CHAPTER III

EXPERIMENTAL

MATERIALS

1. Base gasolines
2. Base diesels
3. LZ 8195 ; as dispersant additive package for gasoline
   Lubrizol
4. LZ 8252 ; as dispersant additive package for gasoline
   Lubrizol
5. LZ 8250 ; as dispersant additive package for gasoline
   Lubrizol
6. LZ 8250 (new) ; as dispersant additive package for gasoline
   Lubrizol
7. LZ 8253 ; as dispersant additive package for gasoline
   Lubrizol
8. Hitech-4961A ; as dispersant additive package for gasoline
   Adibis
9. LZ 9530T ; as dispersant additive package for diesel
   Lubrizol
10. Methyl alcohol
    analytical grade; J.T. Baker Inc.
11. Tetrahydrofuran
    HPLC grade; J.T. Baker Inc..
12. Xylene
    Solvent grade; J.T. Baker Inc.

13. Hexane

    Solvent grade; J.T. Baker Inc.

14. Aluminium oxide 90 active, neutral (70-230 mesh ASTM)

    for column chromatography; Merck

15. Aluminium oxide 90 active, basic (70-230 mesh ASTM)

    for column chromatography; Merck

16. Aluminium oxide 90 active, acid (70-230 mesh ASTM)

    for column chromatography; Merck

17. Nitrogen gas

    indurstrial grade; Thai industrial gas

APPARATUS AND INSTRUMENT

1. Sep-Pak Pump

    Vacuum Manifold, Waters

2. Rotary evaporator

    Rotavapor-R, BUCHI

3. High Performance Liquid Chromtography (HPLC) - pump

    307 pump, GILSON

4 .Gel Permeable Chromatography GPC column

    - PLgel 5 μm 50 A 300x7.5 mm column, Polymer laboratories
    - PLgel 5 μm 100 A 300x7.5 mm column, Polymer laboratories
    - PLgel Mix-E 300 x 7.5 mm column, Polymer laboratories

5. Evaporative Mass Detector (EMD)

    PL-EMD 950, Polymer laboratories

6. Injector

7. Loop 20 μl

8. Syringe 25 μl

PROCEDURE

1.GASOLINE

1.1 Preparation of standard gasoline

A stock solution was prepared by weighing 1.49 g of LZ 8195 (accurate to 0.1 mg) in 1000 ml volumetric flask and gasoline (specific gravity = 0.745)was added to make 2000 mg/kg (ppm wt/wt) standard gasoline. The 2000 ppm standard gasoline was diluted to make standard gasolines containing 400,500,600,700, 800 and 900 ppm of LZ 8195, respectively.

1.2 Injection sample in HPLC/GPC system

The HPLC/GPC system was set up in operating condition for optimized the conditions which varied as follows;

- type of GPC column
- temperature of the Evaporative Mass Detector (EMD)
- the flow rate of Nitrogen gas
- the flow rate of Tetrahydrofuran (THF)

Other conditions of EMD were set up. After that the base gasoline was injected into HPLC/GPC system to check base line of system.

20 microlitres of standard gasoline was injected by 25 microlitres syringe,using a range of 400 ppm to 900 ppm samples. The first peak in the chromatogram was due to the dispersant polymer.

1.3 Calibration curve

Chromatogram from 1.2 was integrated in the first peak which was dispersant polymer molecules in LZ 8195 package. These peak area were shown the concentration (ppm wt/wt) of LZ 8195 in gasoline. Used these peak area from standard gasoline (400-900 ppm) to prepare standard calibration curve.

1.4 Calculation of LZ 8195 in gasoline sample

20 microlitres of unknown gasoline sample (commercial gasoline) was injected and compared peak area at the first peak with the standard calibration curve to determine the amount of LZ 8195 in unknown gasoline sample.

The concentration of LZ 8195 in unknown gasoline sample can be calculated according to the equation :

$$\text{LZ 8195 (ppm wt/wt)} = (Y-C)/S$$

where :

S = slope of calibration curve

Y = peak area of the first peak in chromatogram

C = intercept of calibration curve

The concentration of other dispersant additive packages can be determined with this method.

1.5 Calculation of other dispersant packages in gasoline sample

Other dispersant additive packages for gasoline such as LZ 8252, LZ 8250, LZ 8250 (new), LZ 8253 and Hitech-4961A can be calculated like in LZ 8195.

2. DIESEL

2.1 Preparation of standard diesel

Standard diesels with LZ 9530T were prepared like in gasoline which containing 200, 250, 300, 350, 400 and 500 ppm wt/v.

