2. EXPERIMENTAL AND RESULTS

2.1 Equipments

(1) CHNS/O Analyzer 2400 , Perkin Elmer

(2) FT-IR Spectrophotometer , Nicolet 510

(3) Gas Chromatography-Mass Spectrometer QP 2000 , Shimadzu

2.2 Chemicals

Manufactured by Fluka Chemic Buchs, Switzerland.

1. 1- Chlorobutane (n – Butyl chloride), $CH_3(CH_2)3Cl$, lab grade.
2. Stannic chloride anhydrous, $SnCl_4$, GPR
3. Sodium peroxide, Na_2O_2, puriss
4. Magnesium turnings, lab grade
5. Tri - n – Octylphosphine oxide, $C_{24}H_{51}OP$, AR

Manufactured by BDH Chemical Ltd., England.

1. Toluene, C_7H_8, Analar
2. Nitric acid 65%, HNO_3, GR
3. Petroleum ether 40-60°C, lab grade
4. Sulfuric acid 96%, GR

Manufactured by E. Merck, Darmastadt, Germany.

1. Calcium chloride , $CaCl_2$, lab grade
2. Ethanol absolute, C_2H_5OH, GR, 99.8%
3. Diethyl ether anhydrous, $(C_2H_5)_2O$, GR
4. L (+) Ascorbic acid, $C_6H_8O_6$, GR

5. Sodium hydrogen carbonate, $NaHCO_3$, GR

Manufactured by May and Baker Ltd., Dagenham, England.

1. Sodium in liquid paraffin, Lab Grade
2. Starch powder, lab grade
3. Aluminum powder, AR

Manufactured by Carlo Erba.

1. Sodium hydroxide pellets, NaOH, GR
2. Potassium iodide, KI ,AR
3. Potassium hydroxide, KOH, AR
4. Sodium sulphate anhydrous, Na_2SO_4, AR

Manufacture by J.T. Baker.

1. Acetone, $(CH_3)_2CO$, Analar
2. Hydrochloric acid, HCl 37%, GR
3. Arsenic trioxide, As_2O_3, AR

Manufactured by Unilab, Australia.

1. Lithium chloride, LiCl, AR
2. Sodium chloride, NaCl, AR

Manufactured by Ichimaru, Japan.

1. Iodine resublimed, AR

Cassiterite (SnO_2) was obtained from The Mineral Resource Department Region 3 (Chiang Mai)

2.3 Preparation of solution for the determination of tin in tin compounds.[21, 33]

2.3.1 Standard 0.1 N iodine solution

Dissolve 20 g of iodate - free potassium iodide, AR, in 30–40 mL of water in 1-Litre volumetric flask. Weigh out about 12.7 g of resublimed iodine on a watch glass on a rough balance, and transfer it by means of a small dry funnel into the concentrated potassium iodide solution. Insert the glass stopper into the flask and shake in the cool until all the iodine has dissolved. Allow the solution to acquire room temperature, and make up to the mask with distilled water, kept in a cool, dark place.

2.3.2 Standardization of 0.1 N iodine solution by 0.1 N arsenious oxide (As_2O_3).

Weighs out accurately about 2.5 g of finely powdered, AR, arsenious oxide, transfer to a 400-mL beaker, and dissolve it in a concentrated solution of sodium hydroxide, prepared from 2 g of ion-free sodium hydroxide, AR, and 20 mL of water. Dilute to about 200 ml., and neutralize the solution with hydrochloric acid, using a strip of litmus paper as indicator. When the solution is faintly acid, remove the litmus paper by means of a stirring rod and carefully rinse both the rod and the paper. Transfer the contents of the beaker quantitatively to a 500- mL volumetric flask, add 2 g of pure sodium bicarbonate, and when all the salt has dissolved, dilute to the mark.

Measure out from a burette 25.0-mL of arsenite solution into a 250-mL flask, add 25-50 mL of water, 5 g of sodium bicarbonate, and 2 L. of starch solution. Swirl the solution carefully until the bicarbonate has dissolved. Then titrate slowly with the iodine solution, contained in a burette, to the first blue color

Calculate the normality of the iodine solution. A 0.1 N solution of arsenite oxide contains 4.946 g. As_2O_3 per Liter. In this experiment the weigh of is As_2O_3 2.4902 g. so the concentration of As_2O_3 is 0.1007 N and the results of standardization were shown in Table 2.1. From the result concentration of iodine solution is 0.1004 N.

Table 2.1 standardization of I_2 solution 0.1 N

Titration	Volume of I_2 solution (mL)
1	50.20
2	50.15
3	50.15
Mean	50.17

2.3.3 Preparation of 0.5 N iodine solution.

Dissolve 100 g of iodate-free potassium iodide, AR, in 30-40 mL of water in 1-Liter volumetric flask. Weigh out about 63.5 g of crystal iodine transfer into the concentrated potassium iodide solution, and shake in the cold until it has dissolved. Allow the solution to acquire room temperature, and make up the mask with distilled water.

2.3.4 Standardization of 0.1 N iodine solution by 0.5 N arsenious oxide (As_2O_3).

Weigh out about 12.5 g of As_2O_3 and prepare 0.5 N As_2O_3 like the method in 2.3.2. In this experiment the weigh of As_2O_3 is 12.4003 so that concentration of As_2O_3 solution is 0.5003 N. The results of standardization of 0.5 N iodine solution were shown in Table 2.2. From the result the concentration of iodine solution is 0.5033 N

Table 2.2 standardization of I_2 solution 0.5 N

Titration	Volume of I_2 solution (mL)
1	49.05
2	50.00
3	50.05
Mean	49.70

2.4 Preparation of solutions for synthesis of bis(tributyltin) oxide.

(1) Preparation of 50% NaOH solution.

Weight 50 g NaOH and dissolve in 100 mL distilled water

(2) Preparation 5% quinine (w/v)

Weight 5 g of quinine and dissolve 100 mL HCl: H_2O (1:1)

(3) Preparation of 5 % ascorbic acid (w/v)

Weigh 5 g of ascorbic acid and dissolve in 100 mL distilled water

(4) Preparation of 5% tri –n- octylphosphine oxide, TOPO

Dissolve 5 g of TOPO in 100 mL toluene and add 2-3 ml of 6 M HCl

2.5 Physical measurement of organotin compounds.

2.5.1 Infrared spectroscopy

The IR spectra of organotin compounds were recorded by smearing the sample on the NaCl plate and detecting in the range 4000-400 cm^{-1} on FT-IR spectrometer, Nicolet 510. The equipment was calibrated by polystyrene film.

IR spectra were recorded for all products, which obtained in each step in the preparation of bis(tributyltin) oxide. The results were shown in Figure 2.5-2.12.

2.5.2 Determination the percentage of carbon and hydrogen in organotin compounds

The percentages of carbon and hydrogen in organotin compounds were carried out by CHNS/O Analyzer as results were shown in Table 2.3.

2.5.3 Determination the percentage of tin in organotin compounds by iodometry [35-37]

Weigh the sample 0.3 – 0.5 g. transfer to flask 500-ml., add mixture of concentrate nitric acid and sulfuric acid (1:1) 60 ml. and digest on hot plate until brown gas was appeared about 6 hour. The sample was cooled, add distilled water 150 ml. and hydrochloric acid 60 ml. Add 5 g of aluminum powder to reduce Sn(IV) to Sn(II) under carbon dioxide atmosphere by using 10% sodium hydrogen carbonate as show in Figure 2.6. When the reduction complete, cool down to 15 - 20°C. Add 1% starch solution 5 ml. and titrate with iodine standard solution 0.1004 N through permanent blue. (In the titration must add a little of sodium hydrogen carbonate all time to produce carbon dioxide.) The results of this experiment were shown in Table 2.4

Calculation the percentage of tin

From the factor

1 ml of 0.1 I_2 solution = 0.005935 g. of Sn

There for

$$\%Sn = \frac{0.005935 \times N \times V \times 100}{0.1 \times \text{wt.sample (g)}}$$

N = concentration of I_2 solution (0.1004 N)

V = volume of I_2 solution in titration to end point.

2.5.4 Calculation of the boiling points of organotin compounds [35]

The boiling point of organotin compounds in this experiment could not determine under atmosphere pressure. Because of their boiling point are elevated temperature and they are decomposed at elevated temperature but may be determine by diminishing the pressure on its surface, it is possible to determine at a lower temperature.

Estimation of boiling point of organotin compound

One useful relationship between pressure and boiling point is given in equation 2-1, where P is the pressure over the liquid and T is the boiling point at this pressure. In this equation both boiling temperatures are expressed in degrees Kelvin (K = $^{\circ}$C + 273) and $bp(n)$ is normal boiling point. The boiling of organotin compounds were shown in Table 2.5

$$\log\left(\frac{760}{P}\right) = 5.46\left(\frac{bp\,(n)}{T} - 1\right) \quad \text{--------------- (2-1)}$$

2.5.5 Identify the structure of organotin compounds by Mass spectrometry

The mass spectrum of organotin compounds were recorded by direct insertion technique .The results were shown in Figure 2.17-2.18

2.6 Preparation of bis(tributyltin) oxide by Grignard reaction. [3, 8, 22-26]

The preparation of bis(tributyltin) oxide has three steps, firstly tetrabutyltin was prepared by Grignard method, secondly tributyltin chloride was prepared by disproportion reaction, and thirdly bis(tributyltin) oxide was prepared by alkaline hydrolysis. As see in the following equation. (2-2 – 2-5)

$$4\ BuCl + 4\ Mg \longrightarrow 4\ BuMgCl \text{ ------------------------- } (2\text{-}2)$$

$$4\ BuMgCl + SnCl_4 \longrightarrow Bu_4Sn + MgCl_2 \text{ ----------------- } (2\text{-}3)$$

$$3\ Bu_4Sn + SnCl_4 \longrightarrow 4\ Bu_3SnCl \text{ ---------------------- } (2\text{-}4)$$

$$2\ Bu_3SnCl + 2\ NaOH \longrightarrow (Bu_3Sn)_2O + 2\ NaCl \text{ -------- } (2\text{-}5)$$

2.6.1 Preparation of tetrabutyltin, Bu_4Sn [22,27]

Weigh 24 g (1mol) magnesium turning transfer to a tree-necked flask equipped with a stirrer, reflux condenser and a graduated dropping funnel (Figure 2.1). A mixture of n-butyl chloride and dry ethyl ether [23] (10 mL of total of 92.5 g, 1 mol dissolved in 100 mL of absolute ether) was added with a crystal of iodine. The reaction was initiated by slight warming. After initiation, 100 mL of ether was added and the remainder of the n-butyl chloride-ether mix was added as rapidly as possible to maintain rapid reflux. After the addition was complete, the mixture was heated to gentle reflux for ½ hour to 1 hour at a temperature of about 36 °C. Absolute toluene 100 ml. was added and heating was continued at a temperature within the range 36 -110 °C. until the ether was removed by distillation. Anhydrous stannic chloride (27.2 mL, 0.235 mol in 100 mL of absolute toluene) was then added rapidly and the temperature increased. After 2-3 hour of heating above 100 °C. And after the distilling head vapour temperature had reached 110°C., the heating was stopped and the mixture was cooled. The cooled mixture was filtered and the filter cake was washed with toluene. Washings and filtrate were stripped of toluene and the organotin were fractionated. The product was mainly n-Bu_4Sn with small amounts of n-Bu_3SnCl and n-Bu_2SnCl_2. The crude Bu_4Sn was distillate by reduces pressure distillation, the colourless liquid distillate was kept at 106-118°C /0.7 mmHg. But in this experiment the main product was n-Bu_3SnCl, which was confirmed by IR spectra as shown in Figure 2.8 and by the percentage of carbon and hydrogen from analysis; found: C=45.20, H= 8.67; calcd: C=55.36, H=10.45 for $(C_4H_9)_4Sn$, calcd. : C=44.27, H=8.36 for $(C_4H_9)_3SnCl$ (Table 2.3).

