CHAPTER III

RESEARCH METHODOLOGY

3.1 DETERMINATION OF SILICONE CONTENT ON VARIOUS RELEASE LINERS AND LABELS ADHESIVE SITE USING FT-IR ANALYSIS

3.1.1 PROCEDURE (52)

This experiment uses Nicolet Magna 760 E.S.P with MCT detector see Figure D1 in appendix D, attenuated total reflectance (ATR) Attachment, Vertical type as variable ATR Spectra Tech, #300, P/N#0012-010 see Figure D2 in appendix D and crystal type used as KRS-5 (thallous bromide-iodide) and 50x10x3 mm, 45°, parallelogram, for VATR P/N #0050-703.

3.1.2 METHOD FOR CREATING SILICONE STANDARD CURVE

Prepare 1 mg/ml standard stock solution of dimethyl polysiloxane then dilute to 0.1 mg/ml and 0.01 mg/ml standard solution and keep in a 2 ml vial with properly seal.

3.1.2.1 Generation of 0-10.0 μg curve

Step 1 to create the 0-10.0 μg curve

Draw 5 μl of the 0.1 mg/ml standard silicone oil solution into the cleaned syringe and deposit the solution near the **first deposition point** of the ATR crystal. This volume equates to 0.5 μg of silicone. Try to keep the droplet centered on the ATR crystal and away from the edges while the hexane evaporates. Replace the ATR crystal in the FTIR. Collect an FTIR spectrum of this sample and subtract the background. Repeat the above procedure until an appropriate baseline is obtained. If all is satisfactory, then record the baseline corrected peak height of the 800 cm^{-1} band associated with this concentration of silicone.

Step 2 to create the 0-10.0 μg curve

Deposit an additional 5 μl of the solution (as described above) on the **next deposition point.** Overall, this is the second point of deposition. This volume equates to an additional 0.5 μg of silicone for a combined total of 1.0 μg of silicone on the crystal and collect an FTIR spectrum of this sample and ratio it against the background. Record the baseline corrected peak height of the 800 cm^{-1} band associated with this concentration of silicone.

Step 3 to create the 0-10.0 μg curve

Deposit an additional 10 μl of the solution (as described above) on **the next deposition point.** Overall, this is the third point of deposition. This volume equates to a total of 2.0 μg of silicone on the crystal and collect an FTIR spectrum of this sample and ratio it against

the background. Record the baseline corrected peak height of the 800 cm^{-1} band associated with this concentration of silicone.

Note: Check the peak heights of the 800 cm^{-1} silicone band for the three (3) concentrations (0.5 μg, 1.0 μg, and 2.0 μg) at this time. If the peak heights have not doubled (within 10%) from the first to the second deposition (0.5 μg to 1.0 μg) and from the second to the third deposition (1.0 μg to 2.0 μg). Then data acquisition must be stopped. The ATR crystal is cleaned and the operator should begin a new measurement from section 3.1.2.1.

Step 4 to create the 0-10.0 μg curve

Repeat Step 3, increment the deposition point by one each time and deposit 10 μl of solution per increment until a total of 10 μg (11 deposition points) of silicone has been deposited onto the ATR crystal.

