



The Chemical Analysis of Triphenyltin(IV)*p*-hydroxybenzoate by SquareWave Voltammetry

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ABSTRACT

The method validation of chemical analysis for triphenyltin(IV) *p*-hydroxybenzoate compound by squarewave voltammetry has been performed. This compound has successfully been synthesized, fully characterized and applied as anticorrosion inhibitor. The squarewave voltammetry was chosen as this method has excellent sensitivity and the chemical analysis was easily conducted. The validation parameters used were linearity, limit of detection, precision and sensitivity, for this purpose the measurements of standard solution of triphenyltin(IV)*p*-hydroxybenzoate prepared were varied its concentrations. The concentrations used were 1.6×10^{-4} M; 3.2×10^{-4} M; 4.8×10^{-4} M; 6.4×10^{-4} M; and 8.0×10^{-4} M. The measurements were set at conditions of potential windows of +700 mV to +1,400 mV, scan rate potential of 100 mV/s, working electrode Au, auxiliary electrode Pt, reference electrode Ag and supporting electrolyte used was NaCl solution 0.02 M in H₂O-DMSO (3 : 1). The results showed that the method validation analysis gave regression linear equation of $i_p = 6.1857C + 7.945$, coefficient correlation (*r*) 0.995128, standard deviation percentage (%RSD) 1.96%, limit of detection (LoD) 0.099 mM and sensitivity (S) 6.1857 μ A/mM

Keywords: method validation, square-wave voltammetry, triphenyltin(IV)-*p*-hydroxybenzoate.

INTRODUCTION

Organotin(IV) compounds are continuous to attract attention not only due to their interesting structural features but also the wide spectra of their strong biological activities¹⁻³. Their activities are mainly determined by the number and the type of organic ligand attached to the Sn metal center^{1,3}. These compounds and their derivatives have been widely used and known in many biological activity tests such as antifungal⁴⁻⁷, anticancer and

antitumour⁸⁻¹², antiviral¹³, antibacterial^{14,15} and anticorrosion¹⁶⁻²⁰.

The derivatives of triphenyltin(IV) compounds with ligands of *o*-, *m*-, and *p*-hydroxybenzoic acids have successfully been synthesized and have been tested their anticancer and anticorrosion activity^{12,21}. In the anticorrosion test of triphenyltin(IV)-*p*-hydroxybenzoate, it was able to inhibit the corrosion on the hard rolled plate (HRP) steel with concentration of 100 ppm with

percentage efficiency inhibition (%EI) of 80.41%²¹. The structure of this compound is in Fig. 1. This compound was prepared by the reaction of triphenyltin(IV) hydroxide and *p*-hydroxybenzoic acid with methanol as solvent and temperature reaction of 60°C and reflux times of 4 h. similar to analogous compounds previously prepared^{11,12,20,21}.

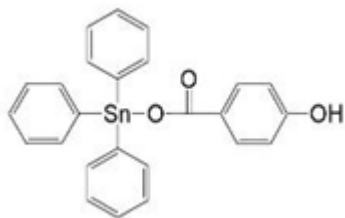


Fig. 1. Structure of triphenyltin(IV)-*p*-hydroxybenzoate

Based on the application of this compound so far, in the future triphenyltin(IV) *p*-hydroxybenzoate and other derivatives may be produced in the large scale and will be extensively used in the environment. However, the analysis method to trace and detect the presence of this compound and similar compounds in the environment is yet available. Thus, the analysis method to overcome the problem that may arise has to be prepared to study the behaviour of these compounds. The analyses of the tin metal and other heavy metals have been performed by voltammetry method²². Voltammetry is an analysis method which rapidly grows compare to other methods as it has some advantages such sensitivity, selectivity, the simple instrument and the ease of the analysis procedure²³. Some applications of voltammetry are in the analyses of environment, pharmacy, the synthesis of coordination and organic compounds²⁴.

In square wave voltammetry, the pulse is given to working electrode in the form of symmetrical square on the base potential like stairs. The advantage of this voltammetry is its high sensitivity and very fast scan rate²². The current is measured twice in one-cycle square wave, which are at the end of forward pulse and at the end of back pulse²². Therefore, in this paper, we reported the new method of voltammetry analysis for triphenyltin(IV)-*p*-hydroxybenzoate compound in order to be useful for further application in the future.

EXPERIMENTAL

Materials

Triphenyltin(IV)-*p*-hydroxybenzoate was available in our laboratory and has been previously prepared and carefully characterized by some spectroscopy techniques, *aqua pure water* obtained from the laboratory of National Agency of Drugs and Food Controls, Bandar Lampung, Indonesia, sodium chloride (NaCl) and dimethylsulphoxide (DMSO, (CH₃)₂SO) was obtained from MERCK and were used as received. ER 644 integrated potentiostat DAQ with three electrode system was used where the gold as working electrode, silver wire as reference electrode, and platinum as counter electrode.