Consideration the preparation of n-Bu_4Sn step by step as seen in following equations. It was found that the main product might be n-Bu_3SnCl if the reaction was not complete.

$$BuMgCl + SnCl_4 \longrightarrow BuSnCl_3 + MgCl_2 \text{ -----------(2-6)}$$

$$BuSnCl_3 + SnCl_4 \longrightarrow Bu_2SnCl_2 + MgCl_2 \text{ -----------(2-7)}$$

$$Bu_2SnCl_2 + SnCl_4 \longrightarrow Bu_3SnCl + MgCl_2 \text{ -----------(2-8)}$$

$$Bu_3SnCl + SnCl_4 \longrightarrow Bu_4Sn + MgCl_2 \text{ -------------- (2-9)}$$

From equation 2-9 if the reaction was not complete, the main product might be Bu_3SnCl. So Bu_3SnCl could be prepared directly by Grignard method.

2.6.2 Preparation of tributyltin chloride, Bu_3SnCl [25,27]

Tributyltin chloride can be prepared by Grignard method as shown in equations 2-2 and 2-10.

$$3\ BuMgCl + SnCl_4 \longrightarrow Bu_3SnCl + 3\ MgCl_2 \text{ ----------- (2-10)}$$

Weigh 12 g (0.5 mol) magnesium turning transfer to a tree-necked flask equipped with a stirrer, reflux condenser and a graduated dropping funnel, (Figure 2.1). A mixture of n-butyl chloride and dry ethyl ether 53 mL (46.25 g, 0.5 mol dissolved in 50 mL of absolute ether) was added with a crystal of iodine. The reaction was initiated by slight warming. After initiation, 50 mL of ether was added and the remainder of the n-butyl chloride-ether mixture was added as rapidly as possible to maintain rapid reflux. After the addition was completed, the mixture was heated to gentle reflux for 2 hour at a temperature of about 36 ^{o} C. 50 mL absolute toluene was added and heating was continued at a temperature within the range 36 -110 ^{o}C. Until the ether was removed by distillation. Anhydrous stannic chloride (39.15 g, 0.15 mol in 50 mL of absolute toluene) was then added rapidly and increased the temperature. After 3-4 hour of heating above 100 ^{o}C (not more than 150°C), the heating was stopped and the mixture was cooled. The cooled mixture was filtered and the filter cake was washed with toluene and hydrolyzed the filtrate by 10% of hydrochloric acid 200 mL. The product was dispersed in toluene phase and a little in aqueous phase. The toluene phase (upper phase) was kept by using separatory funnel. The toluene residue was eradicated by distillation. The product was mainly n-Bu_3SnCl with small amounts of n-Bu_2SnCl_2 and n-$BuSnCl_3$. The product was distilled by reduce pressure distillation. The colorless liquid was distilled out at 108 –115 °C/ 0.7 mmHg. The theoretical yield was 49 g and the actual yield was 42.05 g (86% of theoretical yield). The percentage of carbon and hydrogen from, analysis; found: C=43.62, H=7.89; calcd: C=44.27, H=8.36. for $(C_4H_9)_3SnCl$.

2.6.3 Preparation of Bis(tributyltin) oxide, $(Bu_3Sn)_2O$. [26]

Bis(tributyltin) oxide can be prepared by alkaline hydrolysis as in equation 2-11.

$$2\ Bu_3SnCl + 2\ NaOH \longrightarrow (Bu_3Sn)_2O + 2\ NaCl \text{ ---------- } (2\text{-}11)$$

The crude tributyltin chloride of 42.05 g. (0.1292 mol), were dissolved in 135 ml. absolute ethyl alcohol and refluxed with 10.4 ml. 50% sodium hydroxide for 4 hours. Then the alcohol was distilled out, the residue was filtered to remove the precipitate and the filtrate was distilled by reduce pressure distillation. At 115-118°C/ 0.1 mmHg, the desired bis(tributyltin) oxide distilled out in an amount of 22.15 g., which is a colorless liquid corresponds to a yield of 67.32 % of theory base on the reactant tin compound. The percentage of carbon and hydrogen analysis: C=48.92, H= 9.02; calcd :C=49.86, H=9.62 for $((C_4H_9)_3Sn)_2O$.

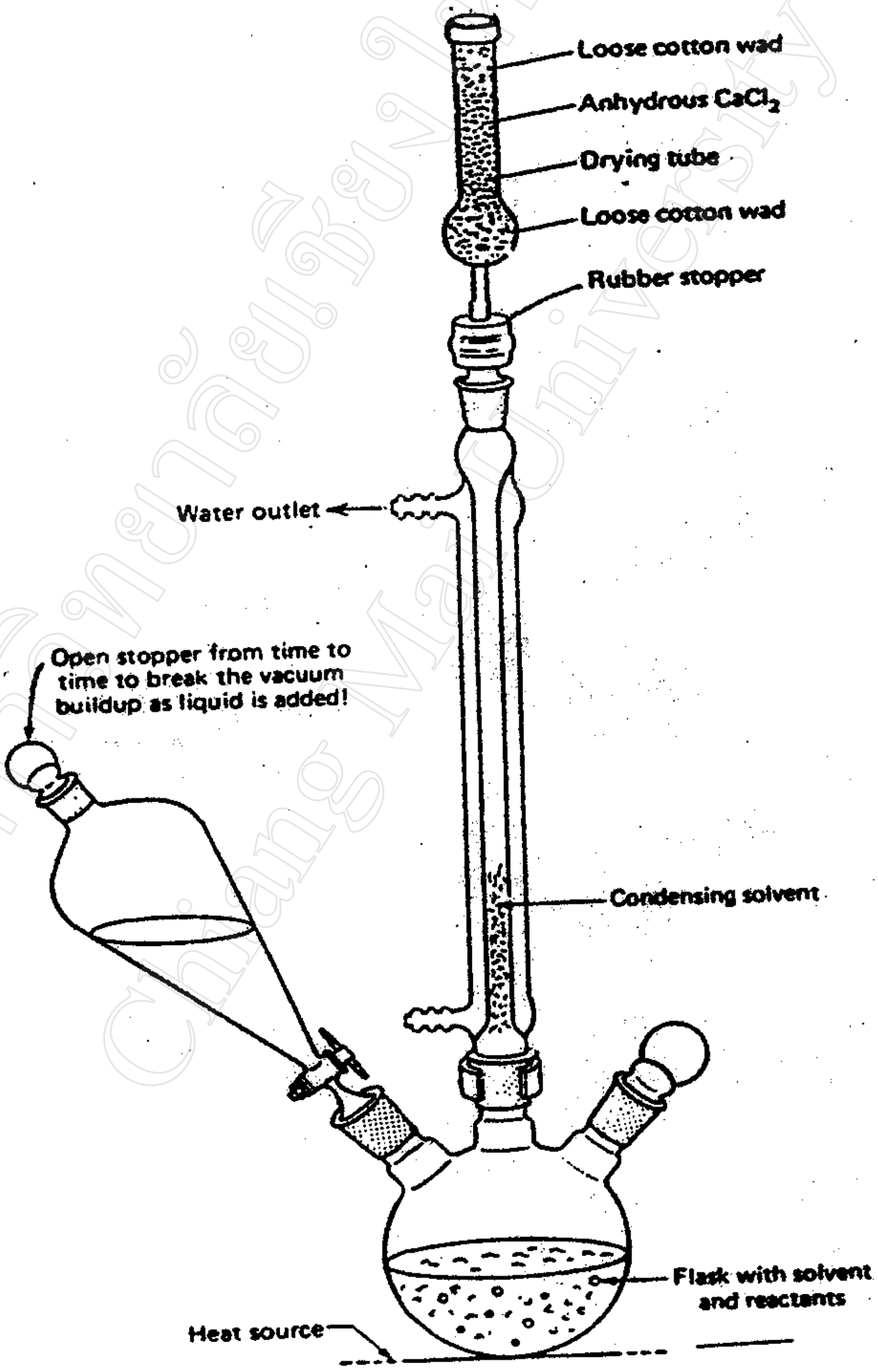


Figure 2.1 Reflux and addition by three-neck flask. [35]

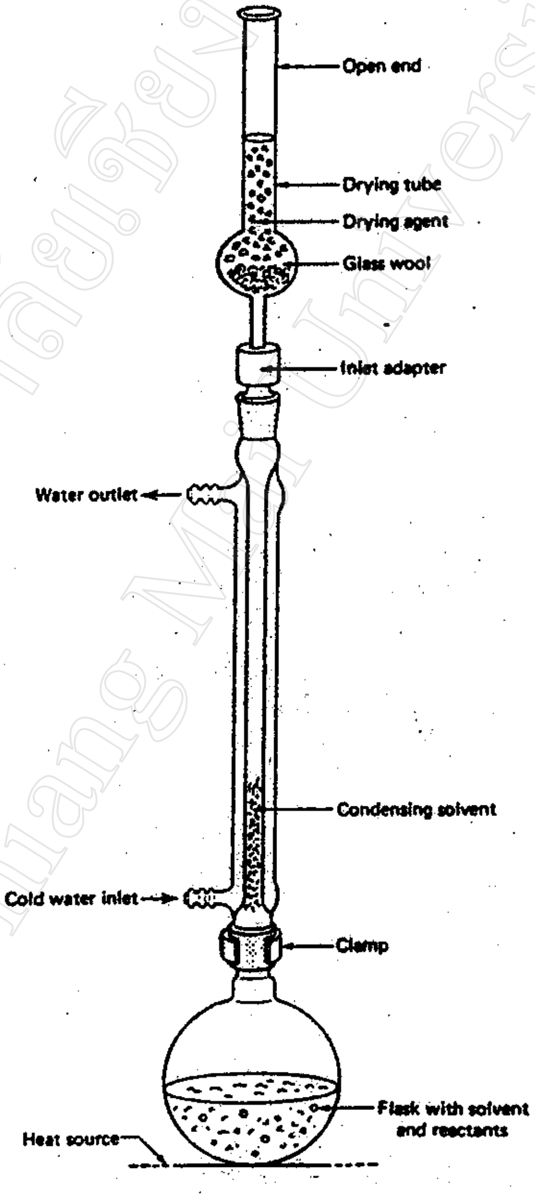


Figure 2.2 Reflux setup [35]