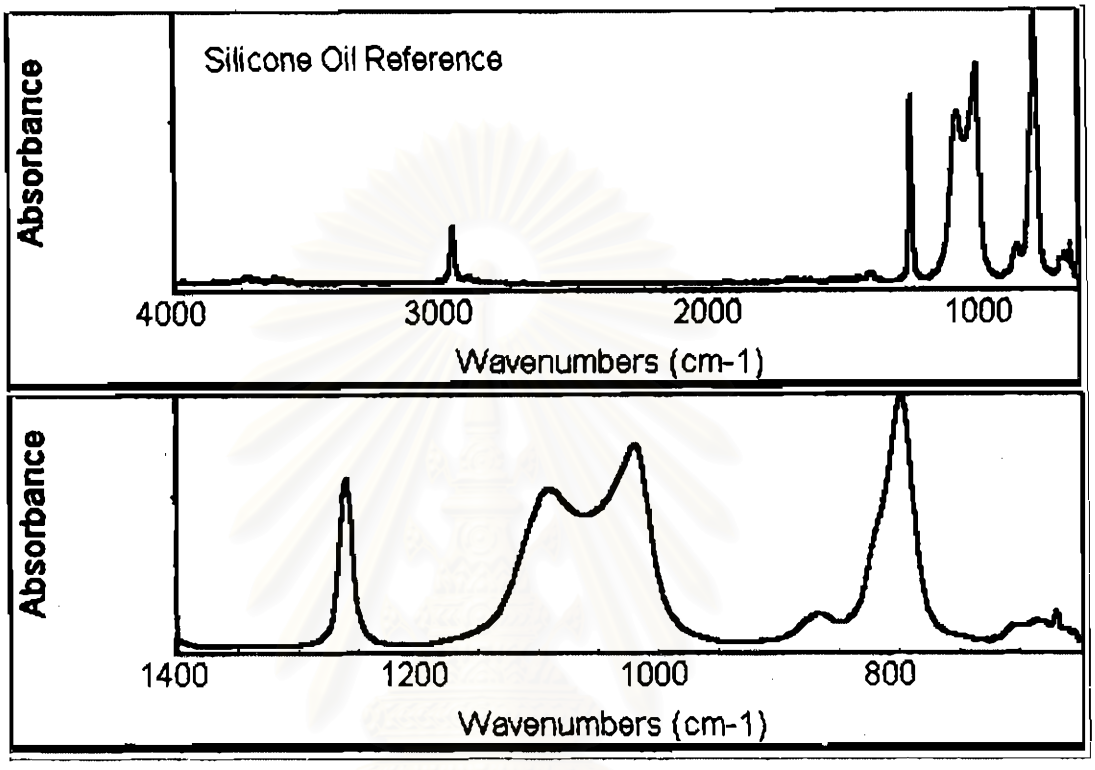
Step 5 to create the 0-10.0 μg curve

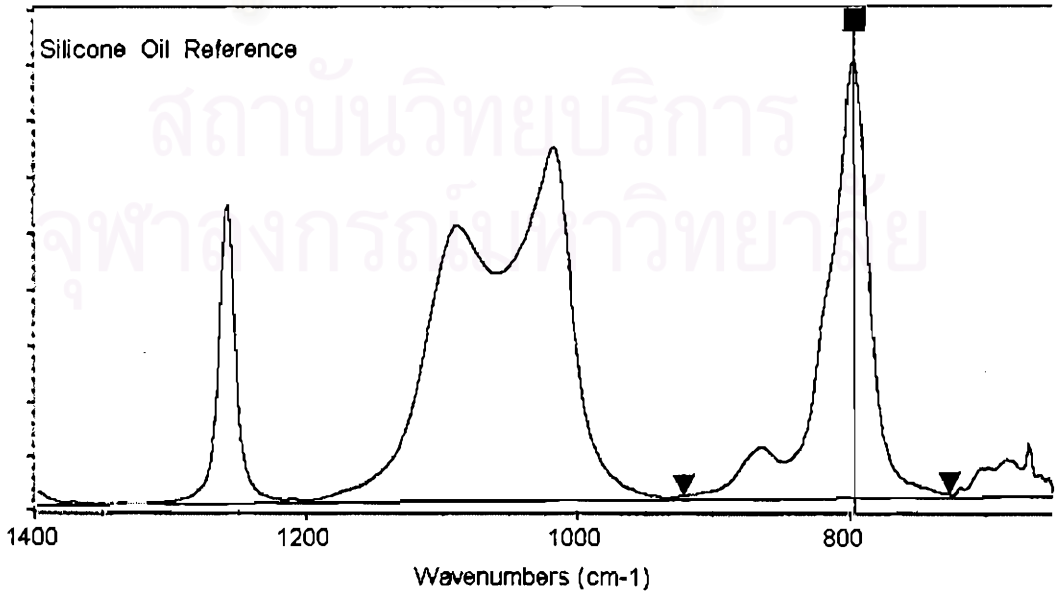
After completion of Step 4, there should be a total of 11 data points ranging from 0.5-10 μg of silicone generated. From each spectrum obtained, calculate the baseline corrected peak height for silicone. The following baseline points are suggested:

Compound	**Peak** (cm^{-1})	**Starting Point** (cm^{-1})	**End Point** (cm^{-1})
Silicone	800 ± 10 cm^{-1}	925-900	750-730

See Figure 3.1 for silicone identification and peak height determination.

