CHAPTER III

EXPERIMENTAL

Apparatus and Instrumentations

1. Aldrich kugelrohr apparatus
   model 213-196-2
2. High Vacuum Pump
   Edward's model E2M2 20035
3. Fourier-Transform Infra red Spectrophotometer
   Perkin-Elmer model 1760x
4. Fourier-Transform Nuclear Magnetic Resonance Spectrophotometer
   Bruker model AC-F 200
5. Mass Spectrometer
   JEOR model JMS-DX 300
6. CFR standard Engine
   ASTM method D 2699
7. Hydrometer FRTCO model 141.5
   ASTM method D 1298
8. Ried Vapor Pressure Bronze tube Brass. Socket
   ASTM method D 323
9. Distillation Herzog
   ASTM method D 86
10. Gas Chromatography

Hewlett-Packard model 5890 Series II

11. Non-Dispersive Infrared Analyzer (NDIR)
    Techno test model 483
12. Timing light
    Techno test model 136

Reagents and their Purification

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 (THF) and toluene anhydrous
   Commercial grade; removed traces of water
   by refluxing with sodium metal and distilling
   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; Fluka, Switzerland
10. Tetrabutyltin

Reagent grade; Fluka, Switzerland

11. Magnesium perchlorate

    Analysis Grade (83%), Merck

12. Benzene

    Reagent grade; Farmitalia Carlo Erba

13. Toluene

    Reagent grade; Baker analyzed

14. Methylene chloride

    Reagent grade; Farmitalia Carlo Erba

15. Miscellaneous solvents

    Distilled before use

Synthesis of Tetrahexyltin by Grignard Reaction

n-Hexyl magnesium bromide was prepared from magnesium turning (9.00g, 0.37mole) and n-hexyl bromide (58.00ml, 68.15g, 0.41mole) in THF (100ml) contained in a 500ml three-necked round bottom flask fitted with a Dean-Stark glass apparatus for trapping water occured from the reaction, condenser and drying tube, dropping funnel, and magnetic stirrer. The reaction was initiated by addition of a small quantity of iodine to the flask and n-hexyl bromide was added dropwise from the dropping funnel. When the addition was completed, THF was distilled off from the reaction mixture using the Dean-Stark apparatus. Toluene (100ml) was added and then anhydrous stannic chloride (9.7ml, 21.5g, 0.082mole) was added dropwise with continuous stirring. The reaction mixture was refluxed for 3 hour. The excess Grignard reagent was decomposed by adding a small amount of saturated ammonium chloride solution. The toluene layer was evaporated under reduced pressure to yield the crude product which was distilled at reduced pressure(3mmHg) to give tetrahexyltin 32.0ml (32.32g, 85.87% yield based on stannic chloride), bp. (at 3mm Hg) 180-182°C.

