

THIN LAYER CHROMATOGRAPHIC AND SPECTROPHOTOMETRIC ANALYSIS OF ETHYL TIN COMPOUNDS

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A procedure has been described for the separation of tetraethyl tin, tri-, di-, and monoethyl tin chlorides by thin layer chromatography on silica gel G type 60, using the mixture of ethylacetate, acetic acid and pyridine as solvent system. The quantitative estimation of each of these compounds were made possible by measuring the colour intensity in the visible region using the solution of diphenyl thiocarbazon in chloroform (pH 8.4) as colour producing reagent. R_f values were found to be 0.81, 0.53, 0.36 and 0.24 for the tetraethyl tin tri-, di-, and monoethyl tin chlorides, respectively.

INTRODUCTION

Dithizone also known as diphenylthiocarbazon is a well known reagent not only for detecting small amounts of metals but also for their quantitative determinations. Miller and co-workers [1,2] used this reagent for determination of small amount of mercury ethyl and phenyl compounds. Later on a methods was developed [3] for the qualitative and quantitative differentiation of the mixtures of triethyl tin and diethyl tin chlorides. Some authors [4,5] have used pyrocatechol violet for location of the spots on TL plates previously eluted with suitable solvent mixture and measuring the absorption at 580 nm.

A quick and sensitive method for the separation of tetraethyl tin tri-, di-, and monoethyl tin chlorides on silica gel G type 60 is reported. A spectrophotometric method has been developed for the determination of each of these compounds using dithizone as colour producing reagent. This method comprises of mixing a solution of ethyl tin compounds with that of dithizone in chloroform at pH value of 8.4. The pH has been adjusted with the buffer solution. The spectrophotometric measurements become possible since each type of the above mentioned ethyl tin compounds absorbs at 510 nm after getting separated on the TLC plate. Using this method even micro amounts of ethyl tin compounds can be detected efficiently and accurately. This method may be used for the determination of ethyl tin compounds in biocides, plastics and polymer samples.

EXPERIMENTAL

Reagents and Solutions. All the reagents used were of analytical reagent grade and no further purification was

found necessary. Silica gel used was of G-type 60 and was obtained from E. Merck, Darmstadt, W. Germany. Dithizone solution was made by dissolving 5.0 mg of the reagent in 100 ml of chloroform. This solution was then stored in dark.

For the preparation of the borate buffer solution, 19.00 g of sodium borate decahydrate and 10.00 g of boric acid were dissolved in 1000 ml of distilled water. This yielded a buffer solution of pH 8.4.

Preparation of Ethyl Tin Compounds. The method of Pope [8] was used for the preparation of the tetraethyl tin. Mono-, di-, and triethyl tin compounds were prepared as described by Dillard and Gilman [9,10]. The melting points of triethyl tin chloride and diethyl tin chloride found to be 15°C and 89°C, respectively are in very good agreement with the previously reported values [7]. Similarly, the boiling point values of 175°C and 196°C for the tetra ethyl tin and monoethyl tin chloride, respectively, are comparable to the earlier literature [7].

Chromatographic Separation of Ethyl Tin Compounds. The separation of the four ethyl tin compounds were effected on the 20 x 20 cm standard Desaga plates with a coat of 0.5 mm thick silica gel using a mixture of ethyl acetate, acetic acid and pyridine in the volume ratio of 0.8:1.5:0.5 as the mobile phase. 0.01 ml, 0.04 ml and 2.04 ml of 2.5% solution of the ethyl tin compounds in ethyl acetate was applied to the TLC plates using Desaga microdozer 80. The development was carried out in covered glass tank at room temperature in subdued light. Ascending development to a height of 15 cm normally-occurred in 60 minutes. The spots were located by spraying the dithizone solution.

Spectrophotometric Determination of Ethyl Tin Compounds. For the spectrophotometric determination of the four above mentioned ethyl tin compounds, the four different red spots which appeared on the TLC plate after spraying 0.05% solution of dithizone were scratched separately. The silica scrap of each spot was then extracted several times with chloroform, filtered and concentrated. The concentrate was then treated with the aqueous borate buffer solution, shaking thoroughly, and left for few minutes for complete development of red colour. The absorbance of this red solution was measured at 510 nm using a Hitachi Model 323 spectrometer. From the absorbance, the concentration of ethyl tin compound was determined using the calibration plot.