Figure 3.1 Silicone peak height determination and identification





Plot "mAbs vs. Concentration (μg silicone)" and determine the equation of the line that best represents the data (Linear Regression). This is the standard linear plot for the 0-10 μg range. A linear regression program will generate the slope, y-intercept, and correlation coefficient in the form of y = mx + b where y = measured mAbs

m = line slope

b = y-intercept

x = concentration in μg

3.1.2.2 Generation of 0-1 μg curve

Repeat the above procedure to create the standard curve for 0-1.0 μg range using the 0.01 mg/ml standard solution.

3.1.3 Standard Curve Criteria

In addition, it is suggested that the following criterion be used in determining the validity of the regression equations.

3.1.3.1 The y-intercept value should not be greater than 10% of the slope value.

3.1.3.2 If the value of the y-intercept is greater than 10% of the slope value, determine the change in the slope if the linear regression line was forced through the origin (0,0).

3.1.3.3 If this change is within 5% of the original slope value, then the original equation with the y-intercept value can be used.

3.1.4 FT-IR Sample Recovery

Definition: Sample recovery is defined as the percent sample transferred from the evaporating dish to the ATR crystal.

3.1.4.1 Add 0.5 μg of silicone from the standard solution into a precleaned petri dish

3.1.4.2 Add 2 ml of hexane into the evaporating dish and swirl in the dish to insure mixing

3.1.4.3 Evaporate to approximately 1 ml using low heat. (Do Not Boil!)

3.1.4.4 Transfer the residue from the evaporating dish onto the ATR crystal using a precleaned syringe, in a drop-wise fashion. (ONE SHOULD RINSE THE EVAPORATING DISH 3 TIMES WITH HEXANE IN ORDER TO ASSURE A HIGH SAMPLE RECOVERY)

Note: Multiple rinsing beyond three times may be necessary if a high concentration of contaminants are present. In general, one should not notice additional residue on the ATR crystal if a high recovery has been attained.

3.1.4.5 Collect the IR spectrum and calculate the concentration from the measured Absorbance using the standard curve (0-1 μg range) generated earlier

Example: For line equation, $Y = mX + b$

Y = measured mAbs

m = line slope

b = Y-intercept

X = concentration of unknown in micrograms

if the measured mAbs is 9.6, then, unknown, $X = \frac{9.6 - b}{m}$

3.1.4.6 Calculate % Recovered as follows:

$$\% \text{ Recovered} = \frac{\text{measured } (\mu g)}{0.5} \times 100$$

3.1.4.7 Repeat the above for the 1.0 μg standard for high concentration calibration curve

Note: Repeat step 1-6 three times for each concentration.

3.1.5 Sample Extraction for FT-IR analysis

Cut a sample minimum at least 4 x 4 sq.cm. then rinse the sample with hexane into an evaporating dish using hexane 30 ml and evaporate the extracted solution at 65°C until the solution remain a few microlitre. Use a clean syringe draw remaining solution and deposit it onto KRS-5 then repeat this step four times and collect an FT-IR spectrum. Rinse the evaporating dish with a few dropper of hexane and then evaporate the extracted solution at 65°C until the solution remains a few microlitre again. Then use a clean syringe draw remaining solution and deposit it onto KRS-5 and collect an FT-IR spectrum.

Note: A positive identification of a silicone oil compound requires the presence of four (4) absorption bands at the following wavenumbers.

$800\ cm^{-1} \pm 10\ cm^{-1}$

$1020\ cm^{-1} \pm 10\ cm^{-1}$

$1090\ cm^{-1} \pm 10\ cm^{-1}$

$1260\ cm^{-1} \pm 10\ cm^{-1}$

3.1.5.1 Calculation

The concentration of silicone was calculated from the measured absorbance using the standard curve generated earlier.