Preparation of Solution

Triphenyltin(IV)-*p*-hydroxybenzoate solution (10⁻³ M)

12.75 mg of triphenyltin(IV)-*p*-hydroxybenzoate was weight out and dissolved by stirring with 6.25 ml DMSO, and was added with *aqua pure water* in 25-ml volumetric flask, to give concentration of triphenyltin(IV)-*p*-hydroxybenzoate 1 x 10⁻³ M. The concentrations of 1.6 x 10⁻⁴ M; 3.2 x 10⁻⁴ M; 4.8 x 10⁻⁴ M; 6.4 x 10⁻⁴ M; and 8.0 x 10⁻⁴ M were then prepared from the solution stock, each concentration was prepared in 10 ml.

Supporting electrolyte solution (NaCl 0.02 M)

29.25 mg of NaCl was weight out and dissolved with 50 ml *aqua pure water* in volumetric flask to give NaCl solution NaCl 0.1 M. 2 ml of NaCl 0.1 M was taken and diluted to 10 ml with volumetric flask to give NaCl solution of 0.02 M.

Measurement of Blank Solution with square wave voltammetry

Blank solution was prepared by mixing 2.5 mL DMSO and 7.5 ml *aqua pure water* in 10-ml volumetric flask, and was homogenized. The measurement was performed by pouring 2 ml of blank solution in 2.5 ml erlenmeyer and was added with 0.5 mL NaCl 0.02 as supporting electrolyte. Then the voltammogram was measured at potential of + 700 mV to +1400 mV.

Measurement of voltammogram triphenyltin(IV)-*p*-hydroxybenzoate with square wave voltammetry

The solutions of triphenyltin(IV)-*p*-hydroxybenzoate with concentration variations of 1.6×10^{-4} M; 3.2×10^{-4} M; 4.8×10^{-4} M; 6.4×10^{-4} M; and 8.0×10^{-4} M with supporting electrolyte NaCl 0.02 M were measured at potential window of +700 mV to +1400 mV. Each concentration was measured for 5 times. The similar procedure in the measurement of blank solution was performed for each concentration of this solution.

The statistical analysis (Method Validation)

The data obtained were then evaluated their statistical parameters which include linearity, precision, limit of detection and sensitivity.

Linearity

The determination of linearity was done by measuring each standard solution containing triphenyltin(IV)-*p*-hydroxybenzoate with certain concentration with square wave voltammetry for 10 times. The calibration curve was obtained by measuring the peak current of the standard solution. The current response from voltammogram for each analysis to the standard solution was then plotted against concentration. The calibration curve was then calculated with regression linear equation ($y = a + bx$) and the linearity was expressed by correlation coefficient (r).

Precision

The precision was determined using the concentration values of the current obtained by calibration curve. The values of mean, standard deviation (SD) and relative standard deviation percentage (%RSD) were then calculated²⁵. The %RSD was determined using the Equation 1²⁶.

$$\% RSD = \frac{SD}{x} \times 100\% \quad (1)$$

Limit of Detection (LoD)

Limit of detection was determined by the use of regression linear on calibration curve. Based on the measurement, the LoD was calculated using the Equation 2²⁶.

$$LD = \frac{3 \times SD}{b} \quad (2)$$

Sensitivity

Sensitivity was determined by analyzing the slope of calibration curve.

RESULT AND DISCUSSIONS

Voltammogram of standard solution triphenyltin(IV)-*p*-hydroxybenzoate

The voltammogram of standard solution triphenyltin(IV)-*p*-hydroxybenzoate with square wave voltammetry is shown in Figure. 2.

The voltammogram of the standard solution for triphenyltin(IV)-*p*-hydroxybenzoate due to the increase of oxidation potential given by the voltammogram, the oxidation peak current (i_p) and oxidation peak potential (E_p) can be identified. The data of oxidation peak current value (i_p) and oxidation peak potential (E_p) of the standard solution measured were tabulated on Table 1 and 2.

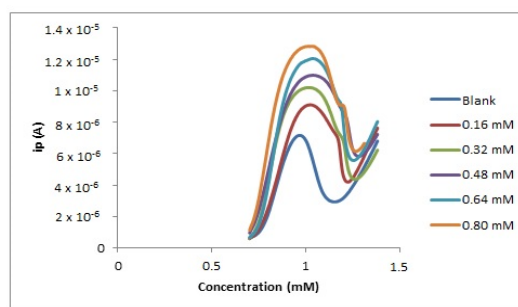


Fig. 2. Voltammogram of concentration variations of standard solution triphenyltin(IV)-*p*-hydroxybenzoate with square wave voltammetry.

Based on Table 1 and 2, the increase of oxidation peak current of standard solution triphenyltin(IV)-*p*-hydroxybenzoate was affected by the concentration of the solution used, where the increase of peak current was higher with the increase of solution measured²². Thus, it can be said that the potential scan rate is directly proportional with peak current obtained. This is fit with the Randles-Sevcik Equation (Eq. 3) where i_p is peak current (A), A is electrode wide (cm^2), D is diffusion coefficient (cm^2/s), C is concentration (mole/cm^3) and v scan rate (V/s)²⁷.

The values of peak potential of blank solution with peak potential of standard solution have to be different. To ensure that the values of E_p of blank solution and standard solutions are different,

Table. 1: The value of E_p standard solution triphenyltin(IV)*p*-hydroxybenzoate.

