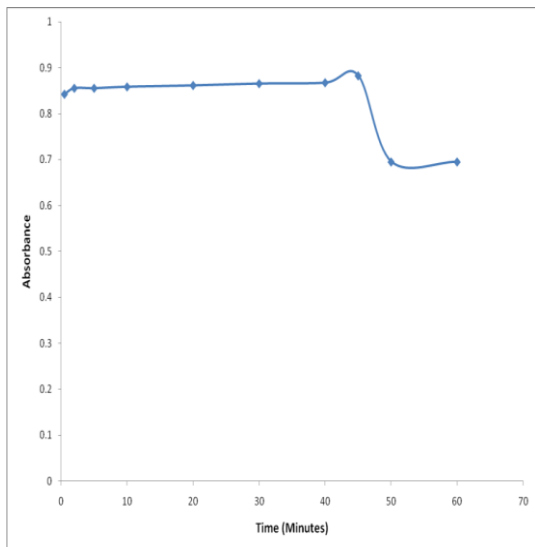


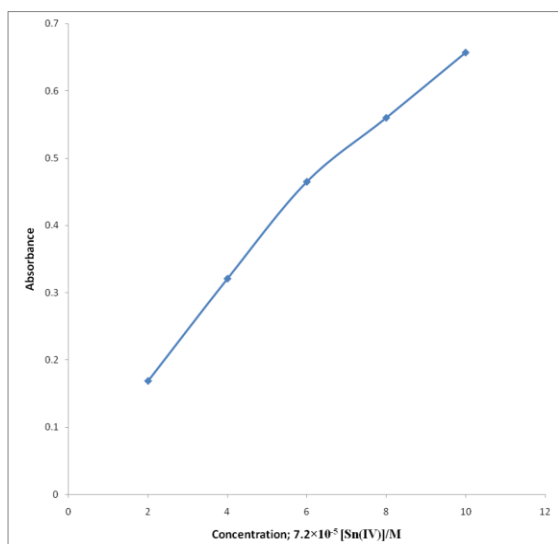
Figure 2: Slope-Ratio Plot for Sn (IV) Complex at Fixed ligand concentration ( $7.20 \times 10^{-4}$  M)

### 3.3 Effect of time on the formation of Sn(IV)-DPDD complex

The variation of absorbance with time in the formation of Sn(IV)-DPDD complex was investigated by measuring the absorbance at different intervals between 30 seconds to 70 minutes. The reaction between  $7.20 \times 10^{-4}$  M and  $3.60 \times 10^{-4}$  M of Sn(IV) and DPDD respectively exhibited maximum absorbance of 0.889 after 45 minutes of the reaction. Therefore, 45 minutes was taken as the optimum time required for the reaction to take place under the prevailing conditions, and was maintained throughout the determination of Sn(IV). The plot is shown in Fig.3.



**Figure 3:** Effect of time on the formation of Sn(IV) complex



**Figure 4:** Effect of the concentration of the reagent on the formation of Sn(IV) complex

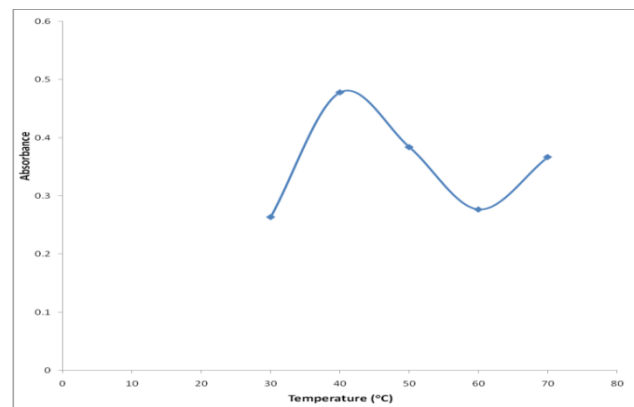
### 3.4 Effect of the concentration of DPDD on the formation of Sn (IV)-DPDD comp

Fig.4 shows the effect of DPDD concentration on the formation of Sn (IV)-DPDD complex. The influence of the DPDD concentration on the absorbance signal of the complex was studied with a fixed amount of Sn(IV) ( $1.44 \times 10^{-4}$  M) and DPDD from  $1.44 \times 10^{-4}$  to  $7.20 \times 10^{-4}$  M. The results show that absorbance increases with increasing amount of DPDD up to  $7.20 \times 10^{-4}$  M. This however suggests that the concentration of DPDD should be at least 5 times more than that of Sn(IV). Thus  $7.20 \times 10^{-4}$  M DPDD concentration was decided upon as being the required amount.