Example: For line equation, $Y = mX + b$

Y = measured absorbance

m = line slope

b = Y-intercept

X = unknown microgram

if the measured milliabsorbance is 9.6, then, unknown, $X = \frac{9.6 - b}{m}$

So, absolute silicone on a piece part is $\frac{XK}{SA}$

Where X = Amount of silicone

K = Recovery factor for each curve range of each standard

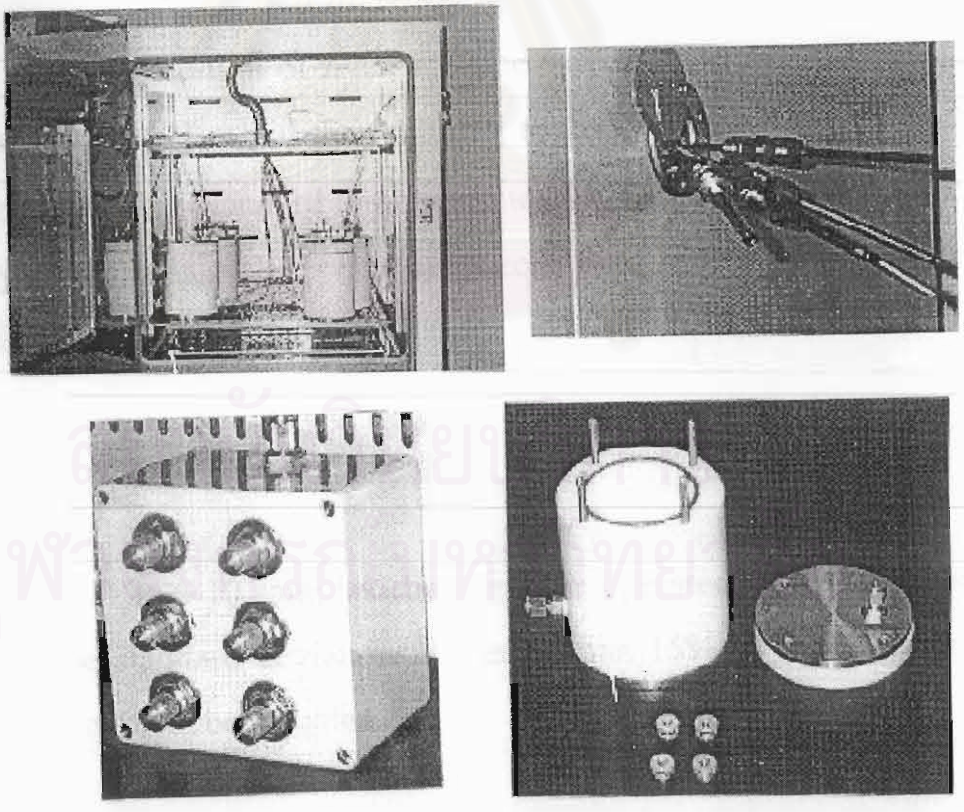
SA = Surface area (cm^2)

3.2 DHS OUTGASSING TEST ANALYSIS

3.2.1 PROCEDURE (53)

Using Gas Chromatograph with Mass Detection (HP) and ATD 400 Perkin Elmer. The Adsorbent Tubes packed with 200 mg Carbotrap C and 100 mg Carbotrap B. The samples will be prepared by using Dynamic headspace sampler chamber (Figure 3.2) and purge with Nitrogen Gas, 99.999% purity.

Figure 3.2 Dynamic Headspace Sampler (DHS Fixture)



3.2.2 Measurement Methods

3.2.2.1 Calibration Procedure

This section includes the procedure for making standard solutions and using the standard solutions to procedure calibration curves. The acceptance criteria for the calibration curves are also outlined.