FTIR (neat) see Figure 3.1

Found 2957, 2923, 2852 cm^{-1}

^1H-NMR ($CDCl_3$) see Figure 3.2

Found 0.79, 0.83, 0.88, 1.26 ppm

^{13}C-NMR ($CDCl_3$) see Figure 3.3

Found 9.26, 14.19, 22.86, 27.14, 31.59, 34.14 ppm

Mass spectrum see Figure 3.4

Found molecular peak at 375; m/e at 123, 207, 291

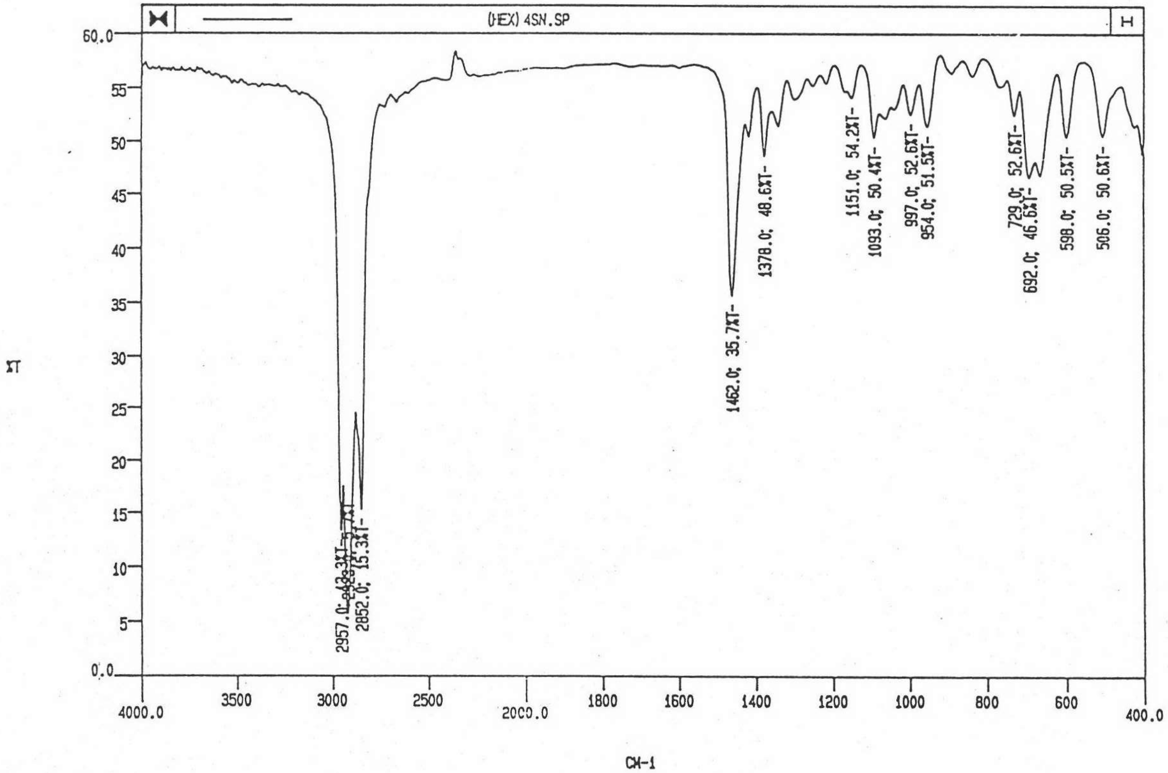


Figure 3.1 FTIR spectrum of tetrahexyltin.