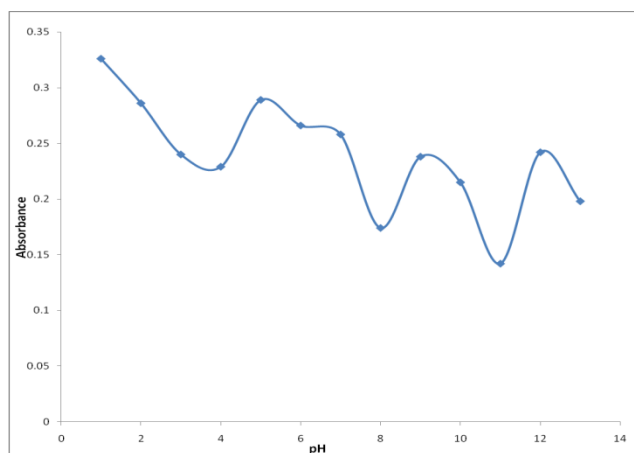
### 3.5 Effect of temperature on the formation of Sn (IV)-DPDD complex

The effect of temperature on the absorbance of Sn(IV)-DPDD complex was studied between  $30^\circ$  and  $70^\circ$  C.  $7.20 \times 10^{-4}$  M DPDD was reacted with  $1.44 \times 10^{-3}$  M Sn(IV) in a thermostated water bath for 45 minutes. The graph depicted in Fig.5 shows that the absorbance is dependent on

temperature. Maximum absorbance of 0.478 was obtained at  $40^\circ$  C and was maintained all through the determination of Sn(IV). The study on the variation of temperature on the absorbance of Sn(IV)-DPDD complex did not go beyond  $70^\circ$  C, to avoid certain physical conditions which are not within the frame work of this study.



**Figure 5:** Effect of Temperature on the Formation of Sn(IV) Complex



**Figure 6:** Effect of pH on the Formation of Sn(IV) Complex

### 3.6 Effect of pH on the formation of Sn(IV)-DPDD complex

The effect of pH on the absorption of the complex was studied at 421.4 nm by measuring the absorbance of  $1.44 \times 10^{-3}$  M Sn(IV) with  $7.20 \times 10^{-4}$  M solution of the ligand over the pH range of 1-13. A graph was plotted of absorbance values against pH (Fig.6), which show a maximum absorbance of 0.324 at pH 1.0. Throughout the studies, a potassium chloride/hydrochloric acid buffer of pH 1.0 was used. This result indicates that Sn(IV)-DPDD complex is highly acidic in nature.

### 3.7 Effect of some interfering ions on the determination of Sn(IV)

Under optimum conditions of the procedure, the selectivity of the proposed method was investigated by the determination of a fixed amount of Sn(IV) (1.99 ppm), in the presence of a series of other ions. The absorbance was compared with the absorbance of the complex in the absence of foreign ion and percentage interference calculated. The limiting value of concentration of foreign ion was taken as

that which caused an error in the absorbance corresponding to twice the standard deviation of the absorbance of the Sn(IV)-DPDD complex. The results are summarized in Table 1.0.

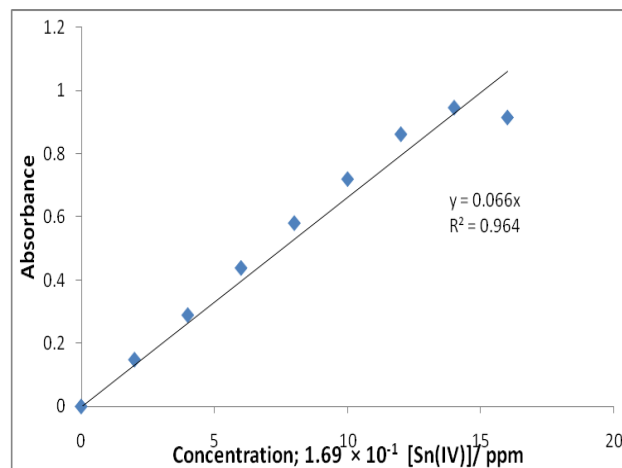
In the determination of Sn(IV)-DPDD complex, the mean absorbance for six determinations is  $0.286 \pm 12.2\%$ . The interference of Fe(III) was eliminated by reduction to Fe(II) with ascorbic acid, and subsequent addition of EDTA to mask Cu(II), Ni(II) and Zn(II).