The Calibration Plot. For each of the four ethyl tin compounds, a separate calibration plot was made in the following manner:

A stock solution of the ethyl tin compound was made by dissolving 50 mg of the compound in 100 ml of chloroform. 0.10, 0.15, 0.20, 0.30, 0.35, 0.40, 0.45, 0.50 and 0.60 ml of this stock solution was drawn out in different 10 ml volumetric flasks each containing 0.5 ml of 0.005% dithizone solution and 1.00 ml of the borate buffer solution. The volume was made up to the mark by addition of chloroform. Each flask was then shaken thoroughly and left for five minutes for complete development of the red colour. The absorbance of each solution was then measured at 510 nm in a matched set of 1 cm thick quartz cell. The absorbance was then plotted as a function of concentration of the ethyl tin compounds. In all the four cases linear plots were obtained in the concentration range of 0.5-8.0 $\mu\text{g}/\text{ml}$ of the ethyl tin compound.

RESULTS AND DISCUSSION

The separation of tetra ethyl tin tri-, di-, and monoethyl tin chlorides were made effective by thin layer chromatography using suitable solvent mixture of ethylacetate, acetic acid and pyridine. The R_f values are given in Table 1. Table 1 shows that R_f value increases as the number of alkyl groups attached to tin atom increases. Further, each of the ethyl tin compounds was quantitatively determined by spectrophotometric method. This method involved running a spectrum of ethyl tin compounds in chloroform in borate buffer solution and developing colour with dithizone. A typical spectrum is shown in Fig. 1. It is evident from the figure that the maximum absorption of such a system occurs at 510 nm. The extinction coefficients for the different tin compounds are also reported in Table 1. These values of extinction coefficients suggest the formation of certain six co-ordinate complexes of ethyl tin compounds with dithizone. It may be emphasized that the red yellow colour does not appear without addition of

Table 1. R_f values and molar extinction coefficients of the ethyl tin compounds.

Compounds	R_f values	Colour under UV light	Molar extinction coefficient (ϵ)
Tetraethyltin	0.81	Light orange	—
Triethyltinchloride	0.53	Light orange	3.88×10^3
Diethyltinchloride	0.36	Light orange	3.99×10^3
Monoethyltinchloride	0.24	Red orange	4.09×10^3

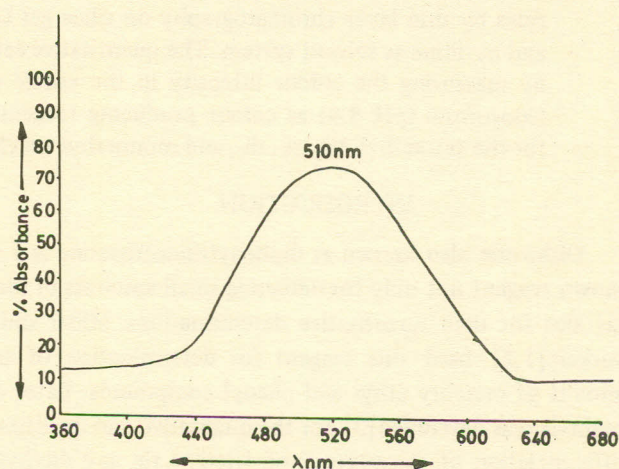


Fig. 1. Absorption spectrum of Ethyltin compounds and dithizone.

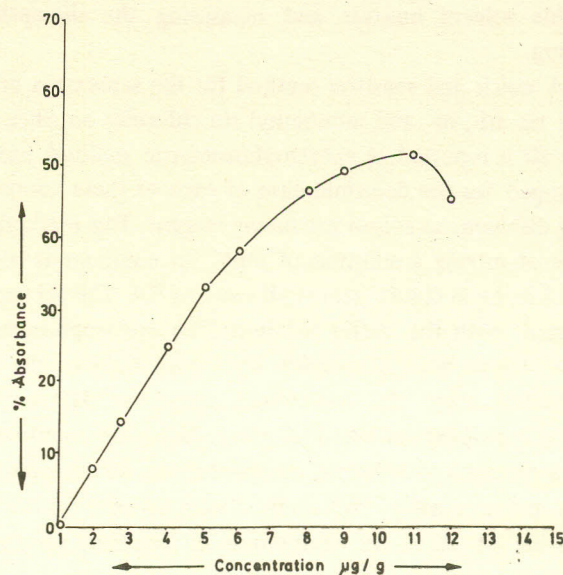


Fig. 2. Calibration plot for triethyltin ethyltin compound.

