CHAPTER 3

EXPERIMENTAL AND RESULTS

3.1 Apparatus and Instruments

1. Aldrich Kugelrohr Apparatus
   model 213-196-2
2. High Vacuum Pump
   Edwards model E2m2 20035
3. Fourier-Transform IR Spectrophotometer
   Perkin-Elmer model 1760X
4. Fourier-Transform NMR Spectrophotometer
   Bruker model AC-F 200
5. Mass Spectrometer
   Jeol model JMS-DX 300
6. CFR Standard Engine
   ASTM method D 2699

3.2 Reagents and Their Purifications

1. Magnesium turnings
   reagent grade; Fluka, Switzerland
2. n-Hexyl bromide
   reagent grade; Fluka, Switzerland
3. Stannic chloride anhydrous
   reagent grade; Fluka, Switzerland

4. Tetrahydrofuran and Toluene anhydrous

   commercial grade; removed trace of water by refluxing with sodium metal and distilled before use

5. Iodine crystals

6. Ammonium chloride

   reagent grade; saturated aqueous solution, Fluka, Switzerland

7. Sodium sulfate anhydrous

   reagent grade; Fluka, Switzerland

8. Methyl-tert-butyl ether

   commercial grade; 98% minimum

9. Isopropyl alcohol

   commercial grade; distilled before use

10. Tin-butyl (Tetrabutyl Tin)

    reagent grade; Fluka, Switzerland

11. miscellaneous solvents

    distilled before use

3.3 Synthesis of Tetrahexyltin by Grignard Reaction

n-hexylmagnesium bromide was prepared from magnesium turnings (9.00 g, 0.37 mole) and n-hexyl bromide (58.00 ml, 68.15 g, 0.41 mole) in THF (100 ml) contained in 500 ml three-neck round bottom flask fitted with a dean-stark, glass apparatus for trapping which water that occurred from reaction, condenser and drying tube, dropping funnel, and magnetic stirrer. The reaction had been initiated by adding a small quantity of iodine in flask and hexyl bromide was added dropwise from dropping funnel. When the addition was completed, THF was distilled off from the reaction mixture using dean-stark apparatus. Toluene (100 ml) was added and then anhydrous

stannic chloride (9.7 ml, 21.5 g, 0.082 mole) was added dropwise with continuous stirring. The reaction mixture was refluxed further for 3 hours. The excess Grignard reagent was decomposed by adding a small amount of saturated aqueous ammonium chloride solution. The toluene layer was evaporated under reduced pressure to yield the crude product which was distilled at reduced pressure (3 mmHg) to give tetrahexyltin 33.0 ml (33.33 g, 88.55% yield based on stannic chloride), b.p. (at 3 mmHg) 180-182° C .

FTIR (neat) : ν (cm^{-1}) ; 2957, 2923, 2852 ;
see fig. 3.1

^{1}H-NMR ($CDCl_3$) : δ (ppm) ; 0.790, 0.830, 0.883, 1.269 ;
see fig. 3.2

^{13}C-NMR ($CDCl_3$) : δ (ppm) ; 9.263, 14.193, 22.861, 27.141, 31.592, 34.146 ppm ; see fig. 3.3

Mass Spectrum : base peak at 375, other peaks at 123, 207, 291 ; see fig. 3.4

3.4 Determination of Antiknock Property in Blended Gasoline Bases

The octane number determination, ASTM method D 2699, was performed by Petroleum Authority of Thailand (PTT). Gasoline base was prepared by mixing 50% Light Naphtha (octane number 69.0) with 50% Reformate (octane number 96.4). The research octane numbers (RON) of various composition gasoline bases which were blended with MTBE, IPA, tetrahexyltin and tetrabutyltin were presented in the tables below.

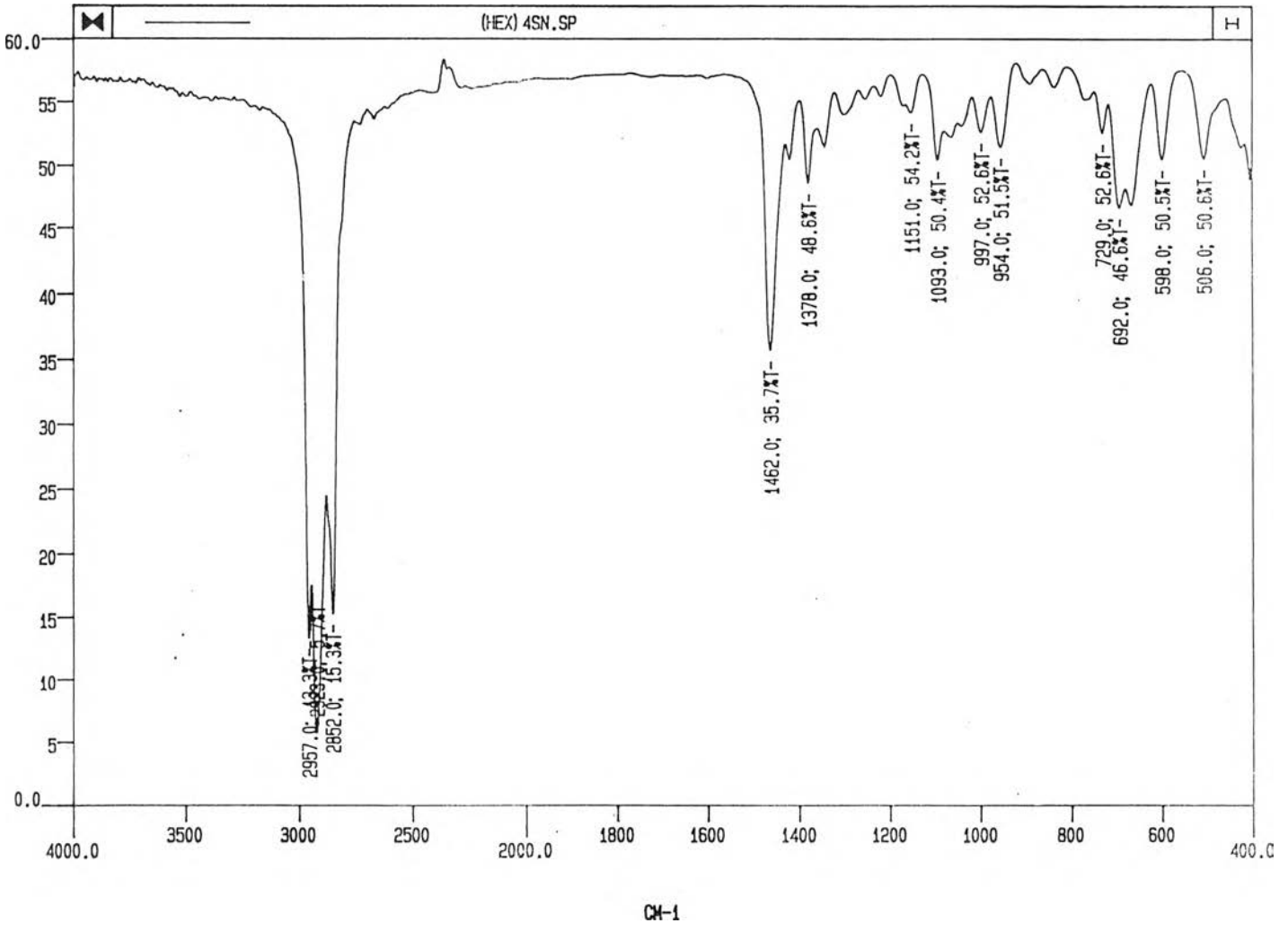
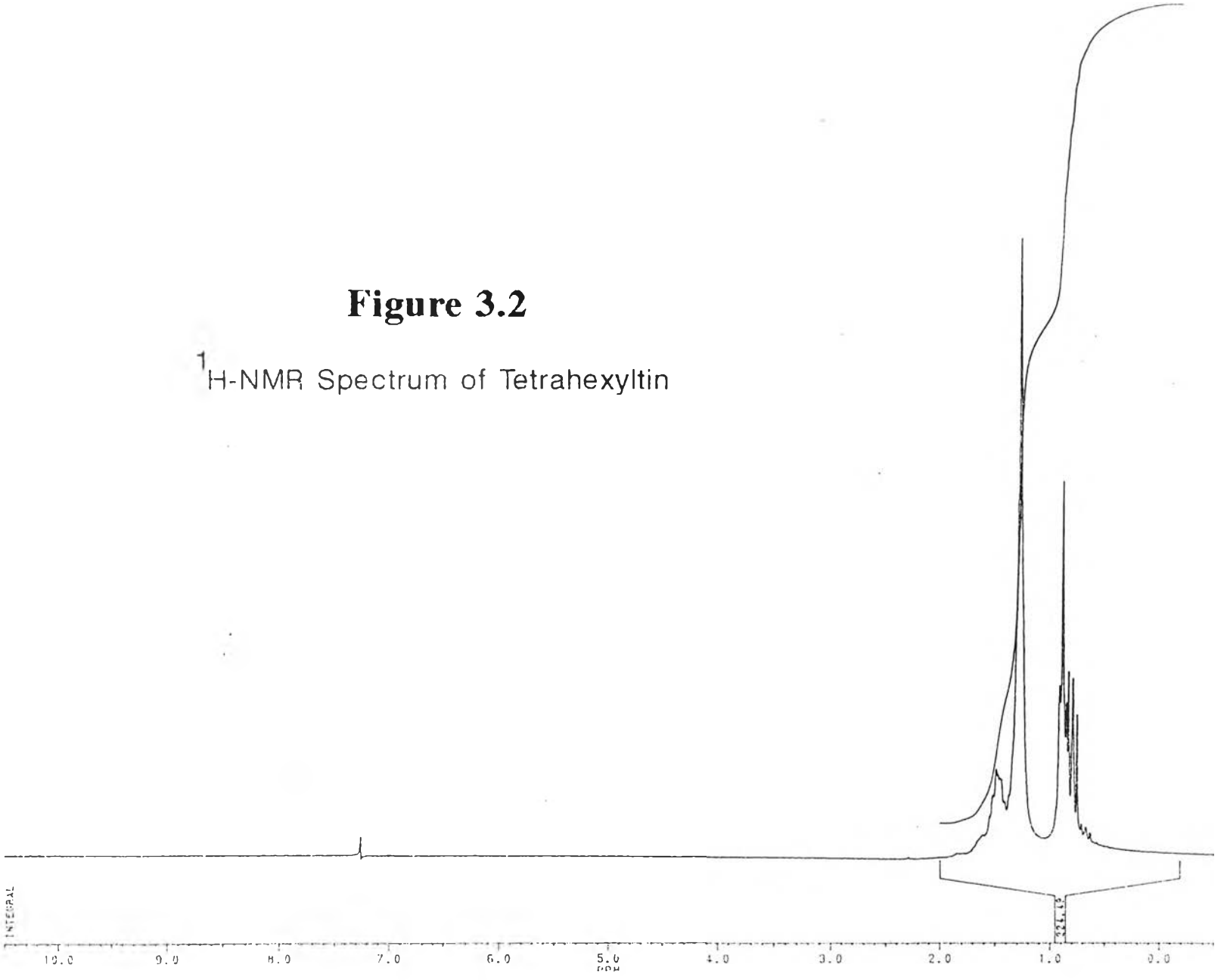