**Table 1:** Effect of Some Interfering Ions on Sn(IV) Complex

Ion Added	Concentration (ppm)	Absorbance	Interference Level (%)
Mo <sup>6+</sup> added as Na <sub>2</sub> MoO <sub>4</sub>	1.2	0.124	-56.64
	1.5	0.135	-52.8
	1.8	0.166	-41.96
	2.1	0.08	-72.01
	2.4	0.204	-28.7
	2.7	0.07	-75.5
	3	0.106	-62.94
Bi <sup>3+</sup> added as Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	0.34	0.191	-33.22
	0.68	0.196	-31.5
	1.36	0.221	-22.73
	2.04	0.228	-20.3
	2.72	0.22	-23.1
	3.4	0.271	-52.5
	4.08	0.212	-25.9
As <sup>3+</sup> added as As <sub>2</sub> O <sub>3</sub>	1.12	0.151	-47.2
	1.4	0.158	-44.8
	1.68	0.187	-34.62
	1.96	0.201	-29.72
	2.24	0.185	-35.32
	2.52	0.24	-16.1
	2.8	0.192	-32.9
Fe <sup>3+</sup> added as FeCl <sub>3</sub>	1.2	0.116	-59.4
	1.44	0.171	-40.2
	1.68	0.038	-86.7
	1.92	0.106	-62.9
	2.2	0.212	-25.9
	2.4	0.167	-41.6
	2.64	0.222	-22.4
Cu <sup>2+</sup> added as CuSO <sub>4</sub> ·5H <sub>2</sub> O	1.08	0.234	-18.2
	1.44	0.219	-23.43
	1.8	0.241	-15.75
	2.16	0.2	-30.1
	2.53	0.2	-30.1
	2.88	0.221	-22.73
	3.24	0.175	-38.81

### 3.8 Analytical characteristics of the method

A calibration curve was prepared according to the general procedure described in the experimental, section 2.5. The Sn(IV)-DPDD complex obeys Beer's law between the concentration ranges of 0.169-2.37 ppm. The calibration curve which was constructed under the prevailing conditions is shown in Fig.7. The molar absorptivity of  $7.20 \times 10^{-4}$  M Sn(IV)-DPDD complex in ethanol was  $1.528 \times 10^3$   $\text{Imol}^{-1} \text{cm}^{-1}$  at 421.nm .



**Figure 7:** Calibration Curve of Sn(IV) Complex

The analytical sensitivity, calibration sensitivity, limit of detection and limit of quantification, as well as other analytical characteristics are summarized in Table II.

**Table 2:** Analytical characteristics of the procedures

Characteristic	Value of Sn(IV) Complex
$\lambda_{\text{max}}$ (nm)	421.4
Molar absorptivity ( $\text{Imol}^{-1} \text{cm}^{-1}$ )	1528
Calibration sensitivity, m (ppm)	0.068
Analytical sensitivity: $m/S_A$ (ppm)	67.00
Limit of detection, $C_L$ ; $3S_A$ (ppm)	0.06
Limit of quantification, $C_Q$ ; $10S_A$ (ppm)	0.023
Linear dynamic range, (ppm)	0.34 – 2.71
Coefficient of variation (%)	2.09

$S_A$  = standard deviation of the blank:

### 3.9 Application to the analysis of alloys (solder and brass)

An aliquot of the solutions of various alloys already analyzed by flame AAS was taken and the content of Sn(IV) in each case determined spectrophotometrically, under the prevailing conditions according to the general procedure. The concentration of the Sn(IV) was extrapolated from the calibration curve. Table 3 summarizes the results obtained for the determination of Sn(IV) in the various alloys with DPDD.

**Table 3:** Determination of Sn(IV) in Solder and Brass with the Reagent

Sample	Amount added (ppm)	Amount found (ppm)	Recovery (%)	RSD (n=3)
Solder I	1.794	1.215	67.73	$\pm 0.02$
Solder II	5.382	4.726	87.81	$\pm 0.01$
Solder III	8.970	7.911	88.20	$\pm 0.01$
Brass I	1.994	1.407	70.56	$\pm 0.03$
Brass II	5.982	5.037	84.20	$\pm 0.01$
Brass III	9.970	7.807	78.31	$\pm 0.01$

The above results show that the direct determination of Sn(IV) using DPDD is possible and could be more effective with simple samples. The proposed method is sensitive for tin(IV). It suffers from lack of specificity to a certain extent, which is common with other methods. For further studies, it appears however, that prior separation (solvent extraction or ion-ex-change separation) of tin(IV) may be necessary with

the proposed method for determining the tin (IV) content of solder and brass alloys.

#### 4. Conclusion

DPDD and its Sn(IV) complex have been successfully synthesized. Sn(IV) was determined after establishing the necessary parameters, and adjusting the conditions of the samples. Interferences were marked with EDTA, and absorbance measured at 421.4 nm under the optimum conditions of Sn(IV)-DPDD complex.

The applicability of the proposed method was evaluated by its application to the direct determination of Sn(IV) in solder and brass previously analyzed by flame AAS. No extraction procedure was required in the study. The proposed method has proved to be promising in the analysis of simple and complex samples. It is rapid, selective and sensitive.

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