3.2.2.1.1 Calibration Procedure for Semi-Quantitative Analysis

Step 1

Preparation of n-hexadecane external and internal standards stock solution at 10 μg/μl then dilute it to 200 ng/μl. Inject 5 μl of the 200 ng/μl working standard to obtain a total of 1000 ng of n-hexadecane directly into the injection ports or directly into the preheated chamber with nitrogen flowing.

Step 2

The 6-10 samples chambers are operated using the standard only. If the standard deviation is greater than 15% of the average, the measurement must be repeated.

3.2.3 Sampling Method

3.2.3.1 Sampling Condition

3.2.3.1.1 Sampling Conditions for DHS

Gas:	Nitrogen (99.999%)
Flow:	50 +/-2 ml/min
Temp/Time:	85 °C/3 hrs
Adsorption Tubes:	Carbotrap C/Carbotrap B

3.2.3.1.2 Conditions for ATD/GC/MS

Gas:	Helium (99.999%)
ATD Flow:	50 +/-2 ml/min
Outlet Split:	1:50 Ratio
Desorb Flow:	50 ml/min
Desorb:	340°C /8 min
ATD Trap:	Carbotrap C packing
Trap Conditions:	350 °C/ 30 min

3.2.3.1.3 GC Conditions

Column:	Restek XTI-5, 0.25mm ID x 0.25um, 30 m
MS:	Sample mass 30 to 550

GC Oven Program: Initial temperature 40 °C for 2 minutes
Rate 8 °C/min
Final temperature 240 °C for 13 minutes
Total run time 40 minutes

3.2.3.2 Sampling Procedure

Condition the adsorbent tubes using ATD 400 and set the laboratory oven to 85 °C. Place the sample chambers in the oven at least one hour prior to use to allow them to reach thermal equilibrium. Measure the pressure sensitive adhesive about 3x3 cm^2. Remove the backing from the adhesive side of the pressure sensitive adhesive and fold the pressure sensitive adhesive to adhesive. Place the sample to be analyzed into a sample chamber and attach the top for outgassing. As for release liner, measure the release liner about 3x3 cm^2 and then place the samples into the chamber for outgassing. Reported as total ng per square centimeter. Place the parts-containing sample chambers into the laboratory oven and attach the incoming gas lines and the gas lines leading to the adsorbent tubes or to the vessel top. Check flow rates of each tubes. Allow the samples to outgas for three hours. Then remove the adsorbent tubes from the lines and place them into the ATD. Program the ATD to desorb the tubes and program the gas chromatograph to sample each tube to be analyzed. Identification of outgassed compounds is performed automatically by the operating GC/MS software. These results are then verified manually by the operator.

3.2.4 Calculation

3.2.4.1 Calculation Equation

The concentrations of the outgassed compounds are then calculated according to the following equation:

[S] = (area sample x (standard concentration ng/area std))/SA

[S] is concentration of the compound in the sample in ng,

Area sample is the area of peak in the sample

Area standard is the area of the 1000 ng hexadecane peak

SA = surface area of sample was used

If more than one part per sample chamber is outgassed, [S] obtained by this equation must be divided by the number of parts used.

3.3 GC/MSD PROCEDURE (54)

Using Gas chromatograph with attachments for split flow HP-5MS capillary column analysis with helium carrier gas (e.g., Hewlett Packard Model 5890 Series II Plus) and detector sensitive to general organic compounds such as mass selective detector (e.g., Hewlett Packard model No.5972).

3.3.1 Measurement Methods

3.3.1.1 Equipment Conditions

The standard instrument settings are shown below,

Column HP-5, capillary Flow rate (at 150°C) is 0.68 ml/min

Mass Spectrometer	Source Temperature 280°C
Injector Temperature	270°C
Mass Range	30-550 amu
Oven Settings	Initial Temperature 35°C
Ramp Rate	15°C per min
Final Temperature	260°C (15 min)

3.3.1.2 Sample preparation

Use 10 µl syringe with methylene chloride 10 µl to localized extract on release liner until methylene chloride evaporates to about 2 µl then inject the 2 µl to GC/MSD for analysis. Identification of extracted compounds is performed automatically by the operating GC/MS software. These results are then verified manually by the operator.