the borate buffer solution at low concentrations. This observation is in accordance with the fact that dithizone occurs in

tautomeric forms of thio-keto and thiol in the pH range of 4.7-12.0

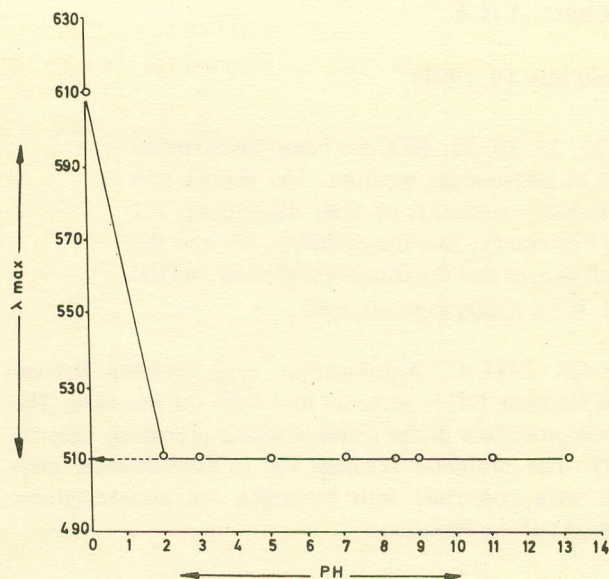
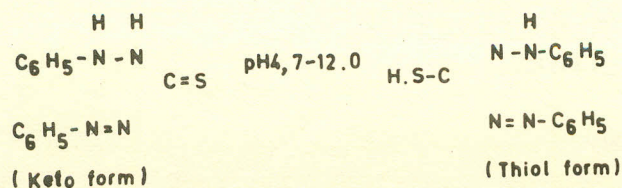


Fig. 3. Effect of pH on λ_{\max} of triethyltin.

The effect of pH on λ_{\max} was investigated for triethyl tin compound. This is illustrated in Fig. 3. The complex shows maximum absorption in the pH range of 3.0-13.0 For pH less than 3, dithizone-triethyl tin complex is unstable and decomposes to its components immediately as evidenced by

the appearance of dithizone peak at 610 nm in the visible spectrum.

Finally, the method is extendingly useful as it can be applied directly for determination of alkyl tin stabilizers in the polymer samples. A previous method[6] requires the reaction of such stabilizers with Grignards reagent before they could be estimated. Also this method does not evaluate individual alkyl tin compounds. The method reported in the present work is rather simple, more convenient and is applicable for evaluation of individual, as well, as collective alkyl tin compounds.

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REFERENCES

1. V.L. Miller, D. Polley and C.J. Gould, *Anal. Chem.*, **23**, 1286 (1951).
2. V.L. Miller and D. Polley, *Anal. Chem.*, **24**, 1622 (1952).
3. W.N. Aldridge and J.E. Cremer, *Analyst*, **82**, 37 (1957).
4. W.H. Oidich, *Dtsch. Lebensun. Rundsch Vienna Aust.* **72**, 421 (1976).
5. J. Koch and K. Figge, *Chromatography*, **109**, 89 (1975).
6. B.W. Rockett, M. Hedlington and W.R. Poyner, *Polymer, Science*, **18**, 745 (1974).
7. R.K. Ingham, S.D. Rosenberg and H. Gilman, *Chem. Reviews*, **60**, 459 (1960).
8. W.J. Pope and S.J. Peachey, *Proc. Chem.Soc.*, **19**, 290 (1903).
9. C.R. Dillard, E.H. McNeill, D.E. Simmons and J. B Yeldell *J.Am.Chem.Soc.*, **80**, 3607 (1958).
10. H. Gilmar L.A. Gist, *J. Org. Chem.*, **22**, 368 (1957).