การวิเคราะห์สารเติมแต่งน้ำมันหล่อลื่นโดยดิฟฟิวส์รีเฟล็กแทนส์อินฟราเรดฟูเรียร์ ทรานสฟอร์มสเปกโทรสโกปี; 4, 4´- METHYLENEBIS (2, 6-DI-TERT-BUTYLPHENOL)

นางสาววัชรี   คตินนท์กุล

ANALYSIS OF LUBRICANT ADDITIVE BY DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY; 4, 4´-METHYLENEBIS (2, 6-DI-TERT-BUTYLPHENOL)

Miss Watcharee   Katinonkul

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science in Petrochemistry and Polymer Science

Program of Petrochemistry and Polymer Science

Faculty of Science

Chulalongkorn University

Academic Year 2001

Thesis Title   Analysis of Lubricant Additive by Diffuse Reflectance Infrared Fourier Transform Spectroscopy; 4, 4´-methylenebis (2, 6-di-tert-butylphenol)

By   Miss Watcharee   Katinonkul

Field of Study   Petrochemistry and Polymer Science

Thesis Advisor   Assistant Professor Sanong Ekgasit, Ph.D.

Accepted by Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………………….. Dean of Faculty of Science

(Associate Professor Wanchai Phothiphichitr, Ph.D.)

Thesis Committee

…………………………………………. Chairman

(Associate Professor Supawan Tantayanon, Ph.D.)

…………………………………………. Thesis Advisor

(Assistant Professor Sanong Ekgasit, Ph.D.)

……………………………………….. Member

(Associate Professor Amorn Petsom, Ph.D.)

……………………………………….. Member

(Assistant Professor Warinthorn Chavasiri, Ph.D.)

วัชรี   คตินนท์กุล : การวิเคราะห์สารเติมแต่งน้ำมันหล่อลื่นโดยดิฟฟิวส์รีเฟล็กแทนส์
อินฟราเรดฟูเรียร์ทรานสฟอร์มสเปกโทรสโกปี; 4, 4´-methylenebis (2, 6-di-tert-
butylphenol) (ANALYSIS OF LUBRICANT ADDITIVE BY DIFFUSE
REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY; 4, 4´
- METHYLENEBIS (2, 6-DI-TERT-BUTYLPHENOL)) อาจารย์ที่ปรึกษา : ผศ.ดร.
สนอง เอกสิทธิ์, 55 หน้า. ISBN 974-03-0198-3

งานวิจัยนี้เป็นการศึกษาเกี่ยวกับการวิเคราะห์ 4, 4´- methylenebis (2, 6-di-tert-
butylphenol) ซึ่งเป็นสารเติมแต่งชนิด phenolic antioxidant ในน้ำมันหล่อลื่น โดยการใช้เทคนิค
ทินแลร์ โครมาโทรกราฟีประยุกต์ใช้ร่วมกับดิฟฟิวส์รีเฟล็กแทนส์อินฟราเรดฟูเรียร์ทรานสฟอร์ม
สเปกโทรสโกปีในการวิเคราะห์ทั้งในเชิงคุณภาพและปริมาณ   งานวิจัยประกอบด้วยการศึกษา
สารตัวอย่างบนแผ่นทินแลร์   โดยใช้ดิฟฟิวส์รีเฟล็กแทนส์อินฟราเรดฟูเรียร์ทรานสฟอร์มสเปก
โทรสโกปี   ซึ่งได้ทำการศึกษาทั้งในเชิงคุณภาพโดยทำการเปรียบเทียบกับเทคนิคทรานสมิชชัน
และการวิเคราะห์เชิงปริมาณโดยเปรียบเทียบผลที่ได้กับการใช้เดนสิทิโอมิเตอร์   จากการศึกษา
พบว่าการนำเทคนิคทั้งสองมาประยุกต์ใช้ร่วมกันนั้นให้ผลดีทั้งในเชิงคุณภาพและปริมาณ
นอกจากนี้ยังช่วยลดขั้นตอน   และค่าใช้จ่ายในการวิเคราะห์โดยสามารถนำสารที่ผ่านการแยก
องค์ประกอบแล้วบนแผ่นทินแลร์มาวิเคราะห์หาปริมาณได้โดยตรงจากกราฟมาตรฐานที่สร้างขึ้น
โดยใช้ดิฟฟิวส์รีเฟล็กแทนส์ฟูเรียร์ทรานสฟอร์มสเปกโทรสโกปี   อย่างไรก็ตามการประยุกต์ใช้
เทคนิคนี้มีข้อจำกัดคือ สารตัวอย่างจะต้องมีความเข้มข้นมากพอเนื่องจากสารจะอยู่บนแผ่นทินแลร์
ที่เคลือบด้วยซิลิกาเจล ซึ่งซิลิกาเจลสามารถดูดกลืนแสงอินฟราเรดในช่วง 1300 – 800 cm^{-1}