No	E_p (Volt)					
	0 M	1.6×10^{-4} M	3.2×10^{-4} M	4.8×10^{-4} M	6.4×10^{-4} M	8.0×10^{-4} M
1	0.97	1.01	1.01	1.035	1.035	1.015
2	0.97	1.01	1.01	1.03	1.035	1.015
3	0.975	1.015	1.01	1.035	1.02	1.035
4	0.975	1.01	1.01	1.035	1.035	1.02
5	0.975	1.02	1.015	1.035	1.035	1.035
Mean	0.97	1.013	1.011	1.034	1.032	1.024
RSD (%)	0.3	0.441	0.221	0.216	0.650	1.001

Table. 2: The value of i_p standard solution triphenyltin(IV)-*p*-hydroxybenzoate.

No	i_p (μ A)					
	0 M	1.6×10^{-4} M	3.2×10^{-4} M	4.8×10^{-4} M	6.4×10^{-4} M	8.0×10^{-4} M
1	7.17	9.09	10.06	10.85	11.88	12.66
2	7.45	9.09	10.09	10.91	11.91	12.67
3	7.72	9.09	10.14	10.92	11.91	12.71
4	7.92	9.1	10.19	10.93	11.99	12.82
5	8.13	9.11	10.2	10.99	12.05	12.83
Mean	7.678	9.096	10.136	10.92	11.948	12.738
RSD (%)	4.9	0.098	0.602	0.458	0.587	0.641

the statistical test was performed using the hypothesis test (F test). It was carried out by comparing the values of F calculation and F from the table, if $F_{\text{calculated}} < F_{\text{Table}}$ then the hypothesis is accepted. Based on the statistical test, the result was $F_{\text{calculated}} > F_{\text{Table}}$ meaning that the hypothesis was rejected or there are significant differences between values of E_p of standard solution and blank solution, so the samples were not from the same variance.

Method Validation

Method validation used including parameters of linearity, limit of detection, precision and sensitivity.

Linearity

Linearity relates to the ability of analysis method to give response directly and proportional to the concentration of analyte in the sample²⁸. This test was performed to know the standard ability to detect the analyte in the sample²⁵. In this test, it can

be done by creating the calibration curve of standard solution towards the response of measurement results. The regression linear equation and correlation obtained from the calibration curve was used to evaluate the relationship between concentration and current produced. The regression linear produced from the measurement of the standard solution with variation concentrations is shown in Figure. 3.

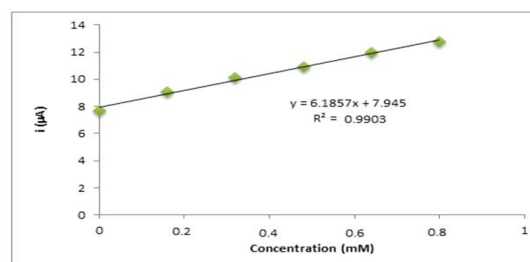


Fig. 3. The calibration curve of triphenyltin(IV) *p*-hydroxybenzoate using square wave Voltammetry.

The linearity test produced the calibration curve with regression linear of $y = 6.1857x + 7.945$ or $i_p = 6.1857 C + 7.945$ with coefficient correlation (r) = 0.995128. Based on these data, 99% of diversity on y values can be explained by the linearity relationship with x^{29} . Therefore, the method applied in this work can be used to analyze the derivatives of organotin(IV) compound with sensitivity of 6.1857 $\mu\text{A}/\text{mM}$.

Precision

Precision relates to the proximity of independent test result obtained under the condition used. The method which a good precision is shown by the value of relative standard deviation (RSD) < 5%²⁶. In this work, the result analysis on the blank sample using this method, the relative standard deviation of this compound was below 5%, *i.e.* 1.96%, thus the RSD of the standard solution used in this work was very good.

Table. 3: The values of r , % RSD, SD and LoD of triphenyltin(IV)-*p*-hydroxybenzoate.

Standard Solution	r	% RSD	SD	LOD (mM)
Triphenyltin (IV)- <i>p</i> -hydroxybenzoate	0.995128	1.96%	0.205091	0.099

Limit of Detection

Limit of detection is the smallest concentration which still can be detected by the instrument. The result of measurement in this work is presented in Table 3.

Method validation of analysis needs to be done in order to ensure and to confirm that the method used was suitable for the analysis. Referring to association of official analytical chemists (AOAC), the data obtained with validation parameter done in this work showed that the analysis performance was suitable for the purpose of the work²⁹.

Sensitivity

Sensitivity relates to the ability of analysis procedure to show the small differences in concentration. It is the ratio of potential increase for each analyte concentration increase²⁶. Based on the result of regression linear in this work, the sensitivity was 6.1857 as sensitivity corresponds to the slope on the regression linear equation.

CONCLUSION

The squarewave voltammetry method has successfully been used to analyzed the triphenyltin(IV)-*p*-hydroxybenzoate. The method validation data were successfully obtained.

Therefore the used of this compound for further application either it is used as anticancer drug or anticorrosion inhibitor or other biological activities may be determined its limit and its analysis in the environment may be determined.

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