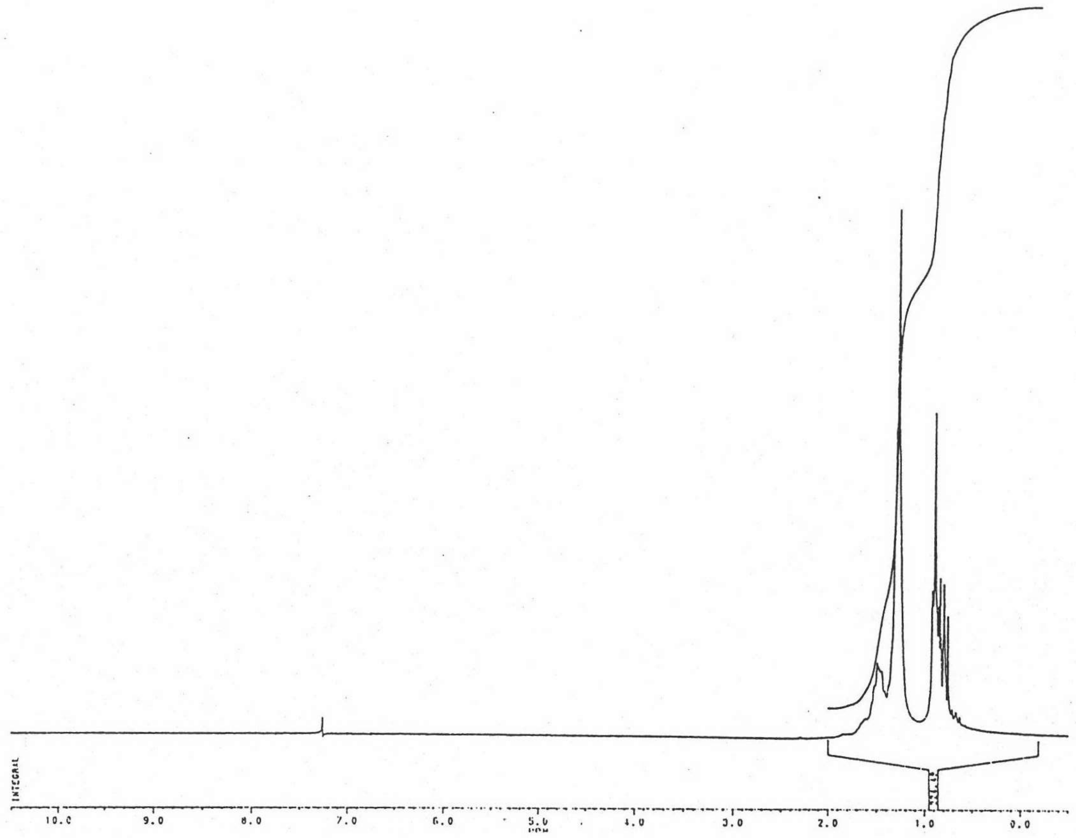


Figure 3.2 ^{1}H-NMR spectrum of tetrahexyltin.

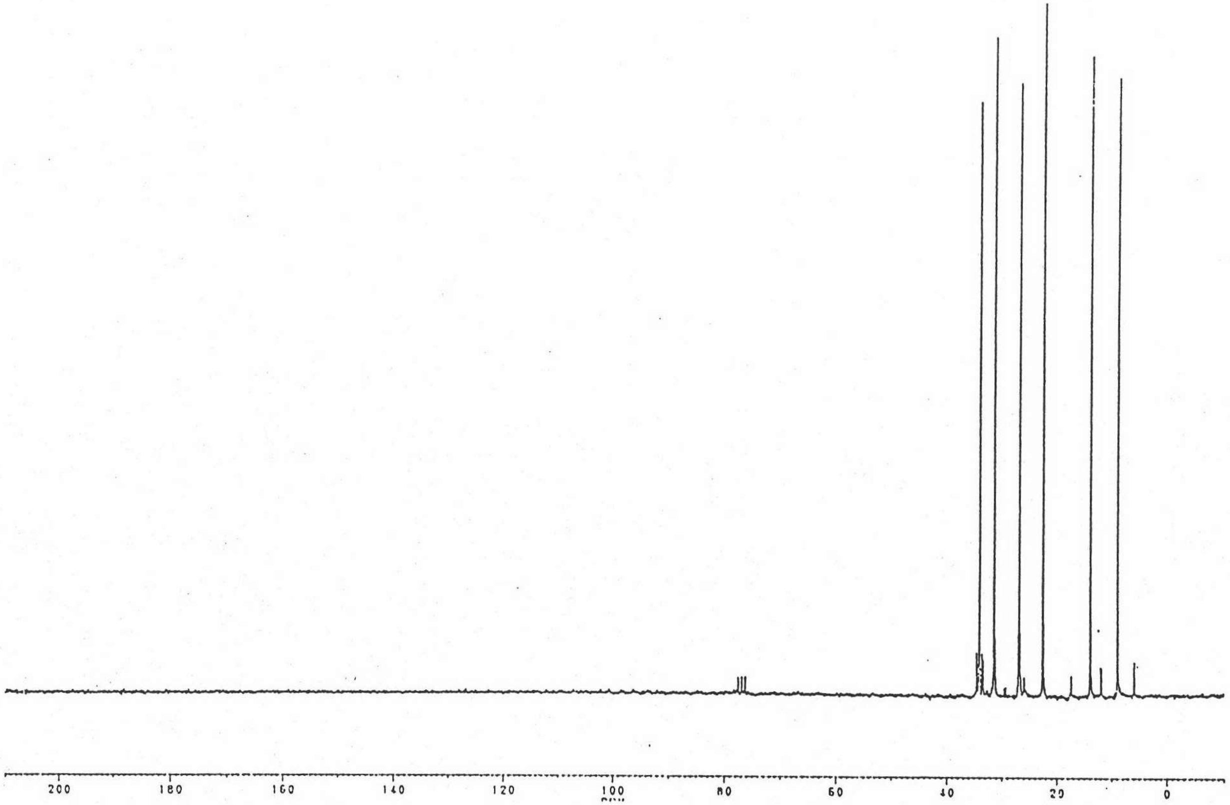
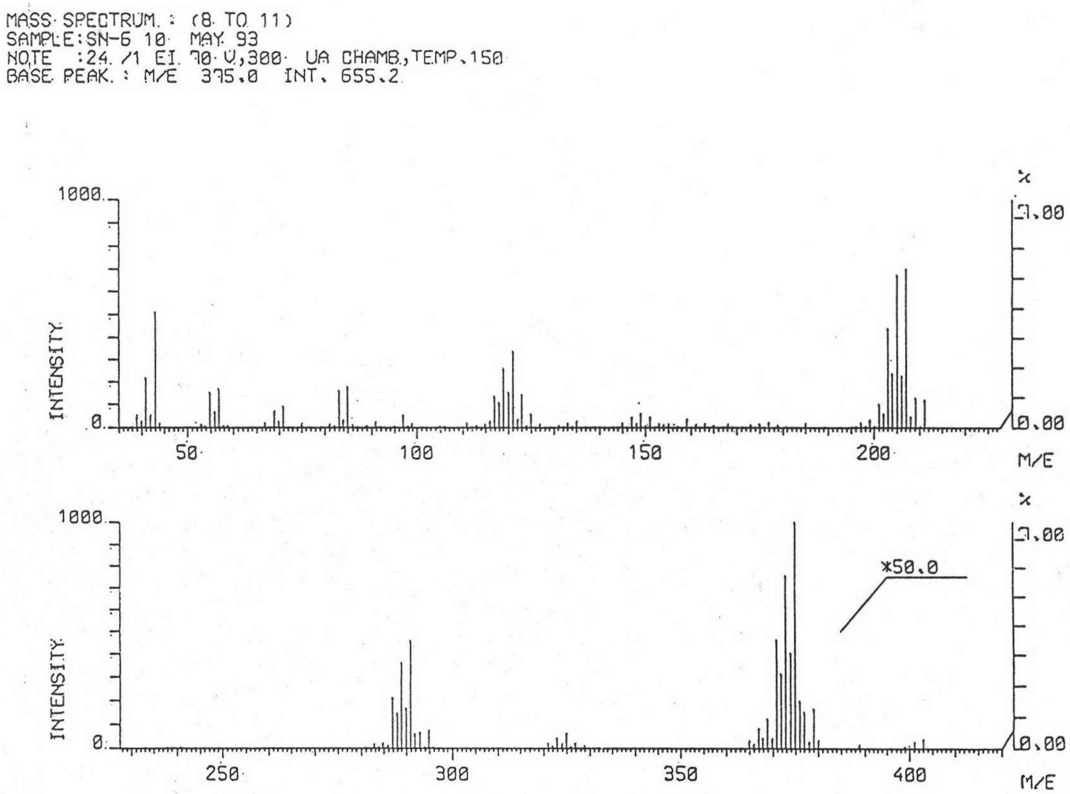