ภาควิชา.............-......................... ลายมือชื่อนิสิต.....................................
สาขาวิชา........ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.. ลายมือชื่ออาจารย์ที่ปรึกษา.........................
ปีการศึกษา.....2544.......................... ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.......-.............

WATCHAREE KATINONKUL: ANALYSIS OF LUBRICANT ADDITIVE BY DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY; 4, 4´- METHYLENEBIS (2, 6-DI-TERT-BUTYLPHENOL). THESIS ADVISOR: ASST. PROF. SANONG EKGASIT., Ph.D. 55 pp. ISBN 974-03-0198-3

This research is the study concerning in both qualitative and quantitative analysis of 4, 4´-methylenebis (2, 6-di-tert-butylphenol), phenolic antioxidant in lubricant using thin layer chromatography (TLC) technique coupled with diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The research consists of the qualitative analysis of the sample coated on TLC sheet compared with transmission technique, the study of DRIFT spectroscopy, the determination of the sample coated on TLC sheet using DRIFT spectroscopy and the confirmation of the determined value from calibration curve by densitiometer. It was found that this applied technique can be used well in both qualitative and quantitative analysis. Beyond this the sample separated by TLC technique can be used in situ with DRIFT spectroscopy that is so convenient, less operating cost, and chemical used. However, this technique can only be applied under limitation that the concentration of the sample must be high enough to overcome the absorption of silica gel coated on TLC sheet because silica gel can absorb infrared in the frequency region 1300– 800 cm^{-1}.

Department………….…………………. Student's signature……………………………….

Field of study…Petrochemistry and Polymer Science… Advisor's signature…….………………………

Academic year……2001…………………... Co-advisor's signature………...……………….

ACKNOWLEDGEMENT

CONTENTS

LIST OF FIGURES

Pages

LIST OF TABLE

LIST OF ABBREVIATIONS

DRIFT : diffuse reflectance infrared fourier transform spectroscopy

FT-IR : fourier transform infrared

TLC : thin layer chromatography

UV : ultra violet

HPLC : High Performance Liquid Chromatography

LIST OF SYMBOLS

μ : micro

λ : wavelength

CHAPTER 1

INTRODUCTION

1.1　The Definition of Lubricant Additives

Lubricant additives are the chemicals added to lubricating materials in order to give them the special properties such as a harsh condition resistivity, detergent property, or viscosity improvement. The additives play an important role in the development of lubricating products and the enhancement of their capabilities. They have been widely used in the engine oils, transmission and hydraulic fluids, gear oils, industrial oils, and process oils. They are also employed in the automotive, marine, aeronautic, petroleum industries, and other industries making use of machinery as well. The additive volume may be as much as 20 percent of the final product composition. The most important type of additives include anti-oxidant agents, anti-wear additives, corrosion inhibitors, viscosity index improvers, and foam suppressors. The function of additives can be summarized as:

- Protect metal surfaces (rings, bearings, gears, etc.)
- Extend the range of lubricant applicability
- Extend lubricant life

1.2　The Analysis of Lubricant Additives

At present, there are many methods for analyzing lubricant additives both qualitatively and quantitatively. However, the appropriate method can be chosen depending on the purpose of the analysis. In general, most methods require same sample pre-treatment procedure [1]. It is relative simple to remove some of the interference from major components by simple extraction or separation procedures. The use of such procedures was proposed twenty years ago and one of the key methods described was dialysis, which has been applied to oil blends not long ago. Dialysis is a physical method for the separation of blended components as a function

of molecular weight and/ or size. It involves the migration of low molecular weight components through a semi-permeable membrane.