Figure 3.1 FTIR Spectrum of Tetrahexyltin

Figure 3.2

^{1}H-NMR Spectrum of Tetrahexyltin



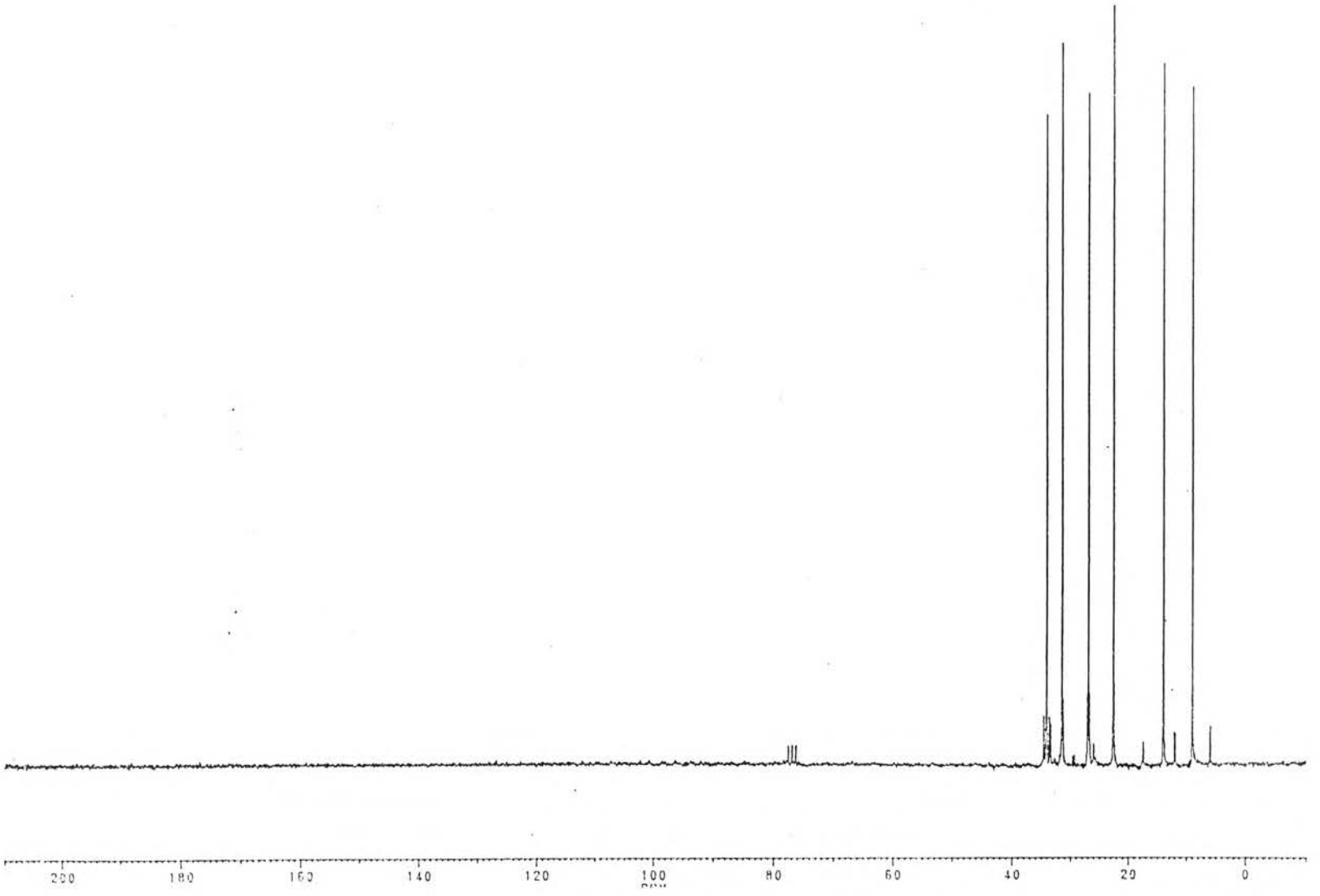


Figure 3.3 ^{13}C-NMR Spectrum of Tetrahexyltin

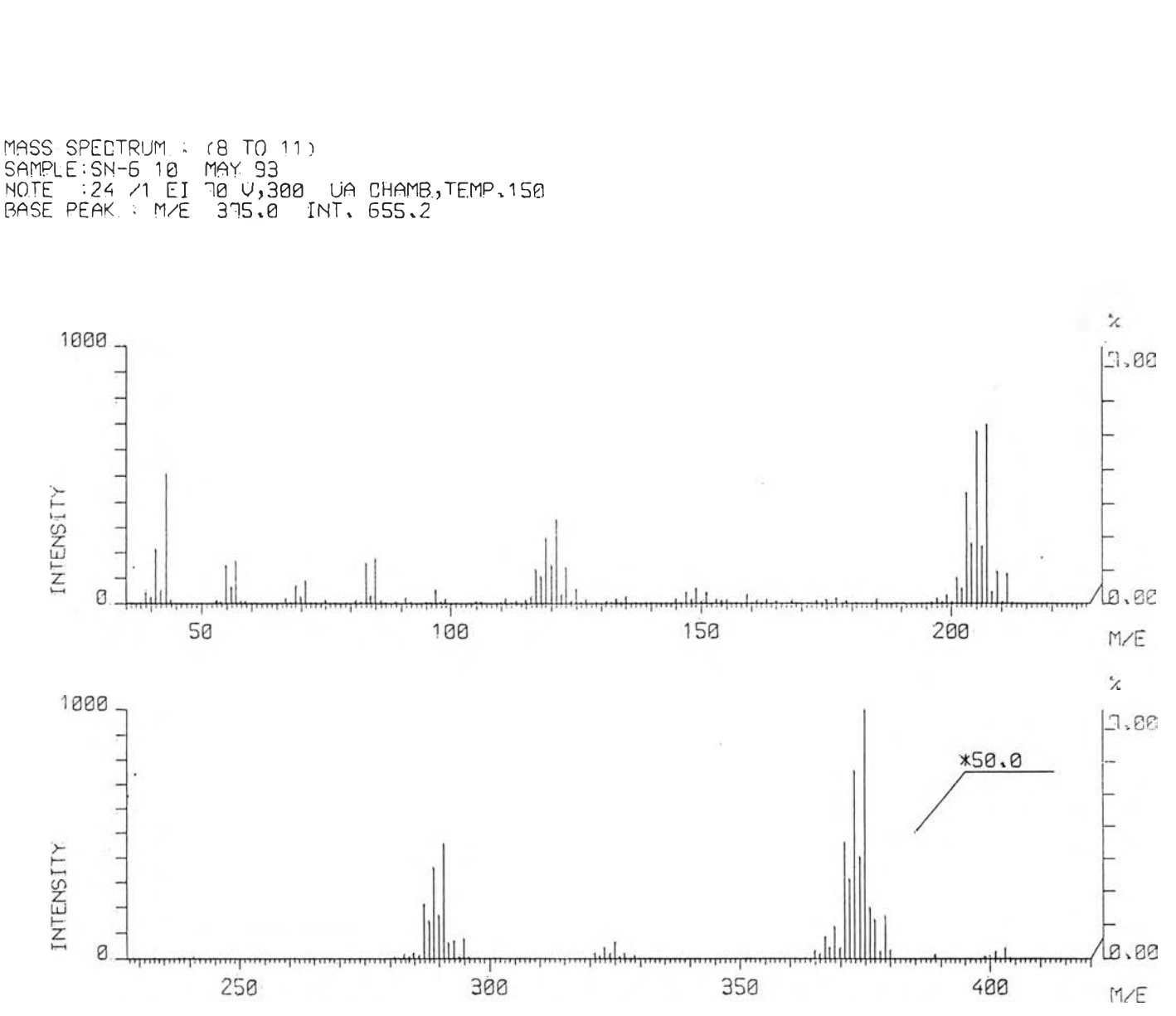


Figure 3.4 Mass Spectrum of Tetrahexyltin

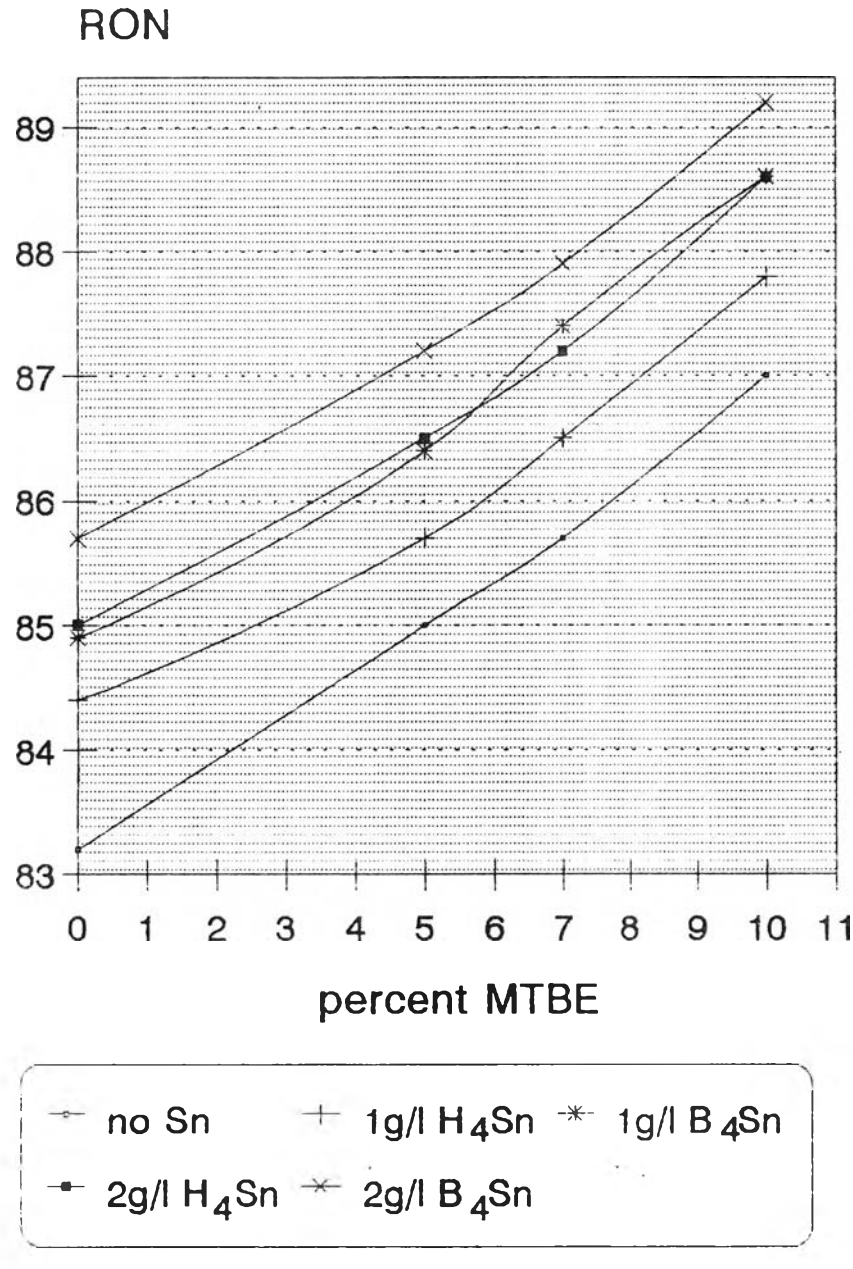
3.4.1 With MTBE, tetrahexyltin and tetrabutyltin

Table 3.1 RON of unleaded gasoline base which was blended with MTBE, tetrahexyltin and tetrabutyltin, see Fig. 3.5-3.6

Blended composition			RON
%MTBE	g/l H_4Sn	g/l B_4Sn	
-	-	-	83.2
-	1	-	84.4
-	2	-	85.0
-	-	1	84.9
-	-	2	85.7
5	-	-	85.0
5	1	-	85.7
5	2	-	86.5
5	-	1	86.4
5	-	2	87.2
7	-	-	85.7
7	1	-	86.5
7	2	-	87.2
7	-	1	87.4
7	-	2	87.9
10	-	-	87.0
10	1	-	87.8
10	2	-	88.6
10	-	1	88.6
10	-	2	89.2