Figure 3.3 ^{13}C-NMR spectrum of tetrahexyltin.



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MASS SPECTRUM. : (8 TO 11)
SAMPLE:SN-6 10  MAY 93
NOTE  :24. /1 EI. 70 V,300  UA CHAMB.,TEMP.150
BASE PEAK. : M/E  375.0  INT. 655.2
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Figure 3.4 Mass-spectrum of tetrahexyltin.

Engine Description

The engine described in Table 3.1 was used for the exhaust emission tests. The engine was warmed up for 30 min. before measurements were taken.

Table 3.1 Description of the test engine

Make/Style	**Toyota Corolla (5K)**
Year	**1982**
Number of cylinder	**4**
Displacement volume(l)	**1.5**
Fuel system	**Carburetor**
Emission system	**Exhaust Gas Recirculation(EGR)**

Test Fuel

The three gasoline fuels used in this study are described in Table 3.2. The gasoline base fuel was prepared by mixing 55% Reformate (octane number 102.3) with 45% Light Naphtha (octane number 74.2). The gasoline fuels were blended with 3% MTBE, 2% IPA, and 1.5g/l tetrabutyltin or tetrahexyltin.

Table 3.2 Composition of gasoline test fuel

Product	Base fuel	Fuel1	Fuel2
Fuel No.	B54	F54-B	F54-H
Composition, %vol.			
Base	100.0	94.9	94.9
MTBE	-	3	3
IPA	-	2	2
Tetrabutyltin	-	0.1	-
Tetrahexyltin	-	-	0.1
TOTAL	100.0	100.0	100.0

Sampling from commercial gasolines were labeled by CG1-CG2

-CG1-CG2 were unleaded regular commercial gasolines, octane number = 92 and

-CG3-CG6 were unleaded premium commercial gasolines, octane number = 97

Exhaust Emissions Testing Procedures

Exhaust emissions (HC and CO) were measured with a Non-Dispersive Infrared analyzer (NDIR). The tests was at least done for three time at each condition of engine (timing and speed)/Fuel.