2.7 Preparation of bis(tributyltin) oxide by Wurtz reaction.

There are three steps in preparation of bis(tributyltin) oxide by Wurtz reaction, as following equations (2-12 – 2-14)

$SnCl_4 + 4\ BuCl + 8\ Na \longrightarrow Bu_4Sn + 8\ NaCl$ --------- (2-12)

$3\ Bu_4Sn + SnCl_4 \longrightarrow 4\ Bu_3SnCl$ ------------------(2-13)

$2\ Bu_3SnCl + 2\ NaOH \longrightarrow (Bu_3Sn)_2O + 2\ NaCl$ --------------(2-14)

2.7.1 Preparation of tetrabutyltin by wurtz reaction (28,29)

All reactions were carried out in 500-mL three–necked flask fitted with a stirrer, a reflux condenser and a dropping funnel, which were shown in Figure 2.1. The solvent, 150 mL petroleum ether 40-60°C and the sodium metal, cut into prices of about 0.5 cm in diameter were introduced into the flask and heat to boiling. From the dropping funnel the mixture of stannic chloride anhydrous 19 g (0.1 mol) and 92.5 g (0.4 mol) of butyl chloride was slowly added with stirring over period of about 30 minutes. As soon as the reaction started (perceptible through the increased rate of reflux) the external heating was stopped. The heat of reaction caused the mixture to boil for ½ - 1½ hours. The mean reaction temperatures observed with the solvents used was, with petroleum ether (40-60°C) at 45-47°C. After being boiled with stirring for a further 4-6 hors the reaction mixture was cooled to room temperature and filtered with suction. The filter cake, consisting of sodium chloride and a very small amount of unchanged sodium, was washed with petroleum ether. After removal the solvent from the filtrate by distillation under atmospheric pressure the residue of crude tetrabutyltin was distilled in vacuum and distillate colourless liquid was kept at 116 - 120°C/0.6 mmHg. The theoretical yield was 34.7 g. The actual yield was 12.11 g which was 34 % of theoretical yield. The percentage of carbon and hydrogen from analysis: C=55.07, H= 9.98; calcd. : C=55.36, H=10.45 for $(C_4H_9)_4Sn$.

2.7.2 Preparation of tributyltin chloride, [25-27]

The preparation of Bu_3SnCl by disproportionation reaction was shown in equation 2-13. Added 12.11 g (0.0349 mol) of tetrabutyltin chloride and 3.1 g anhydrous stannic chloride (0.0119 mol) into 500-mL round bottom flask and reflux at 210-220 °C for 1 ½ hour the apparatus were shown in Figure 2.2. And cooling in the water bath until the temperature decrease. Then the sample was filtrated by Buchner funnel. The filtrate was kept and distillated by reduce pressure distillation (Figure 2.3). Colourless liquid of tributyltin chloride was kept at 115-120°C/1 mmHg. The theoretical yield was 11.36 g. and the actual yield was 6.03 g, which was 53 % of theoretical yield. the percentage of carbon and hydrogen from analysis; found: C=48.72, H=9.45, calcd: C=44.27, H=8.36 for $(C_4H_9)_3SnCl$.

2.7.3 Preparation of Bis(tributyltin) oxide, $(Bu_3Sn)_2O$. [26,28]

Bis(tributyltin) oxide can be prepared by alkaline hydrolysis as in equation 2-11.

The crude tributyltin chloride of 6.03 g (0.0185 mol) were dissolved in 50 mL absolute ethyl alcohol and refluxed with 2.5 mL 50% sodium hydroxide for 4 hours. Then the alcohol was distilled out, the residue was filtered to remove the precipitate and the filtrate was distilled by reduce pressure distillation. At 128-133°C/ 0.2 mmHg, the desired bis-(tributyltin) oxide distilled over in an amount of 1.92 g, which colourless liquid like oil corresponds to a yield of 35 % of theory base on the reactant tin compound. The percentage of carbon and hydrogen from analysis: C=49.52, H= 9.21%; calcd. : C=49.86, H=9.62 for $((C_4H_9)_3Sn)_2O$.

2.8 Preparation of cassiterite ore sample [25]

The cassiterite ore sample was prepared as shown in Figure 2.3

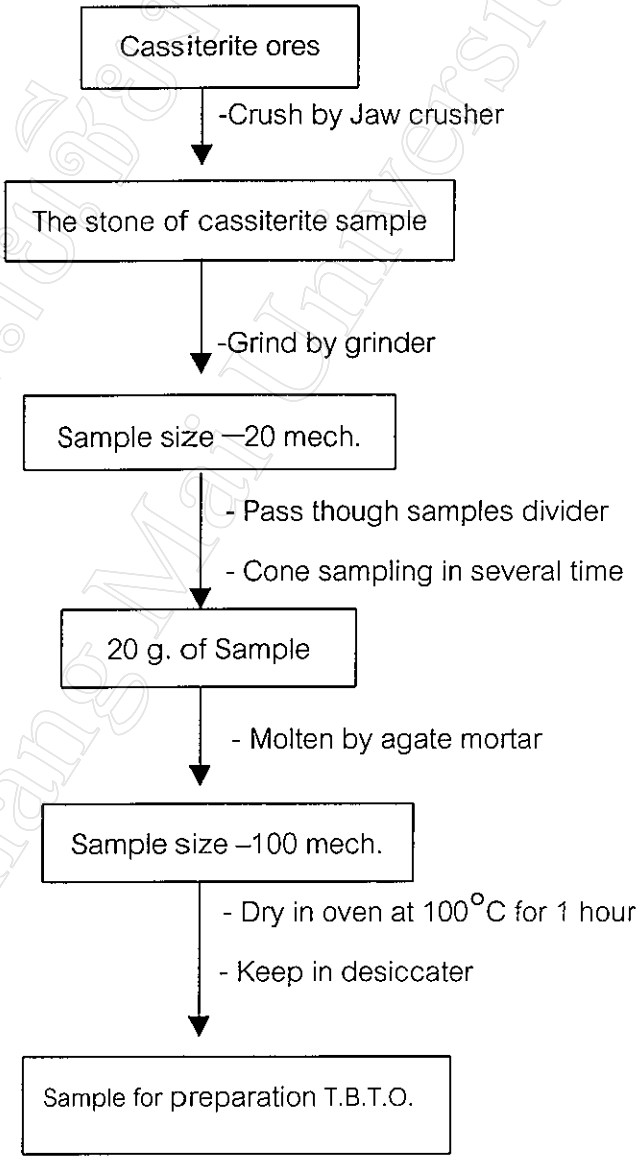


Figure 2.3 The preparation of cassiterite ores

2.9 Preparation of bis(tributyltin) oxide from cassiterite (SnO_2) by Grignard method.

There are three steps in the preparation of bis(tributyltin) oxide, first the preparation of aqueous $SnCl_4$ from cassiterite, second the extraction by toluene and third using $SnCl_4$ in toluene to prepare bis(tributyltin) oxide by Grignard method.

2.9.1 Preparation of aqueous $SnCl_4$ from cassiterite [21,34,35]

The aqueous $SnCl_4$ from cassiterite was prepared by fusion with sodium peroxide, as shown in equations 2-15 and 2-16

$$SnO_2 + 2\,Na_2O_2 \longrightarrow Na_2SnO_3 + 2\,H_2O + 2\,NaOH \text{ ----- } (2\text{-}15)$$

$$Na_2SnO_3 + 6\,HCl \longrightarrow SnCl_4 + 2NaCl + 2\,H_2O \text{ ------------ } (2\text{-}16)$$

Weight 10.0 g of cassiterite (-100 mesh.), which was dried at 100°C for 1 hour, transfer to 100-mL crucible. Add 20.0 g of sodium peroxide and the crucible was covered before heating by Bunsen burner at 700-800°C for 1-2 hour. Until the sample was melt. Cool down at room temperature, dissolved the sample in 150 mL hot water and acidified with 150 mL hydrochloric acid. Add 10 mL 5% quinine to precipitate tungstic acid and heat to warm the sample for ½ hour .The sample was kept at room temperature for 24 hour. Filtrate the cooled sample and the filtrate was kept.

Repeat all steps in this method for 3 times to prepare 900 ml of aqueous $SnCl_4$.

2.9.2 Determination of Sn in aqueous $SnCl_4$. [17,21]

From 900 mL of aqueous $SnCl_4$, 100 ml. of sample was transferred to 500-mL Erlenmeyer flask, add 5 g aluminum powder for the reduction of Sn(IV) to Sn(II) in carbon dioxide atmosphere (Figure 2.4). When the reduction complete, cool down to 15-20°C by cooled water. Add 1-2 g of sodium hydrogen carbonate ($NaHCO_3$) and 5 mL of 1% starch solution. Titrate with 0.5033 N iodine solution though the first permanent blue, 56.5 mL of iodine solution were used.