Many additives are reactive and have polar functional groups. It is therefore possible to separate a blended lubricant by the use of simple column chromatography. Common adsorbents like silica gel, activated alumina, keiselguhr, and Fuller's earth have been used for this purpose. Fractions eluted can be analyzed directly by infrared spectroscopy. These materials are compatible with organic solvents and can be used to separate ionic and polar additives, such as dispersants, metal containing additives, corrosion inhibitors, anti-oxidants, metal deactivators, etc. Column chromatography has been evolved since the early 1970's into the modern and sophisticated technique of liquid chromatography. This technique has been applied to the analysis of blended additives, base oils and lubricant oxidation products.

Several methods for identifying microgram amounts of materials separated by thin-layer chromatography (TLC) using infrared spectrometry have been suggested [2-3]. For all methods, the separation of the sample spot from the adsorbent was achieved by dissolving the sample in a suitable solvent and concentrating the solution before measuring the spectrum of the sample either in a low volume liquid cell or as a KBr microdisc that this procedure may take an hour or half a day to be completed. In this research, a method is described whereby the microgram quantities of materials can be measured without eluting the sample from the chromatoplate and analyzed directly by applying with diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy.

1.3   Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy

Diffuse reflection spectroscopy has been used successfully in many fields as an adjunct to be well known spectroscopic methods, and is often useful where traditional technique fails. Coal, for instance, is extremely difficult to be analyzed by classical techniques, but excellent infrared spectrum can be obtained by diffuse reflectance [4]. Many substances in their natural states (e.g., powders and rough

surface solids) exhibit diffuse reflection, i.e. incident light is scattered in all directions as opposed to specular (mirror-like) reflection where the angle of incidence equals the angle of reflection. In practice, a diffuse reflection spectrum is complex and is strongly dependent on the conditions under which they are obtained. These spectra can exhibit both absorbance and reflectance features due to contributions from transmission, internal and specular reflectance components as well as scattering phenomena in the collected radiation. Diffuse reflectance spectra are further complicated by sample preparation, particle size, sample concentration, and optical geometry effects.

1.4 DRIFT Measurement : Advantages Over Transmission Measurement

Fourier transform infrared spectroscopy (FTIR) has been used in transmission mode for many years to achieve the qualitative and quantitative analysis of solid, liquid and gas samples. However, in the specific domain of opaque materials or surface analysis, DRIFT spectroscopy is more suitable. The information depth is assumed to be in the order of mid-infrared wavelengths for non-absorbing samples and the scattering of light does not affect so much the baseline [5]. The preparation of the samples for DRIFT spectroscopy is fast: the sample is diluted in non-absorbing materials, such as potassium bromide or potassium chloride powder, which minimizes the specular component. In addition, since the sample is ground more gently, and pressing is not involved at all, polymeric changes induced by sample preparation are very unlikely. DRIFT spectroscopy can be achieved using less sample than transmission (KBr pellet) technique. Moreover, the particle size of the ground sample for DRIFT can be much coarser than that needed for preparing a KBr pellet or a mull, where particle sizes need to be 0.5 μm or less to avoid scattering and sloping baselines [6].

1.5   The Objective of This Research

Since thin layer chromatography technique is a very good qualitative technique for identification of components in a mixture. In this research it will be applied with DRIFT spectroscopy as a quantitative analysis. The procedure includes spotting a test material that is 4, 4´-methylenebis (2, 6-di-tert-butylphenol), phenolic antioxidant in lubricant, on TLC sheet, abraded and used as a test material. The DRIFT spectroscopy will be used as a qualitative tool and a quantitative analysis. The calibration curve is constructed from standard solution of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) using similar procedure as the sample so the unknown concentration of sample can be determined.

The determined result that obtains via DRIFT spectroscopy will be confirmed again using densitiometer.