Detailed hydrocarbon measurements were taken from individual exhaust tube samples drawn during the engine test. The samples, which were collected in a 500ml gas sampling tube, were analyzed by a standard GC/FID procedure used for with automobile emissions.

1. Sample Collection

Exhaust gases were collected in a gas sampling tube (500ml) which was evacuated by vacuum pump before sample collected (Figure3.5).

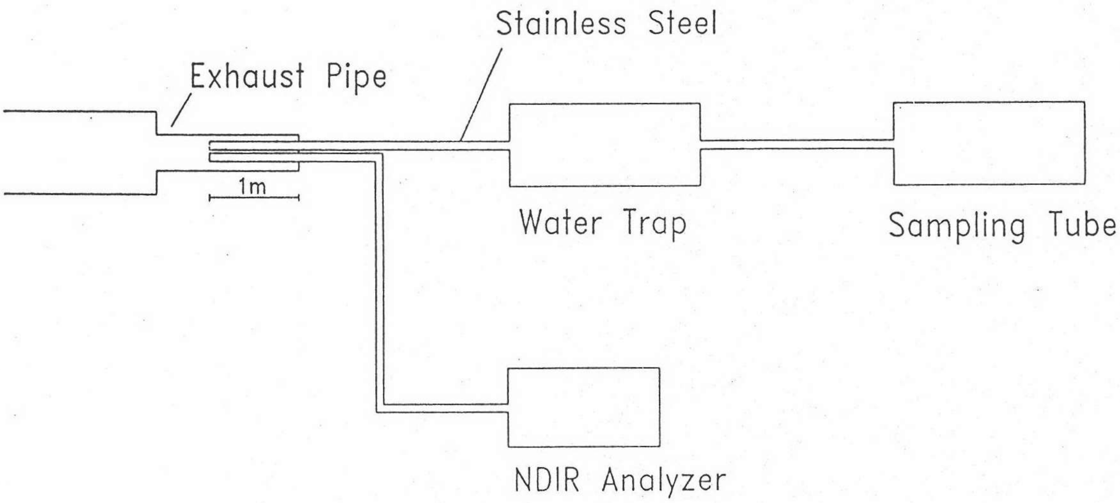

Figure 3.5 Schematic of sample collection for analysis by GC

2. Chromatographic Conditions

The individual hydrocarbons were separated on a DB-1 fused silica capillary column using the experimental conditions listed in Table 3.3.

Table 3.3 Chromatographic condition of individual hydrocarbons analysis

Column	**DB-1 30m × 0.25mm ID fused silica capillary (0.1μm film)**
Carrier gas	**He 32 cm^3/sec.**
Temperature program	**30°C, hold for 2min. 10°C/min. to 100°C, hold for 1 min.**
Detector	**Flame ionization detector (FID) (heated to 300°C)**
Sample injection	**Heated up to 100°C**
Sample size	**1 ml**
Standard size	**1 μl**

3. Compound Identification

Each hydrocarbon was identified by comparing its retention time with those obtained from known hydrocarbon standards or by adding known hydrocarbon standards to the sample.

4. Standard Preparation

1. Standard preparation (Benzene and Toluene) was shown in Table3.4

Table 3.4 Dilution for preparation of standards

Hydrocarbon* Concentration in ppm.	Aliquot of Hydrocarbon	Final Dilution volume in ml
10000	1 ml Pure Hydrocarbon	100
1000	5 ml of 10000 ppm Standard	50
200	5 ml of 1000 ppm Standard	25
20	1 ml of 200 ppm Standard	10

Note : Hydrocarbon was Benzene or Toluene.

2. Standards were stored at 20°C

5. Calculation of Hydrocarbons Concentrations

Total hydrocarbon concentrations in exhaust gases were measured with a flame ionization detector (FID) which was calibrated with benzene and toluene standards. It was assumed that all hydrocarbons gave the same FID response (on a per-carbon basis). Calculation separated two group. Benzene used to compare C_4-C_6 hydrocarbon concentrations. Toluene used to compare C_7-C_8 hydrocarbons (see Appendix I)