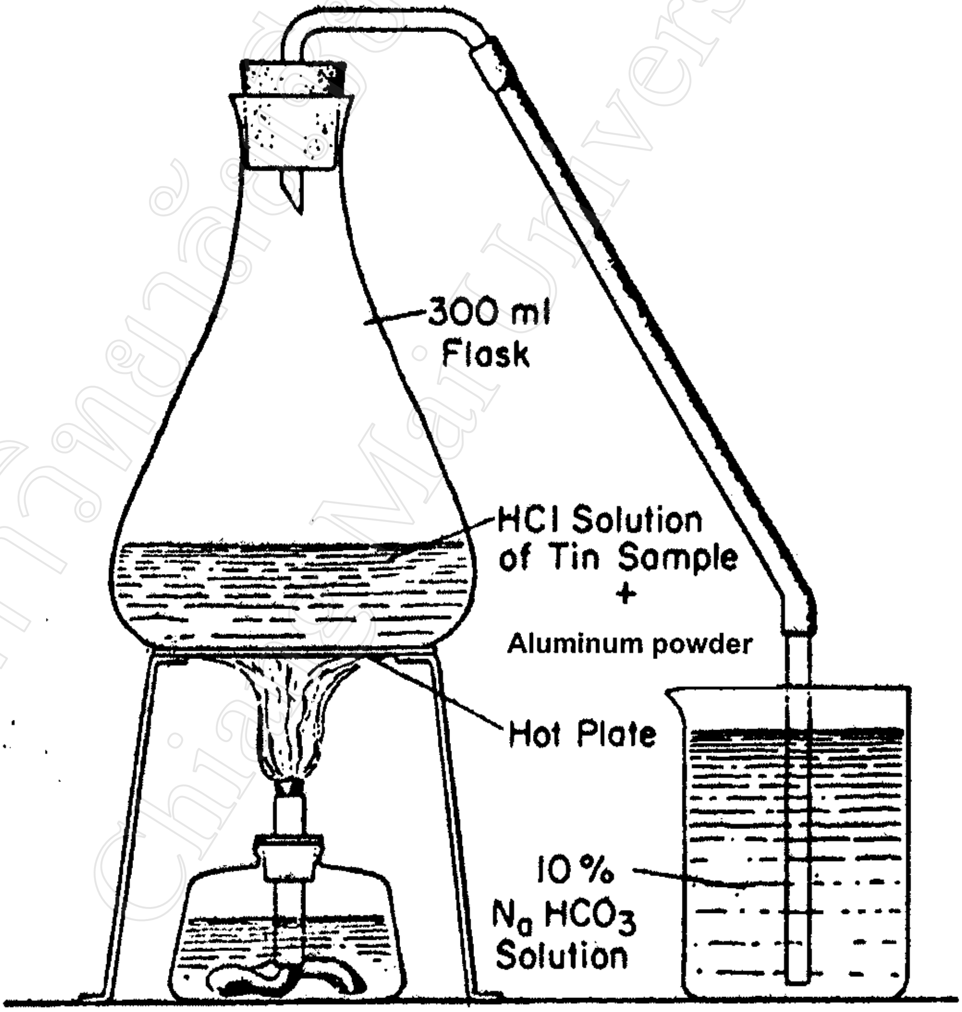


Figure 2.4 The apparatus for reduction Sn(IV) to Sn(II) [33]

2.9.3 Preparation of $SnCl_4$ in toluene from aqueous $SnCl_4$ [33,34]

The aqueous $SnCl_4$ was extracted to $SnCl_4$ in toluene by liquid-liquid extraction in trioctylphosphine oxide (TOPO) extractant.

Transfer 40 mL of aqueous $SnCl_4$ (from 800 mL) to 20 separatory funnel , add 5% 5 mL ascorbic acid to reduce Fe (III) to Fe (II). Until the yellow colour disappear then add 4 mL of 5% TOPO in toluene to extract the $SnCl_4$ in aqueous phase to toluene phase for 20 minute. The toluene phase was kept, transfer the aqueous phase to separatory funnel again and extraction with 5% TOPO in toluene again, repeat the extraction for 10 time. Until the toluene phase was 400 mL and dry with anhydrous $CaCl_2$. When the solution was kept over night the slightly yellow solution was appeared.

2.9.4 Preparation Bu_3SnCl from $SnCl_4$ in toluene by Grignard method [25,17]

The preparation of Bu_3SnCl from $SnCl_4$ in toluene by Grignard method was in equations 2-10. The extraction of $SnCl_4$ from aqueous phase to toluene phase, $SnCl_4$ was dispersed in 60% toluene so $SnCl_4$ in toluene phase is 17.90 g (0.0686 mol), from 29.84 g sample

Weigh 5.26 g (0.218 mol) magnesium turning transfer to a tree-necked flask equipped with a stirrer, reflux condenser and a graduated dropping funnel, (Figure 2.1). A mixture of n-butyl chloride and 20.25 g (0.218 mol) ethyl ether dissolved in 25 mL of absolute ether was added with a crystal of iodine. The reaction was initiated by slight warming. After initiation, 25 mL of dry ether was added and the remainder of the n-butyl chloride-ether mix was added as rapidly as possible to maintain rapid reflux. After the addition was complete, the mixture was heated to gentle reflux for 2 hour at a temperature of about 36 °C. 400 mL stannic chloride in toluene phase (17.90 g, 0.0683 mol) was added rapidly and increased the temperature. After 3-4 hour of heating above 100 °C (not more than 150°C), the heating was stopped and the mixture was cooled. The cooled mix was filtered and the filter cake was washed with toluene and hydrolyzed the filtrate by 10% of 200 ml hydrochloric acid. The product was dispersed in toluene phase and a little in aqueous phase. The toluene phase (upper phase) was kept by using separatory funnel and used rotary evaporator to distillate toluene residue. And distillation by reduces pressure to separate Bu_3SnCl from crude mixture. But in this experiment the crude mixture was brown gel. It can not distillate so the experiment could not continue.

2.7 The experimental results.

(1) The results from the determination of the percentage of carbon and hydrogen in organotin compounds by CHNS/O analyzer were shown in Table 2.3

Table 2.3 Analytical data of the percentage of carbon and hydrogen in organotin compounds.

Organotin compounds	Found		Calculated	
	%C	%H	%C	%H
From Grignard method				
Bu_4Sn	45.20	8.67	55.36	10.54
Bu_3SnCl	43.62	7.89	44.27	8.36
$(Bu_3Sn)_2O$	48.92	9.02	49.86	9.62
From Wurtz method				
Bu_4Sn	55.07	9.98	55.36	10.54
Bu_3SnCl	43.72	8.03	44.27	8.36
$(Bu_3Sn)_2O$	49.52	9.21	49.86	9.62

(2) The results from the determination of percentage of tin in organotin compounds by iodometric titration were shown in Table 2.4

Table 2.4 Analytical data of percentage of tin in organotin compound by iodometry titration

Method of Preparation	Weight of T.B.T.O. (g)	Volume of I_2 solution, mL (0.1004 N)	%Sn	
			Found	Calculated
Grignard method	(1) 0.3825	25.00	38.95	39.82
	(2) 0.3756	24.95	39.58	
	(3) 0.3914	25.80	39.27	
mean	0.3832	25.25	39.27	39.82
Wurtz method	(1) 0.5002	33.25	39.60	39.82
	(2) 0.3907	25.80	39.32	
	(3) 0.4502	29.85	39.52	
mean	0.4470	29.63	39.48	39.82

(3) The results from the determination of the boiling point of organotin compounds were shown in Table 2.5

Table 2.5 Boiling points of organotin compounds

Organotin compounds	bp. From reduce pressure distillation, °C	bp. At 1 atm.(calcd.), °C	bp. from reference$^{(a)}$, °C	bp. At 1atm. from reference$^{(a)}$ (Calcd.), °C
Grignard method				
Bu_4Sn	$106\text{-}118^{(0.7\ \mathrm{mmHg})}$	317-335	$127°C^{(1.7\ \mathrm{mmHg})}$	342
Bu_3SnCl	$108\text{-}115^{(0.7\ \mathrm{mmHg})}$	320-331	$152\text{-}156^{(14\ \mathrm{mmHg})}$	320-330
$(Bu_3Sn)_2O$	$115\text{-}119^{(0.1\ \mathrm{mmHg})}$	391-398	$180^{(2\ \mathrm{mmHg})}$	394
Wurtz method				
Bu_4Sn	$116\text{-}120^{(0.6\ \mathrm{mmHg})}$	337-343	$127°C^{(1.7\ \mathrm{mmHg})}$	342
Bu_3SnCl	$115\text{-}120^{(1\ \mathrm{mmHg})}$	320-327	$152\text{-}156^{(14\ \mathrm{mmHg})}$	320-330
$(Bu_3Sn)_2O$	$128\text{-}133^{(0.2\ \mathrm{mmHg}}$	391-399	$180^{(2\ \mathrm{mmHg})}$	394