Figure 3.5

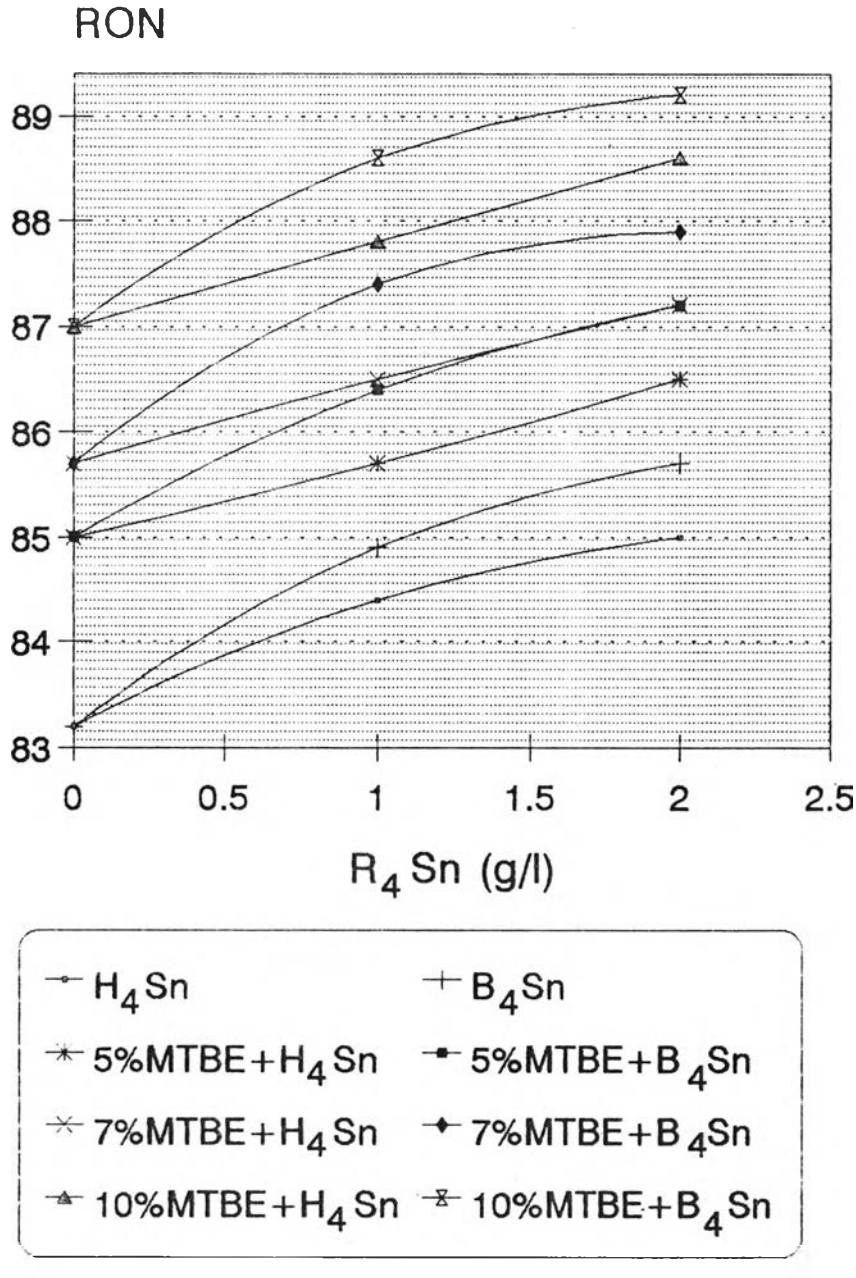
RON of unleaded gasoline base blended with MTBE, tetrahexyltin and tetrabutyltin



base 83.2

Figure 3.6

RON of unleaded gasoline base blended with MTBE, tetrahexyltin and tetrabutyltin



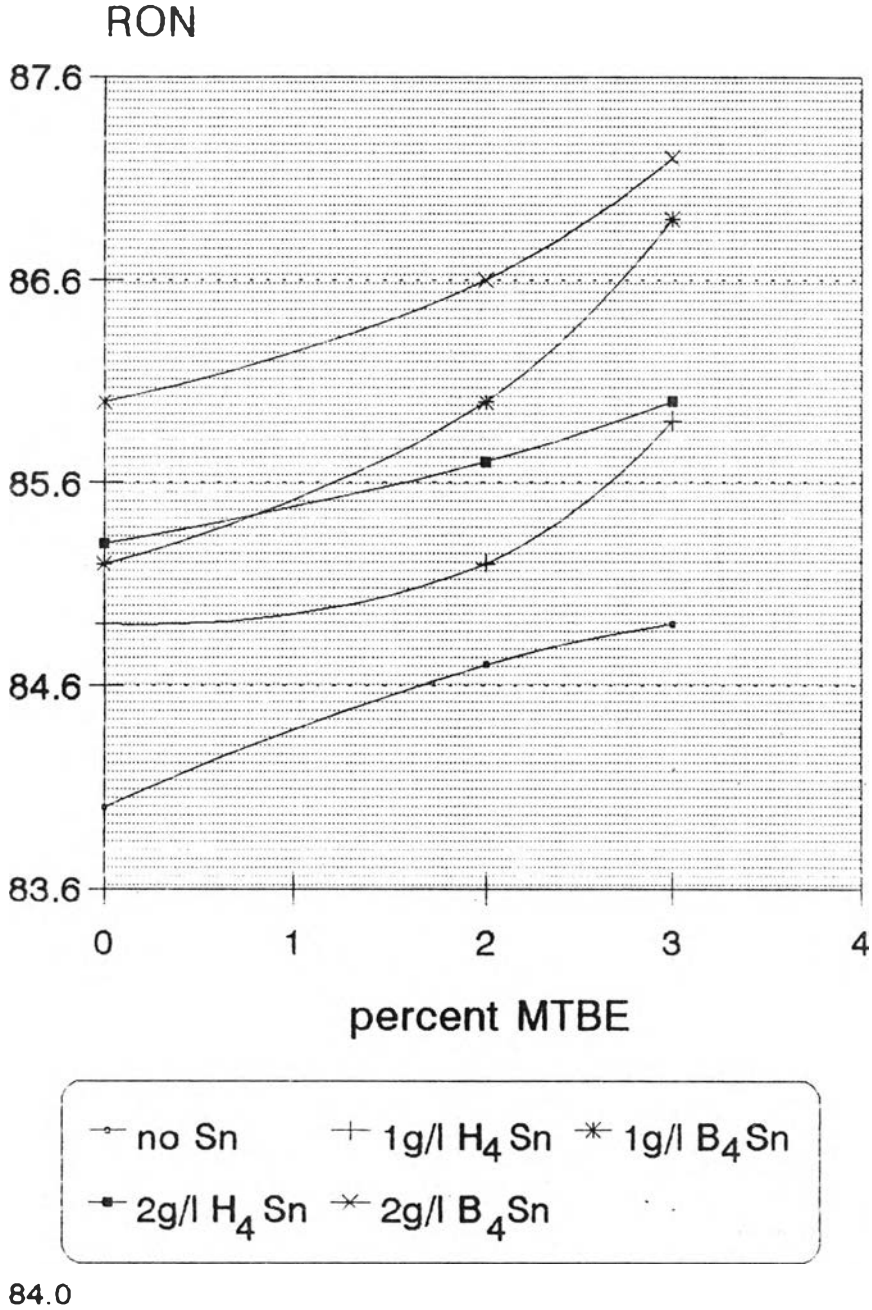
base 83.2

Table 3.2 RON of unleaded gasoline base which was blended with lower MTBE percent, tetrahexyltin and tetrabutyltin, see Fig. 3.7-3.8