2.2 Separation of LZ 9530T from base diesel

Alumina (aluminium oxide 90 active; neutral) 2 g was packed in 5 ml syringe as packed column. The standard diesel was loaded into this syringe.Some solvent was eluted into the syringe to separated the additive (dispersant) away from base diesel. The syringe was eluted again by suitable solvent for separated the dispersant (from LZ 9530T) from away alumina into 100 ml round bottom flask. The round bottom flask was taken to rotary evaporator until the solvent was dried.

For this method we must be carefully to select the suitable absorbent and suitable solvent for optimized condition to separate the dispersant away from base diesel in the final. It have varied conditions to optimized as follow;

- type of absorbent like as alumina neutral, alumina basic and alumina acid

- type of solvent for separated dispersant away from base diesel.
- type of solvent for separated dispersant away from absorbent
- volume of diesel and solvent for loading in syringe.

2.3 Injection sample in HPLC/GPC system

Tetrahydrofuran (THF) was added into the dried round bottom flask. The solution was transfered into 5 ml volumetric flask and add THF until 5 ml.The HPLC/GPC system was set up in operating condition for optimized condition like in gasoline.

20 microlitres of standard diesel was injected by 25 microlitres syringe begin at 200 ppm to 500 ppm into HPLC/GPC system. Notice the first peak in the chromatogram, it was dispersant molecules in LZ 9530T.

2.4 Calibration curve

Chromatograms from 2.3 were integrated in the first peak. This peak area have shown the concentration (ppm wt/v) of LZ 9530T in diesel. Used these peak area from standard diesel to prepare standard calibration curve of LZ 9530T.

2.5 Calculation of LZ 9530T in diesel sample

Unknown diesel sample (commercial diesel) was separated the dispersant away from base diesel, evaporate until dried and make volume by THF in 5 ml volumetric flask. 20 microlitres of sample was injected to HPLC/GPC system and compared peak area at the first peak with standard

calibration curve to determine the amount of LZ 9530T in unknown diesel sample.

The concentration of LZ 9530T in unknown diesel sample can be calculated according to the equation ;

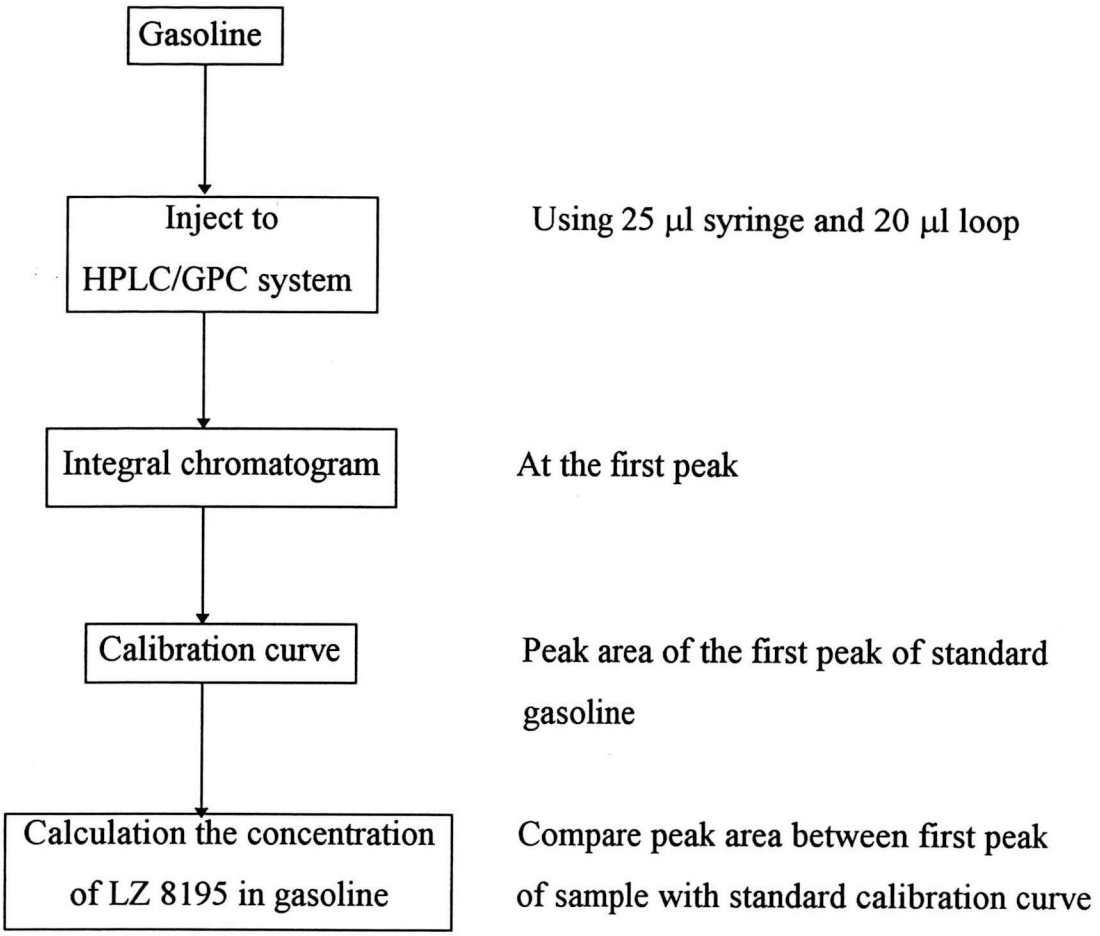
$$\text{LZ 9530T (ppm wt/v)} = (Y-C)/S$$

where;