[a] From referent 38

(4) Infrared spectra and mass spectrum were shown in Figure 2.5 - 2.17

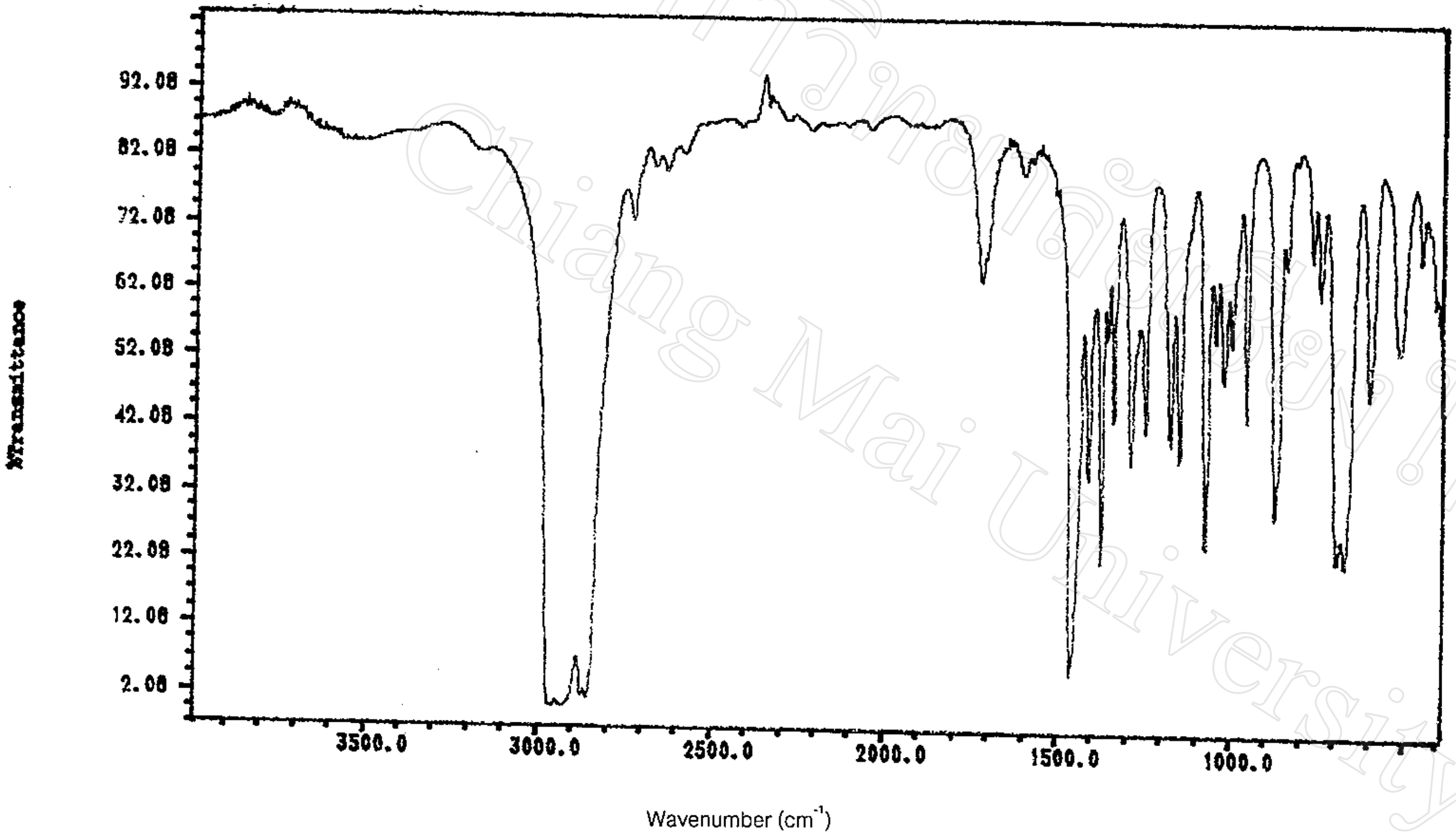


Figure 2.5 IR spectrum of tetrabutyltin from Grignard method

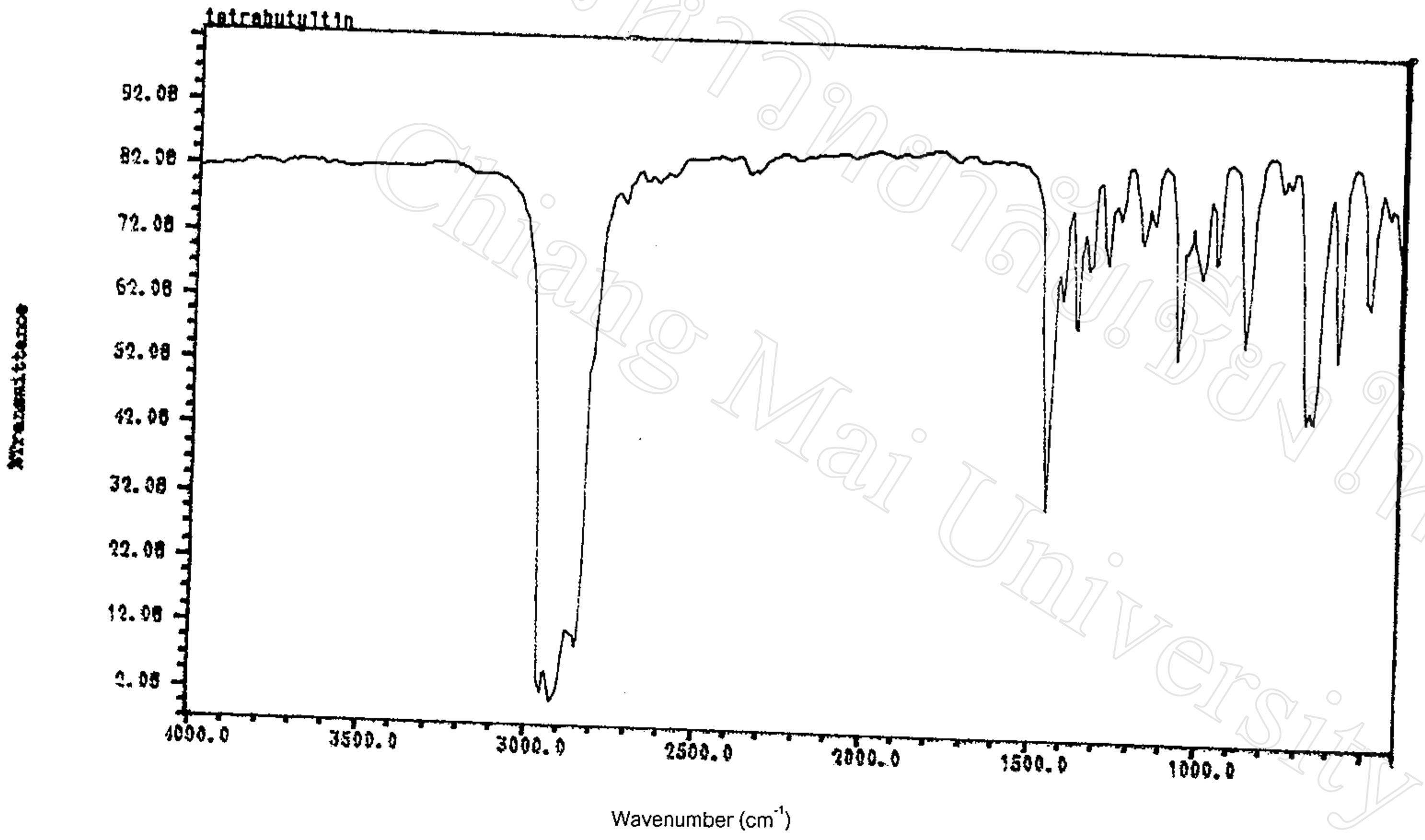


Figure 2.6 IR spectrum of tetrabutyltin from Wurtz method

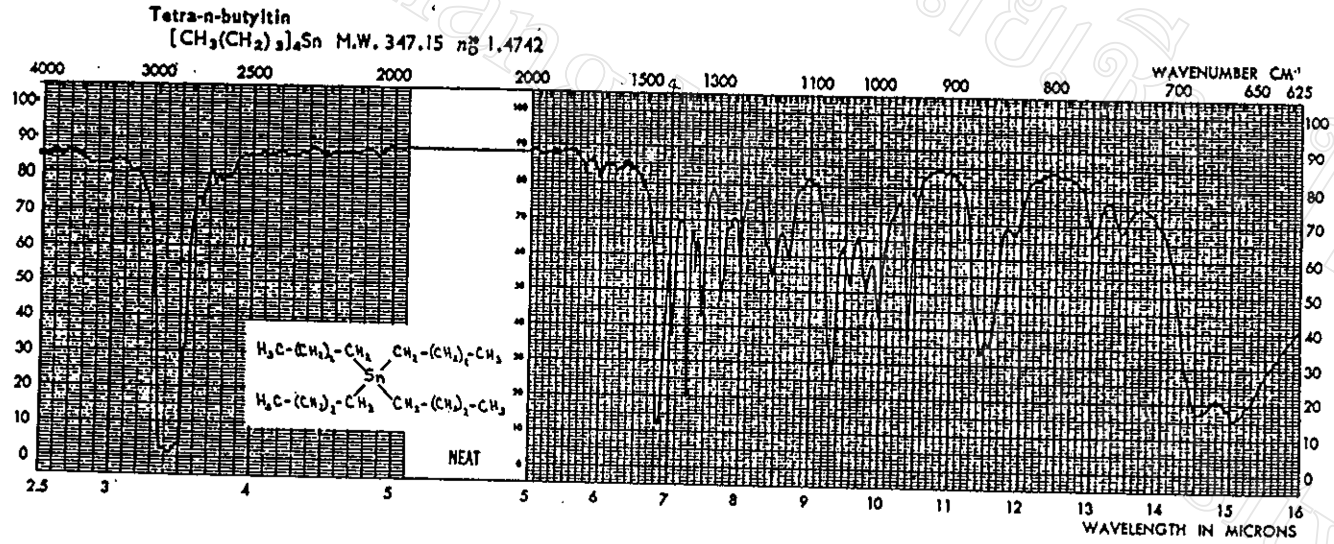


Figure 2.7 IR spectrum of standard tetrabutyltin [40]