Blended composition			RON
%MTBE	g/l H_4Sn	g/l B_4Sn	
-	-	-	84.0
-	1	-	84.9
-	2	-	85.3
-	-	1	85.2
-	-	2	86.0
2	-	-	84.7
2	1	-	85.2
2	2	-	85.7
2	-	1	86.0
2	-	2	86.6
3	-	-	84.9
3	1	-	85.9
3	2	-	86.0
3	-	1	86.9
3	-	2	87.2

Figure 3.7

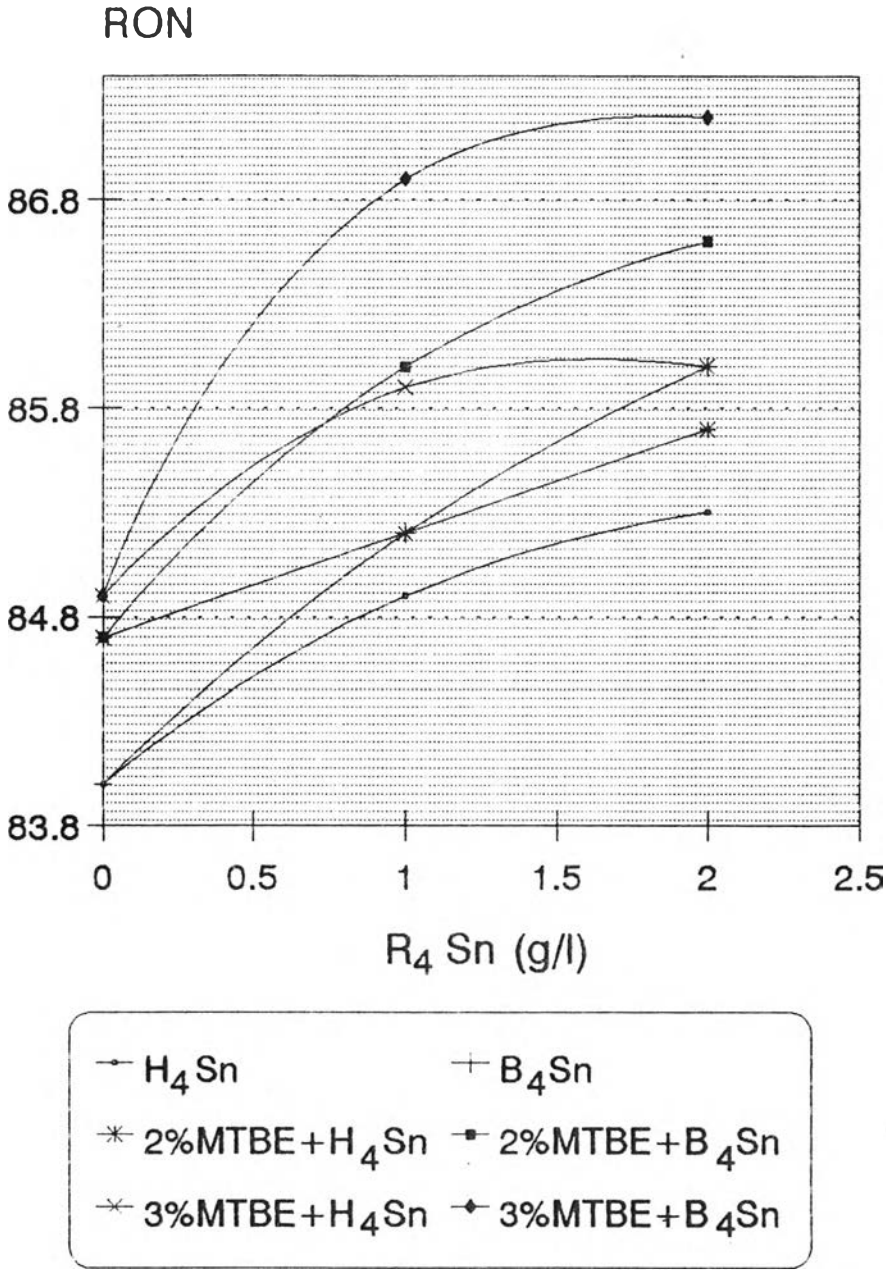
RON of unleaded gasoline base blended with lower MTBE percent. tetrahexyltin and tetrabutyltin



base 84.0

Figure 3.8

RON of unleaded gasoline base blended with lower MTBE percent, tetrahexyltin and tetrabutyltin



base 84.0

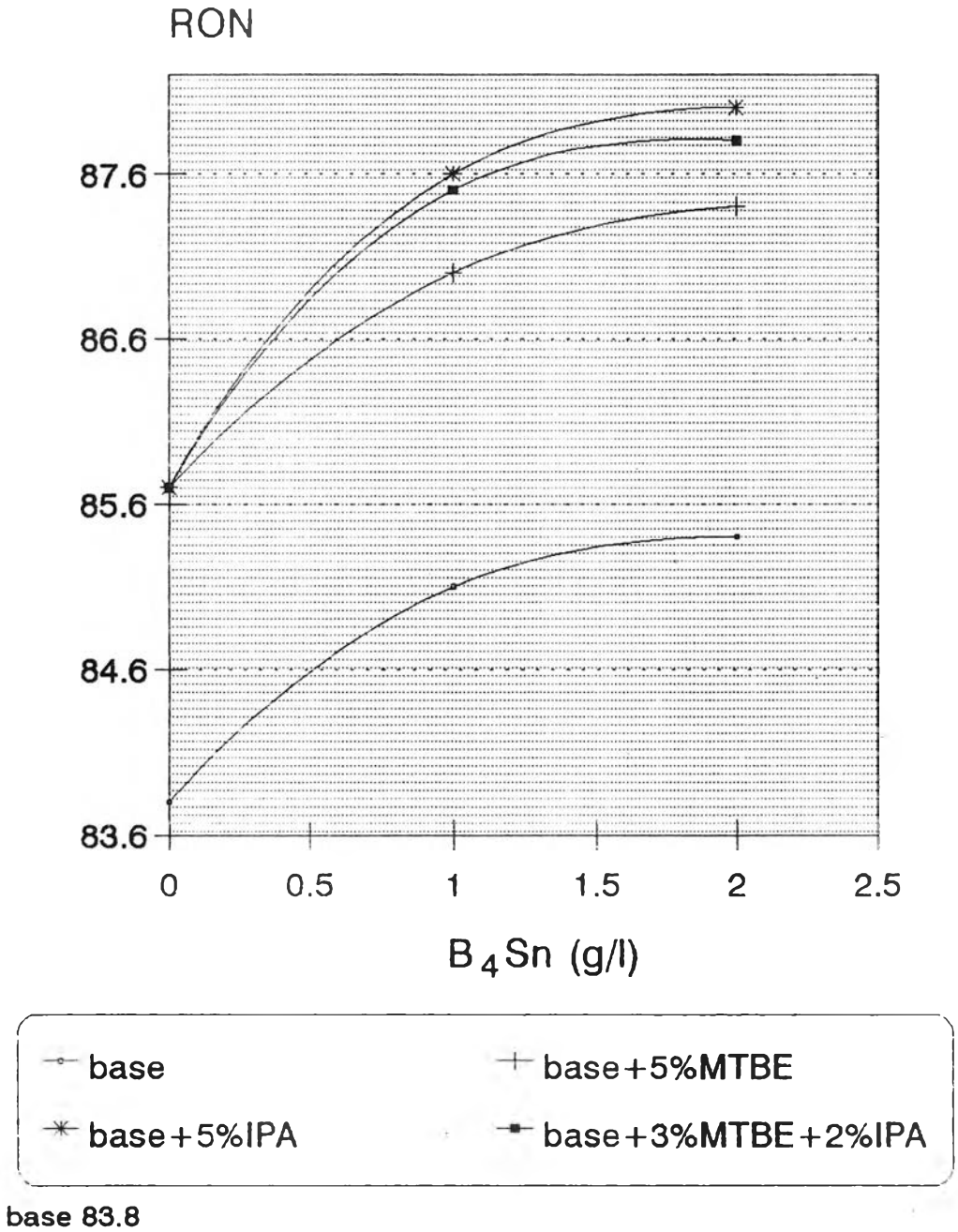
3.4.2 With MTBE, IPA and tetrabutyltin

Table 3.3 RON of unleaded gasoline base which was blended with MTBE, IPA and tetrabutyltin (5% oxygenated test 1), see Fig. 3.9