1.6   Scope of This Research

1.   Study the characteristic of diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy

2.   Perform the qualitative and quantitative analysis of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) spotted on TLC sheet using DRIFT spectroscopy

3.   Compare the determined result obtained via DRIFT spectroscopy with that obtained via densitiometer.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy

2.1.1 Introduction

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy is a reflection or absorption technique where the samples to be analyzed are either "neat" (pure) or prepared as dispersions in nonabsorbing matrices such as halide salts or diamond powder. Neat samples should only be used when measurements are to be made on weakly absorbing spectral regions. Reflection does not occur at exactly the same frequency as the absorption for strong bands, which causes shifts and distortions (Restrahlen). Recently, DRIFT spectroscopy has gained popularity for the study of powders, solids, and species adsorbed on solids [7]. Because its convenient in sample preparation, spending less time, and in some studies identification by conventional transmission spectroscopy can be made difficult because of morphological changes occurring as a result of the grinding or hot compression molding procedures adopted in the preparation of samples. The Kubelka-Munk format of data presentation is favored generally. This format is discussed further in 2.2.3. However, the reflection contribution that comparable to stray light in DRIFT spectroscopy must be reduced by decreasing the particle size, or more tightly packing the material. These procedures cause more interactions of the incoming radiation with the sample.

In such cases diffuse reflectance measurement is more preferable than transmission technique. In addition, DRIFT spectroscopy is also one of a surface characterization technique using infrared reflection method, that has three modes; specular reflection, diffuse reflection, and attenuated total internal reflection. Diffuse reflection occurs off rough surfaces and powdered sample. The reflected radiation comes off in the specular direction and in all other directions as well. In many

situations, for example reflection from a powder, the reflection spectra do not come from the front surface alone. Radiation that penetrates into the material can reappear after scattering or reflecting at a second surface. When this radiation emerges it will experience some absorption depending on the path traversed. Its contribution to the spectrum will have the general character of a transmission spectrum. Spectra of this type are called diffuse reflection spectra [8].
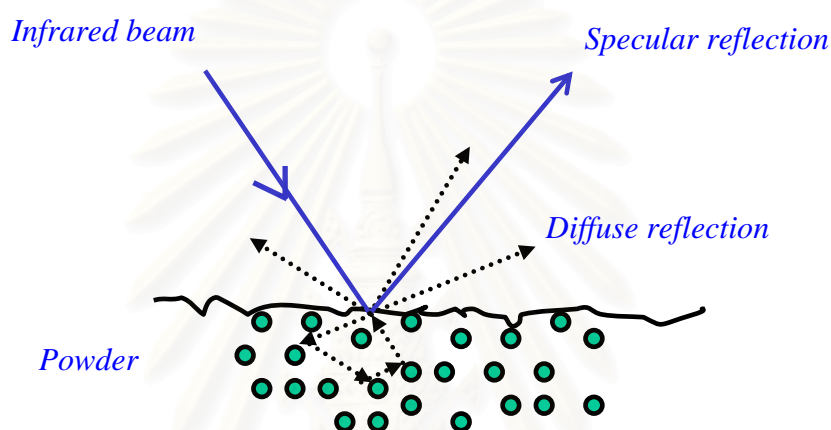
Figure 2.1   Specular and Diffuse Reflectance of powder and rough samples.

2.1.2   Principles of Diffuse Reflectance

The spectral feature depends on the relative amounts of surface reflection and of radiation that has penetrated the sample. The main factors that influence this are the particle size and the strength of the absorption. As the particle size increases the amount of radiation reappearing from within the sample is reduced because more is absorbed before it can be scattered or reflected back to the surface.

Specular reflection is occurred from a glossy sample surface or from a crystal surface, produces inverted bands ("restsrahlen bands") in the diffuse reflectance spectrum which reduce the usefulness of traditional transmission reference spectra. For highly absorbing samples these restsrahlen bands are strong. Grinding and diluting the sample with non-absorbing powder such as KBr, KCl, Ge or Si can minimize or eliminate these effects. Grinding reduces the contribution of reflection from large particle faces. Diluting ensures deeper penetration of the

incident beam, thus increasing the contribution to the spectrum of the transmission and internal reflection component. The resulting spectra have an appearance more similar to that of transmittance spectra than bulk reflectance spectra. If sample dilution is not feasible, the spectra may still be improved using an optical geometry that employed a low incident angle and an off-line collection angle.