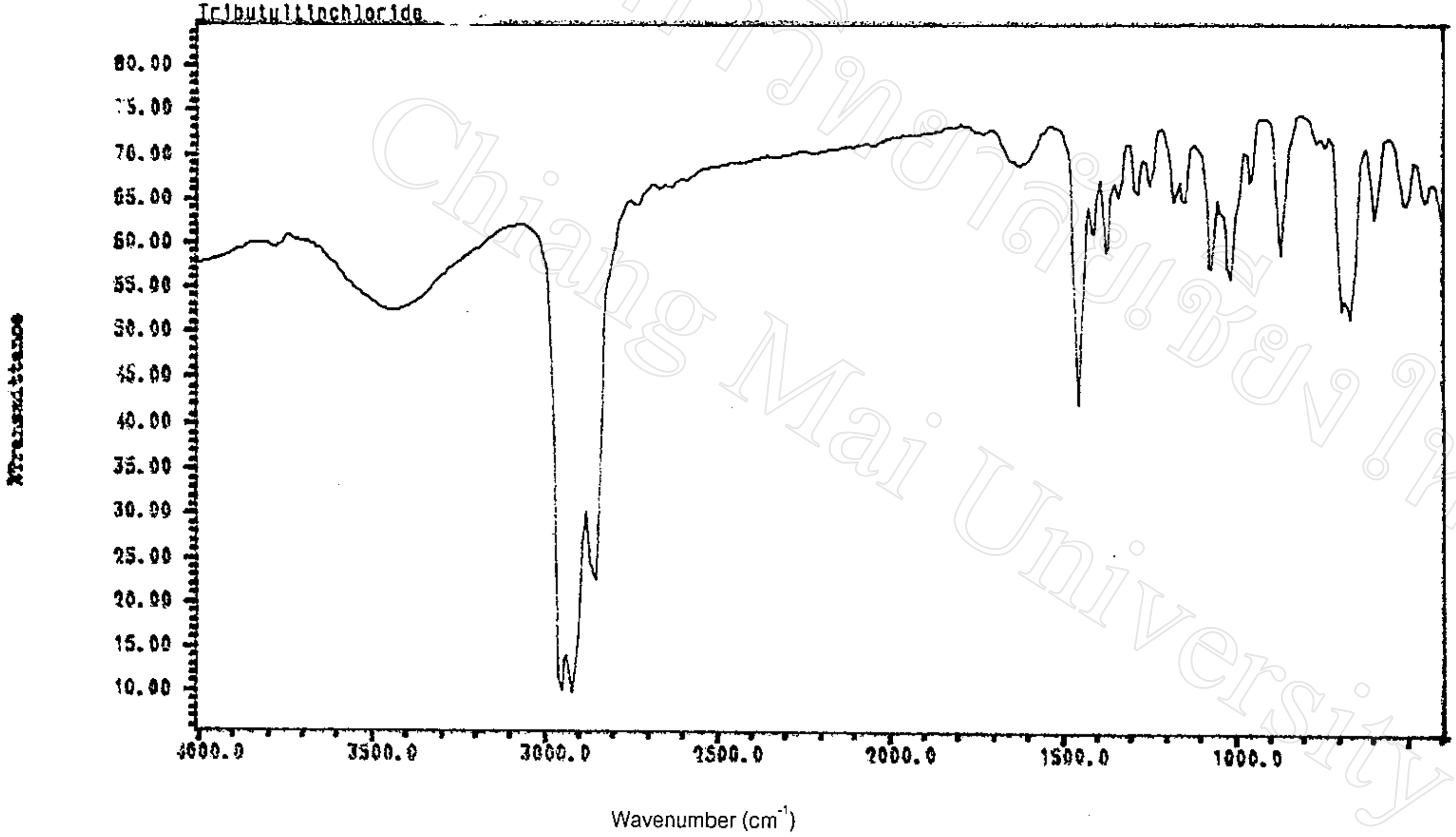


Figure 2.8 IR spectrum of tributyltin chloride from Grignard method

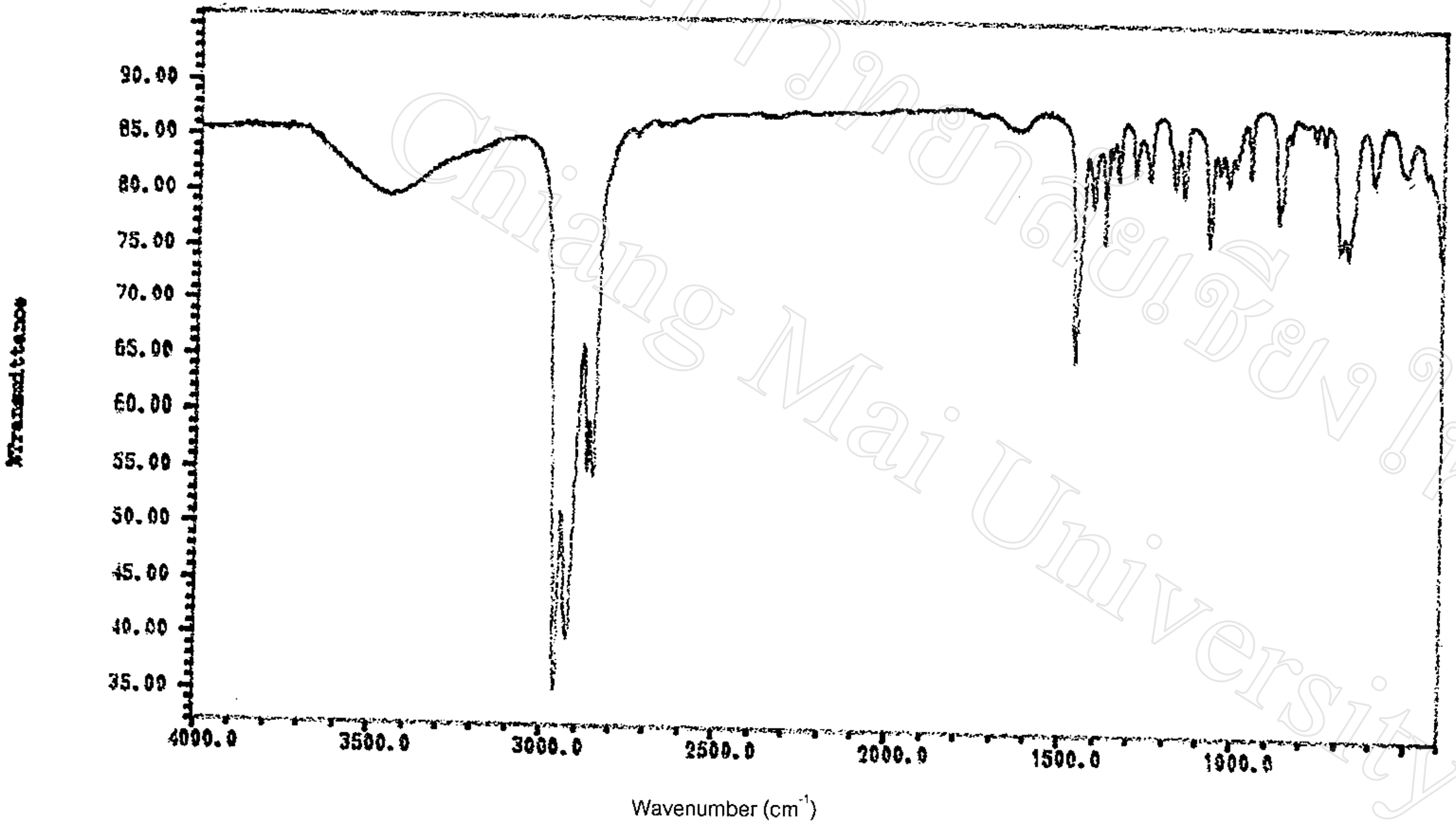


Figure 2.9 IR spectrum of tributyltin chloride from Wurtz method

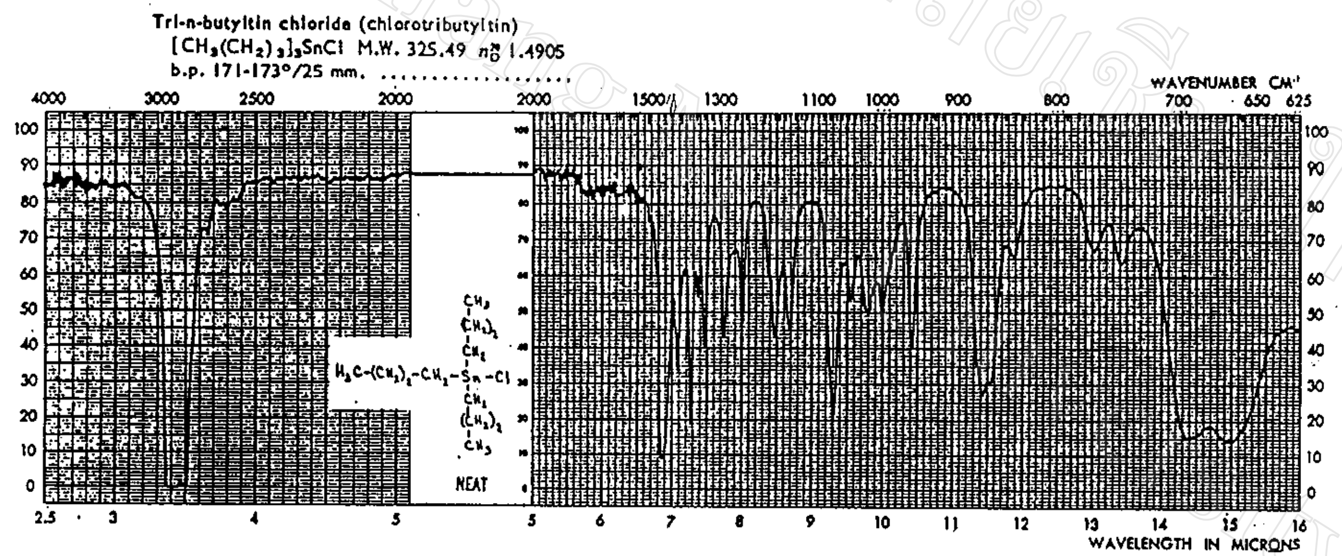


Figure 2.10 IR spectrum of standard tributyltin chloride [40]