Blended composition			RON
%MTBE	% IPA	g/l B_4Sn	
-	-	-	83.8
-	-	1	85.1
-	-	2	85.4
5	-	-	85.7
5	-	1	87.0
5	-	2	87.4
3	2	-	85.7
3	2	1	87.5
3	2	2	87.8
-	5	-	85.7
-	5	1	87.6
-	5	2	88.0

Figure 3.9

RON of unleaded gasoline base blended with MTBE, IPA and tetrabutyltin (5% oxygenated test1)



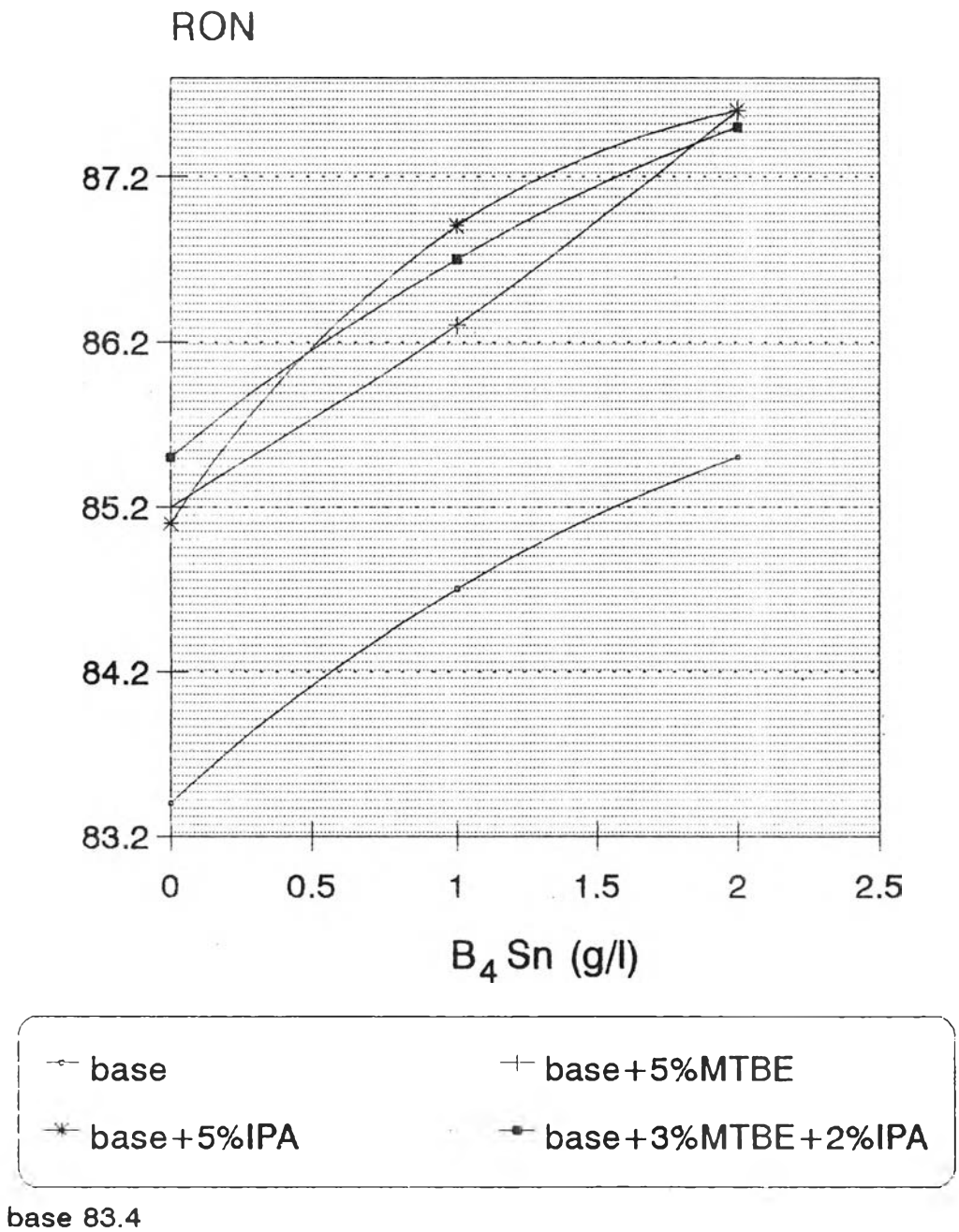
base 83.8

Table 3.4 RON of unleaded gasoline base which was blended with MTBE, IPA and tetrabutyltin (5% oxygenated test 2), see Fig. 3.10

Blended composition			RON
%MTBE	% IPA	g/l B_4Sn	
-	-	-	83.4
-	-	1	84.7
-	-	2	85.5
5	-	-	85.2
5	-	1	86.3
5	-	2	87.6
3	2	-	85.5
3	2	1	86.7
3	2	2	87.5
-	5	-	85.1
-	5	1	86.9
-	5	2	87.6

Figure 3.10

RON of unleaded gasoline base blended with MTBE, IPA and tetrabutyltin (5% oxygenated test2)