The sample is usually ground and diluted with a nonabsorbing materials such as potassium bromide (KBr) or potassium chloride (KCl). The mixture is placed in a small cup about 13 mm in diameter and 3 to 4 mm in depth. (Micro cups can be used when sample size is limited.) The ensuring process is a complex combination of reflection, absorption, and scattering, but the result is that energy is reflected diffusely through a 2π solid angle above the surface of the powder in the cup. This diffusely reflected beam over as wide a solid angle is collected as possible by a large aperture optic, and it is then transferred on to the detector. Spectra are ratioed against a background scan made on a KBr-filled sample cup. The procedure can be shown in Figure 2.2. Infrared beam is penetrated the sample and bounced around beneath the surface and then absorption can occur before it leaves the surface for collection and subsequent analysis.

Infrared beam   *diffuse reflection*
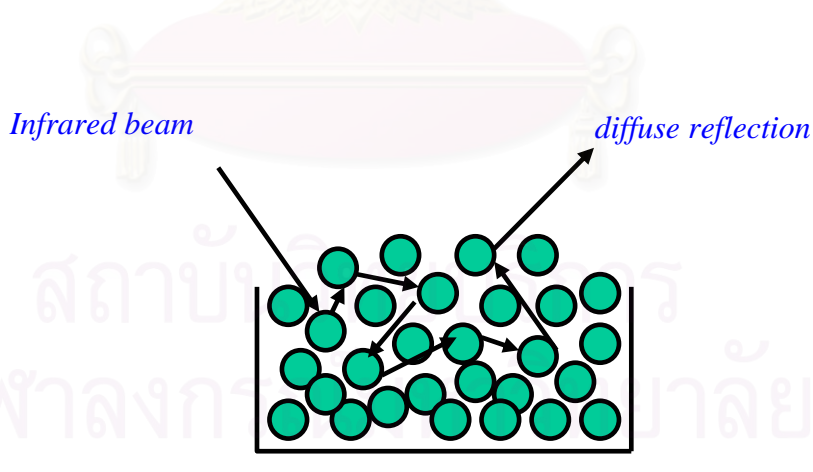
Figure 2.2   Schematic diagram of the diffuse reflection process.

The optical configuration of the diffuse reflectometer used in this work is shown in Figure 2.3. Alignment of the DRIFT spectroscopy accessory is very critical for the proper analysis of samples because DRIFT spectroscopy is an energy loss technique. The additional mirrors of the DRIFT spectroscopy accessory that