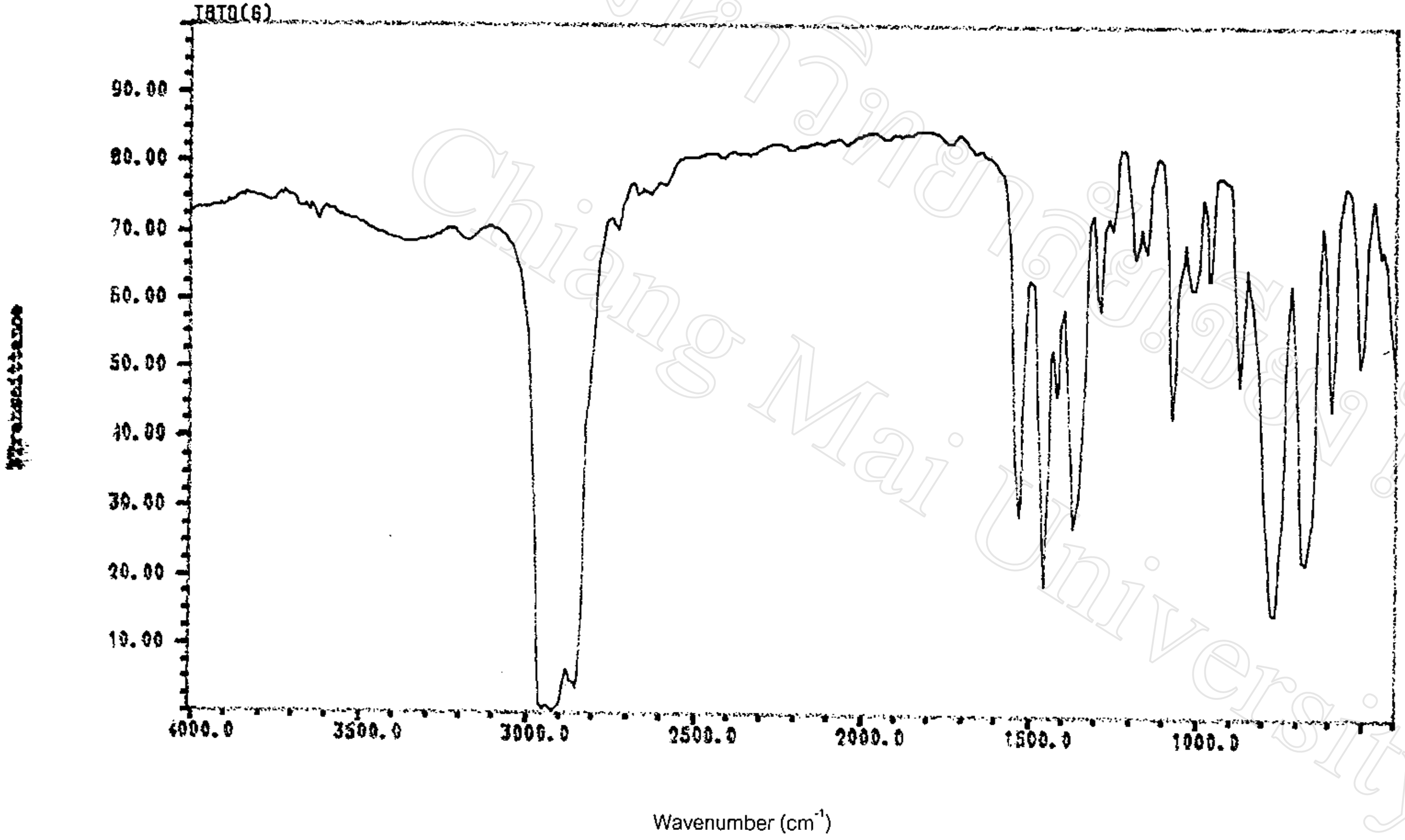


Figure 2.11 IR spectrum of bis(tributyltin) oxide from Grignard method

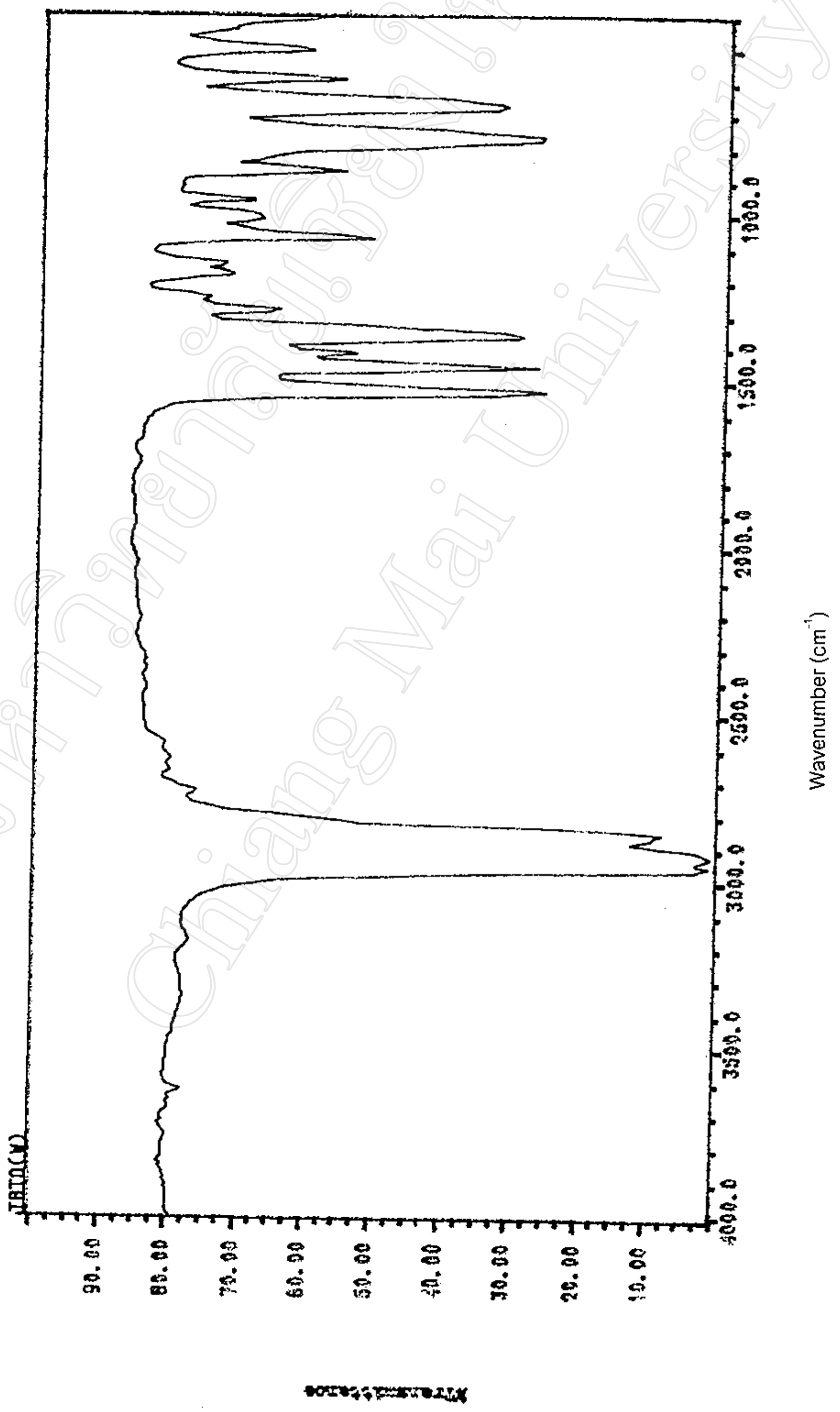


Figure 2.12 IR spectrum of bis(tributyltin) oxide from Wurtz method

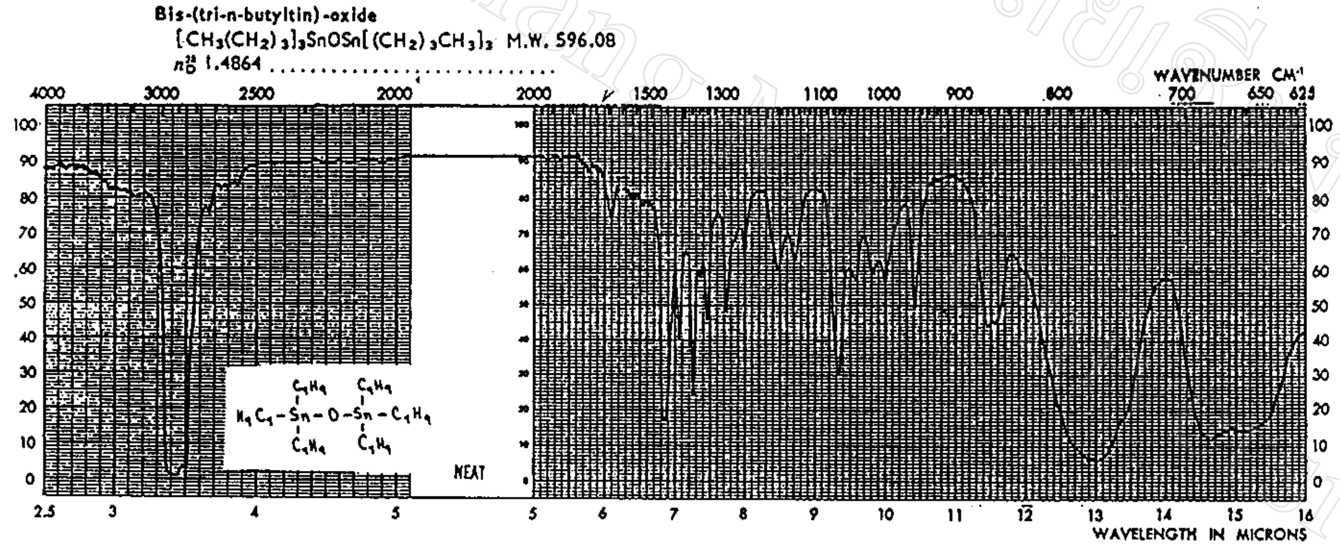


Figure 2.13 IR spectrum of standard bis(tributyltin) oxide [40]

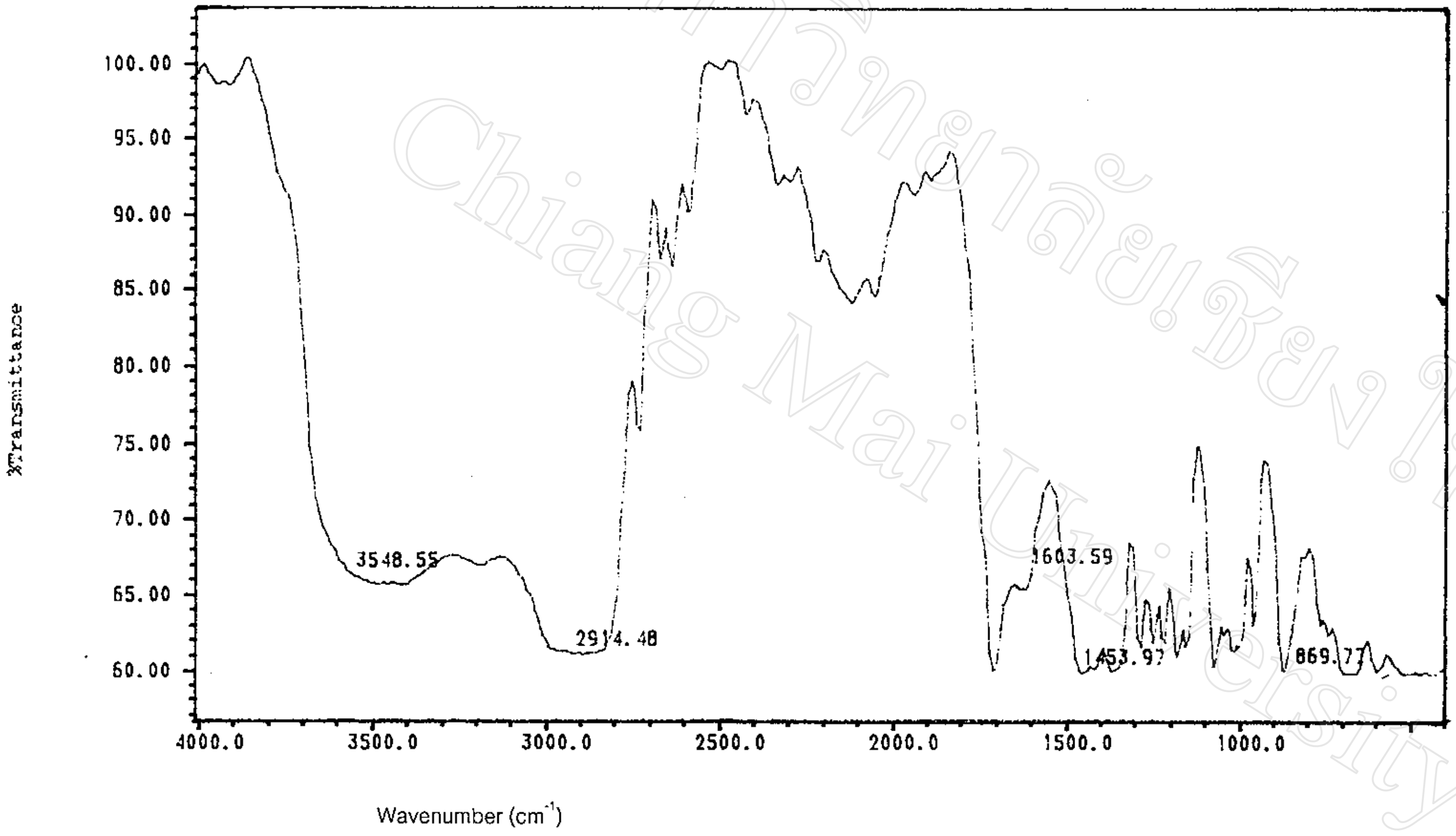


Figure 2.14 IR spectrum of tributyltin chloride from Grignard method by using cassiterite as starting material