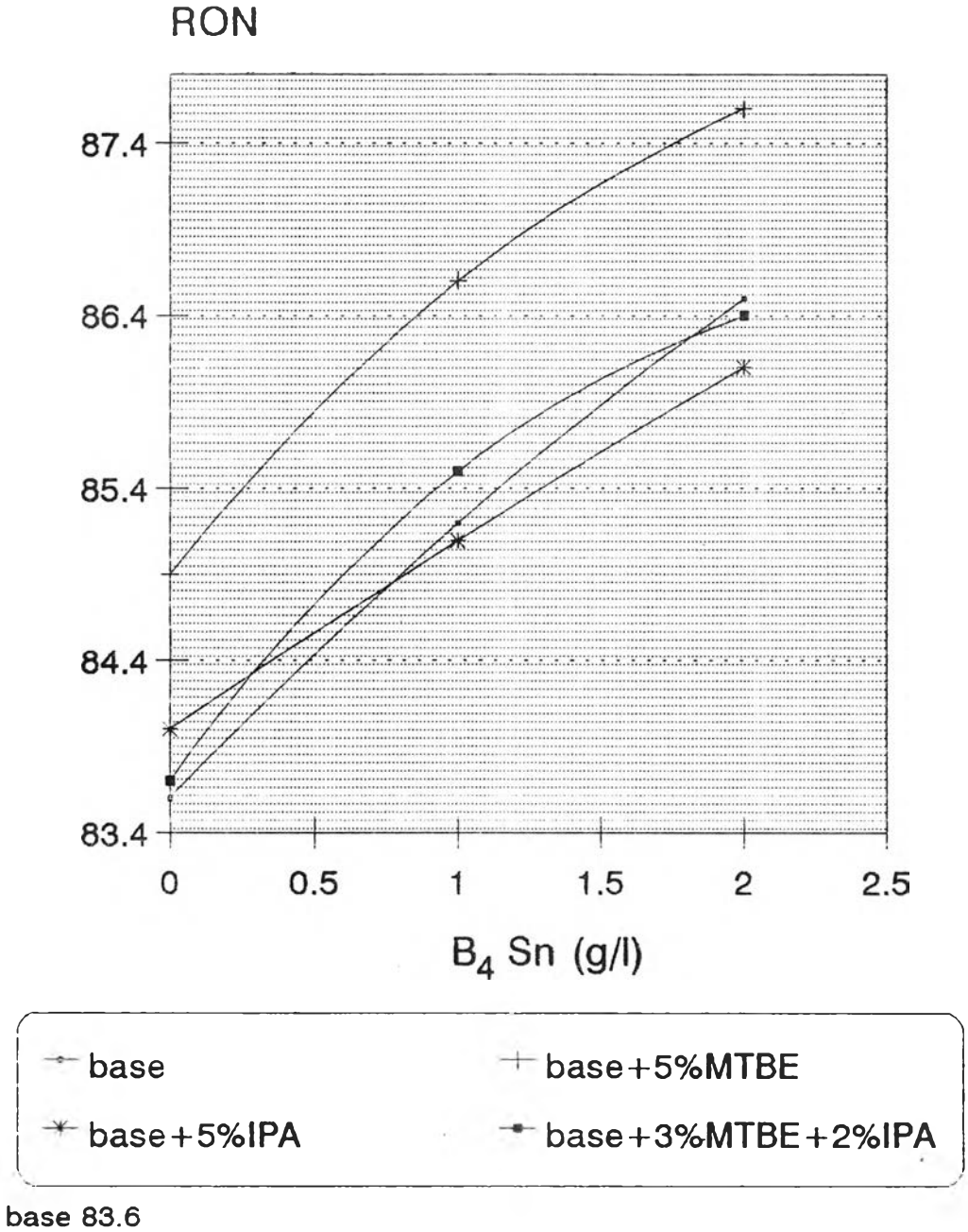
base 83.4

Table 3.5 RON of unleaded gasoline base which was blended with MTBE, IPA (non-distilled) and tetrabutyltin (5% oxygenated test 3), see Fig. 3.11

Blended composition			RON
%MTBE	% IPA	g/l B_4Sn	
-	-	-	83.6
-	-	1	85.2
-	-	2	86.5
5	-	-	84.9
5	-	1	86.6
5	-	2	87.6
3	2	-	83.7
3	2	1	85.5
3	2	2	86.4
-	5	-	84.0
-	5	1	85.1
-	5	2	86.1

Figure 3.11

RON of unleaded gasoline base blended with MTBE, IPA(non-distilled), tetrabutyltin (5% test3)



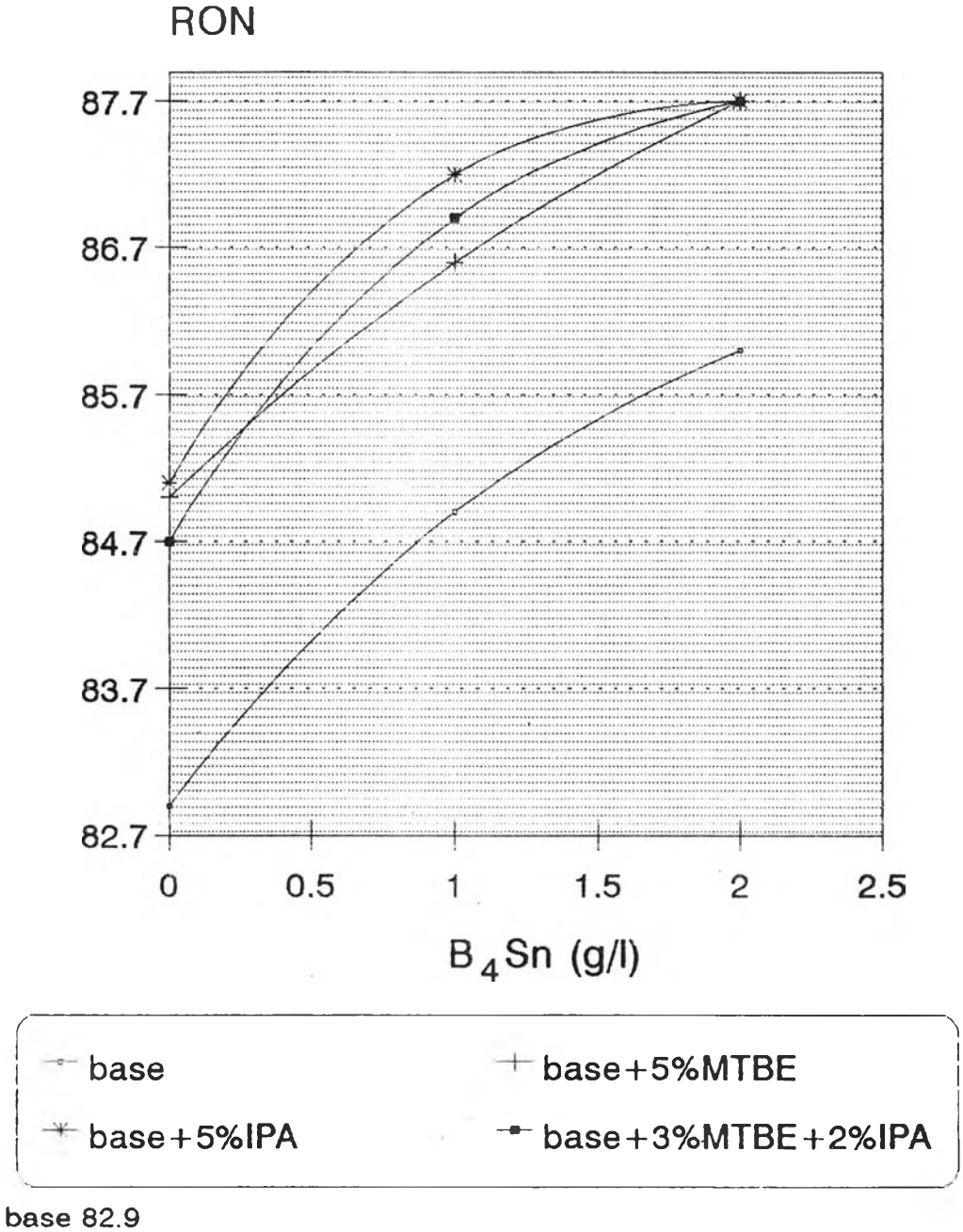
base 83.6

Table 3.6 RON of unleaded gasoline base which was blended with MTBE, IPA and tetrabutyltin (5% oxygenated test 4), see Fig. 3.12

Blended composition			RON
%MTBE	% IPA	g/l B_4Sn	
-	-	-	82.9
-	-	1	84.9
-	-	2	86.0
5	-	-	85.0
5	-	1	86.6
5	-	2	87.7
3	2	-	84.7
3	2	1	86.9
3	2	2	87.7
-	5	-	85.1
-	5	1	87.2
-	5	2	87.7

Figure 3.12

RON of unleaded gasoline base blended with MTBE, IPA and tetrabutyltin (5% oxygenated test4)