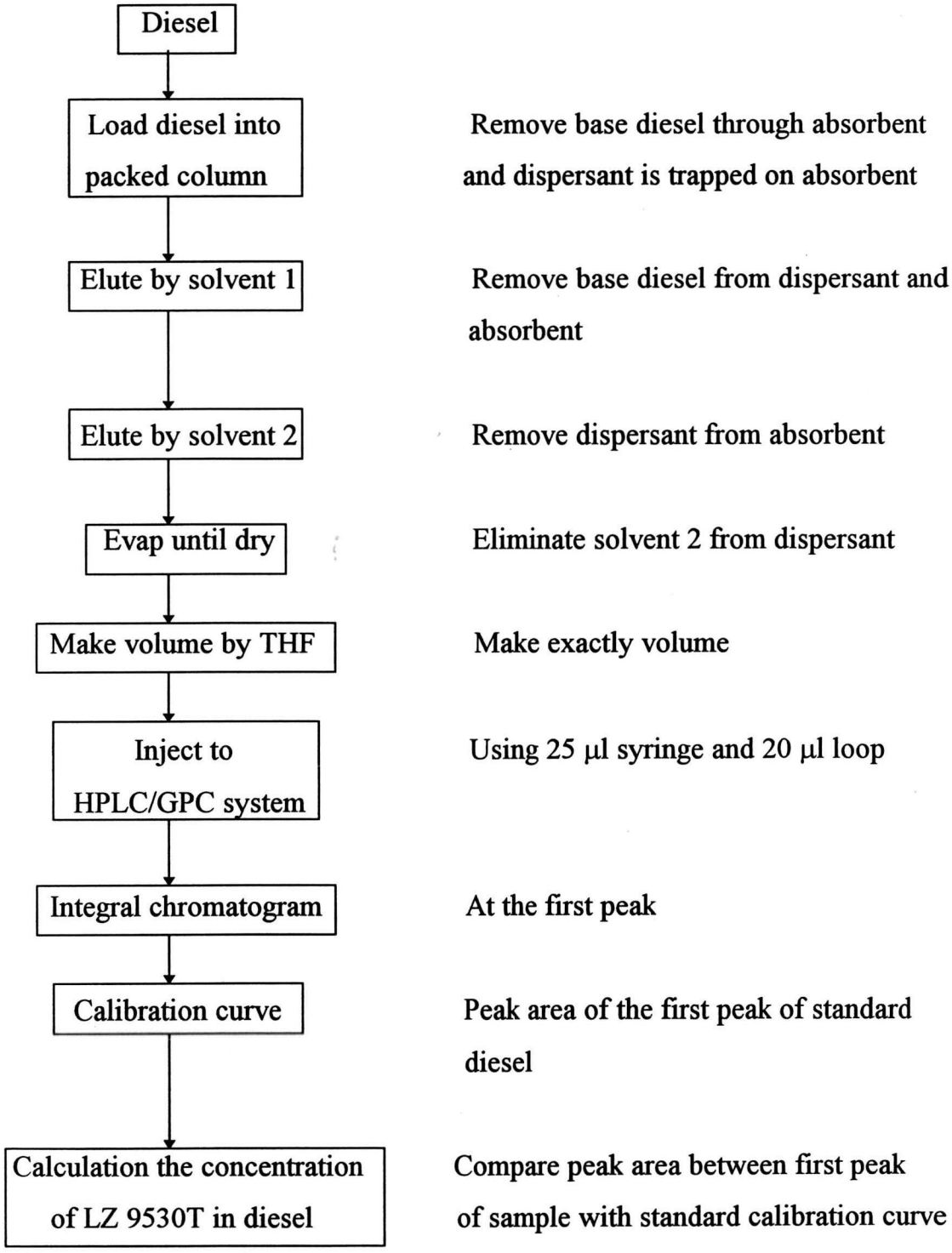
S = slope of calibration curve

Y = peak area of the first peak

C = intercept of standard calibration curve.



Scheme 3.1 The overall process to determine the concentration of LZ 8195 as dispersant additive in gasoline



Scheme 3.2 The overall process to determine the concentration of LZ 9530T as dispersant additive in diesel