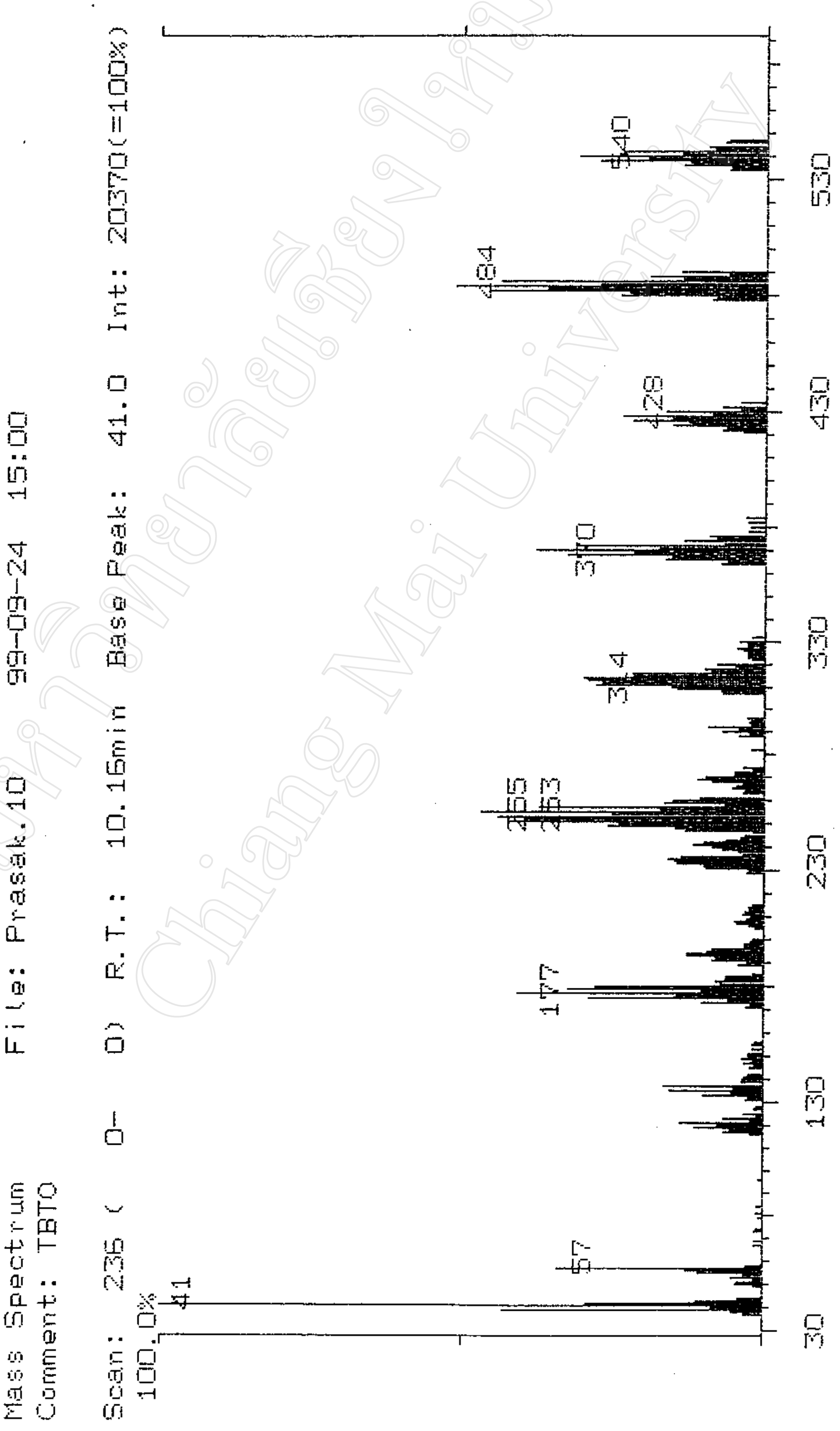


Figure 2.15 Mass spectrum of bis(tributyltin) oxide by Grignard method

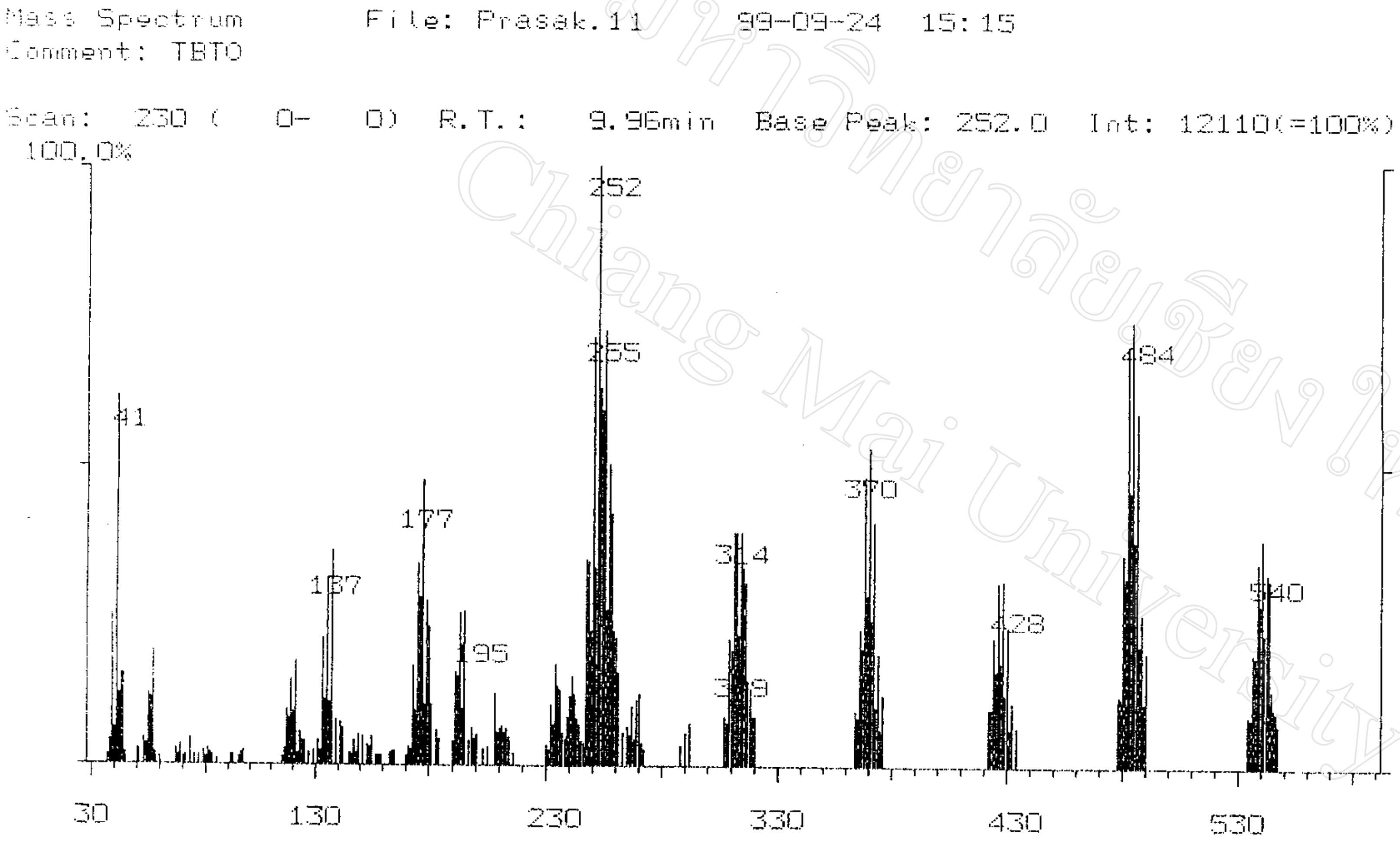
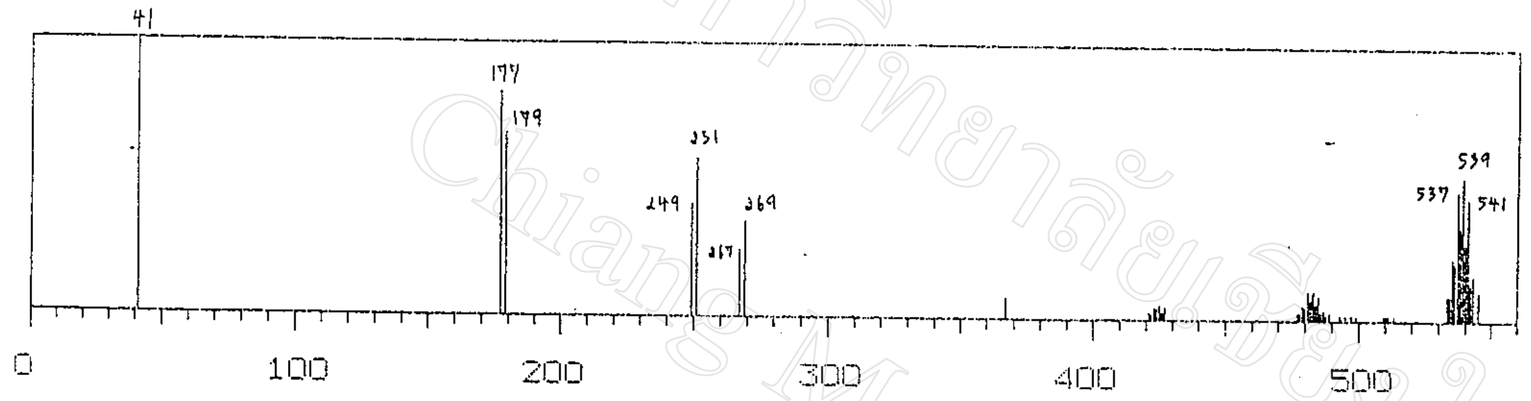


Figure 2.16 Mass spectrum of bis(tributyltin) oxide by Wurtz method

Compound Information



```
CAS :     56-35-9   MW:  598   Class:  6,10          RT:    .00
MF  : C24H54OSn2
Name: Distannoxane, hexabutyl- (8CI9CI)


Mass Table  (m/z-Relative Intensity)
 41-99.9  367- 7.8  427- 4.3  482- 6.6  488- 1.7  507-  .7  533- 8.2  539-52.7
177-81.4  421- 1.9  477- 2.3  483-10.6  489- 2.5  509- 1.1  534- 8.2  540-27.9
179-66.9  422- 1.5  478- 2.3  484- 5.1  493-  .9  510-  .9  535-22.4  541-45.2
249-41.1  423- 4.3  479- 5.1  485- 8.6  495-  .9  511-  .9  536-20.6  542-13.3
251-58.2  424- 2.7  480- 4.3  486- 2.3  497-  .9  512-  .7  537-47.6  543-16.5
267-24.8  425- 5.1  481-10.4  487- 3.1  499-  .9  513-  .9  538-34.6  545-10.6
269-35.0  426- 2.3
```

Figure 2.17 Mass spectrum of standard bis(tributyltin) oxide [39]