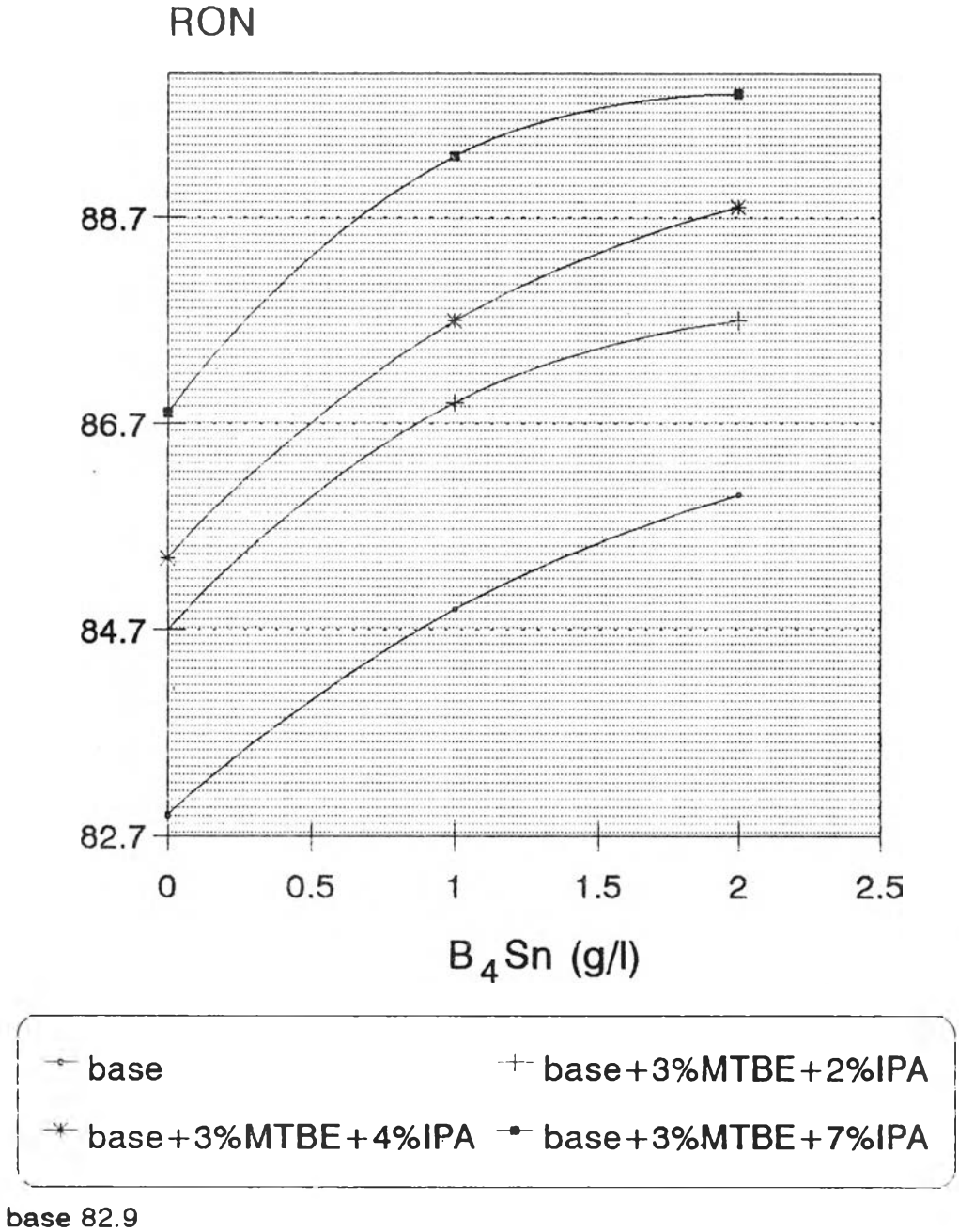
base 82.9

Table 3.7 RON of unleaded gasoline base which was blended with 3% MTBE, IPA and tetrabutyltin (5,7,10% oxygenated), see Fig. 3.13

Blended composition			RON
%MTBE	% IPA	g/l B_4Sn	
-	-	-	82.9
-	-	1	84.9
-	-	2	86.0
3	2	-	84.7
3	2	1	86.9
3	2	2	87.7
3	4	-	85.4
3	4	1	87.7
3	4	2	88.8
3	7	-	86.8
3	7	1	89.3
3	7	2	89.9

Figure 3.13

RON of unleaded gasoline base blended with MTBE, IPA and tetrabutyltin (5,7,10% oxygenated)



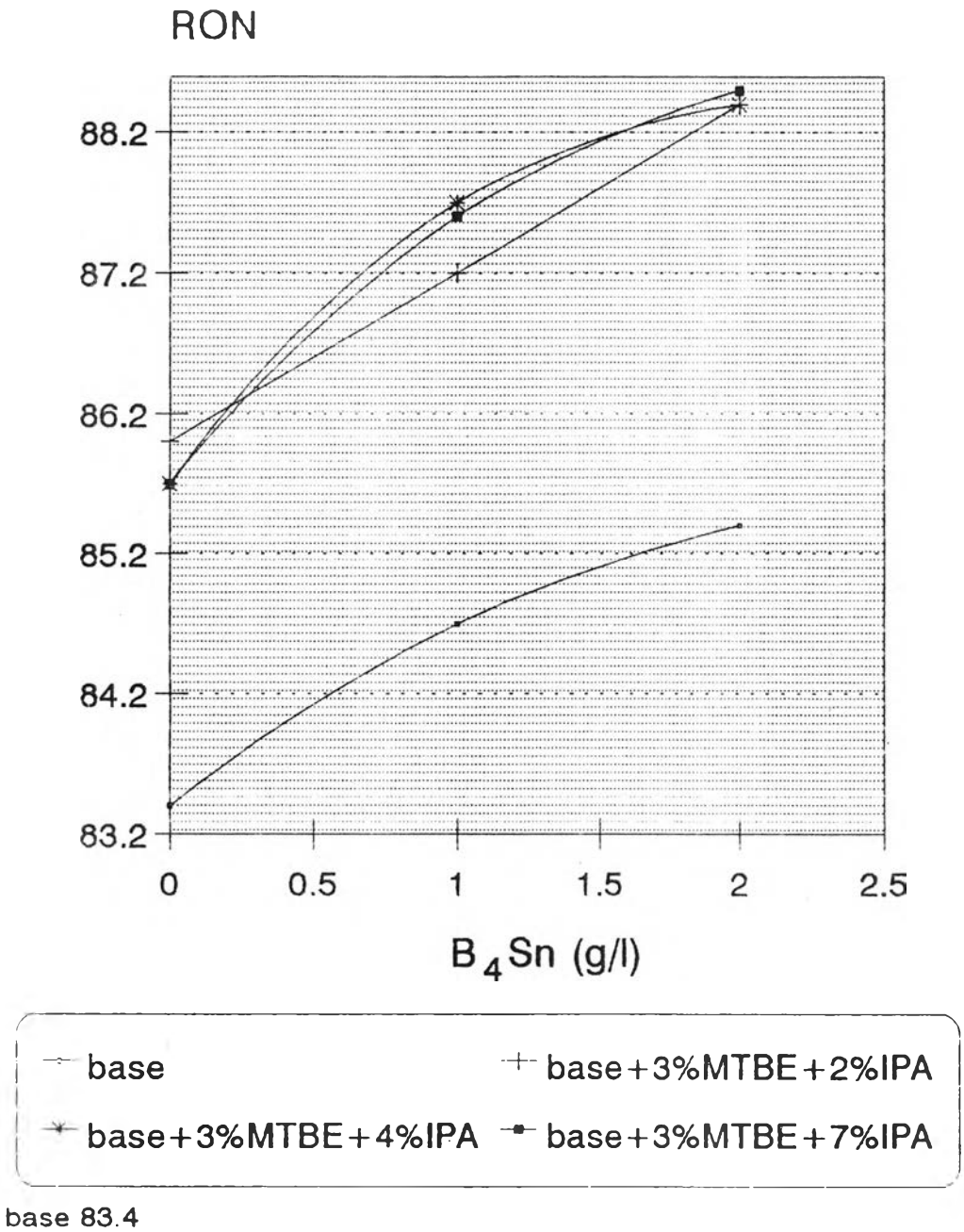
base 82.9

Table 3.8 RON of unleaded gasoline base which was blended with MTBE, IPA and tetrabutyltin (7% oxygenated), see Fig. 3.14

Blended composition			RON
%MTBE	% IPA	g/l B_4Sn	
-	-	-	83.4
-	-	1	84.7
-	-	2	85.4
2	5	-	86.0
2	5	1	87.2
2	5	2	88.4
3.5	3.5	-	85.7
3.5	3.5	1	87.7
3.5	3.5	2	88.4
5	2	-	85.7
5	2	1	87.6
5	2	2	88.5

Figure 3.14

RON of unleaded gasoline base blended with MTBE, IPA and tetrabutyltin (7% oxygenated)



base 83.4