focus the infrared radiation onto the sample and onto the detector all contribute to the loss of energy. Typically, only 10 to 50% of the energy throughput is available for DRIFT spectroscopy analysis, compared to the transmission mode. If the Fourier transform-infrared (FT-IR) spectrometer has multiple aperture settings, the instrument should be set at maximum aperture so that as much of the infrared energy available can be used. The accessory is adjusted level to the optics bench by using a circular level. Next, adjust the height of the accessory to make sure the incident beam hits the center of the first mirror. The rest of the steps are aimed at optimizing the energy throughput to the detector, as monitored by the peak counts or intensity of the interferogram center burst. Place the alignment mirror in the sample cup and adjust its height until no further increases in energy throughput are obtained. An alkali halide powder is used to generate the background spectrum, so this powder should be very dry and under 40 μm in particle size and the cell should be realigned every time the alignment of the instrument is changed or the detector position is moved. This is very critical for obtaining consistent quantitative results [9].
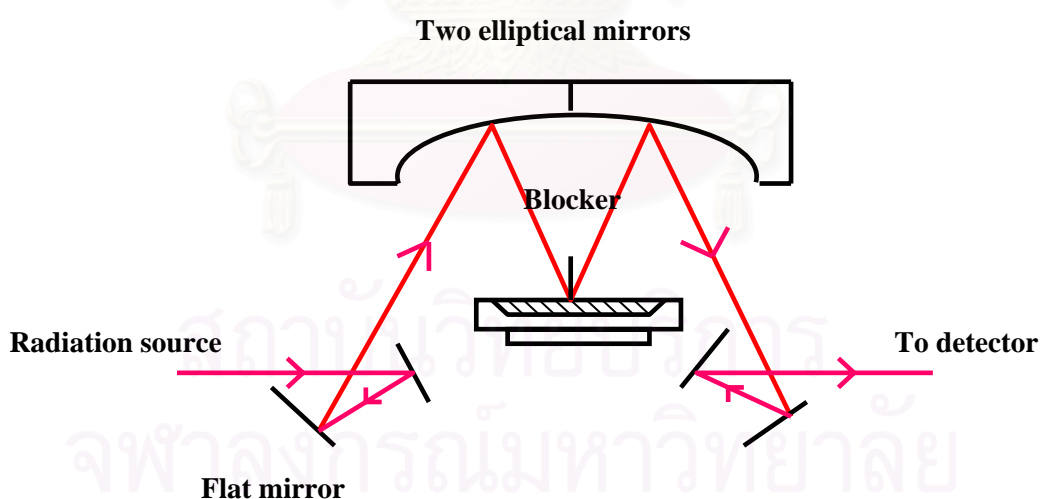
Figure 2.3   Schematic diagram of the "collector" DRIFT cell showing four flat mirrors, and the blocker to help eliminate specular reflected radiation with the path of radiation indicated.

2.1.3 Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectral Intensity

A general theory for diffuse reflectance at scattering layers within powdered sample has been developed by Kubelka and Munk. This theory relates sample concentration and scattered radiation intensity much in the same manner as the Bouger-Beer law of transmittance spectrometry. For an "infinitely thick" layer, the Kubelka-Munk equation may be written as:

$$f(R_\infty) \ = \ \frac{(1 - R_\infty)^2}{2R_\infty} \ = \ \frac{k}{s} \qquad (2.1)$$

where R_∞ is the absolute reflectance of the layer, s is a scattering coefficient, and k is the molar absorption coefficient.

In practice a perfect diffuse reflection standard has not been found and R_∞ in equation 2.1 may be replaced by R_∞', where

$$R_\infty{'} \ = \ \frac{R_\infty{'} \ (sample)}{R_\infty{'} \ (standard)} \qquad (2.2)$$

When $R_\infty{'}$ (sample) represents the single-beam reflectance spectrum of the sample and $R_\infty{'}$ (standard) is the single-beam reflectance spectrum of a selected nonabsorbing standard exhibiting high diffuse reflectance throughout the wavelength regions being studied.

2.1.4 Quantitative Analysis Using DRIFT Spectroscopy

All quantitative infrared analyses are carried out by comparing, directly or indirectly, the absorbance of the unknown at a given wavelength (often the peak of a strong absorption band) with the absorbance of the same material in a standard of known concentration. Peak absorbance, since it is easily measured and is directly relatable to concentration, is the most useful parameter to use in calculations.

However, for quantitative analysis using DRIFT spectroscopy it is necessary to satisfy the basic requirement of a Kubelka-Munk theory that the scattering from the samples and packing density must be kept constantly. The resulting spectrum looks very much like a transmission spectrum of the same sample, except that the relative intensities of the bands will be different in the two spectra. Furthermore, if diffuse reflectance spectra are run on a series of mixtures, the spectra converted to an absorbance format, and a Beer's law plot is attempted, using a peak from one of the components whose concentration is varying, the resulting plot will be non-linear. These problems can be overcome by first performing the Kubelka-Munk transform on the diffuse reflectance spectrum.

The Kubelka-Munk theory predicts a linear relationship between the molar absorption coefficient, k, and the maximum peak value of $f(R_\infty)$ for each band, provided s remains constant. Since s is dependent on particle size and range, these parameters should be made as consistent as possible if quantitative data are needed. It has been shown that for dilute samples in low absorbing or nonabsorbing matrices:

$$k \ = \ 2.303\,\varepsilon\, c \tag{2.3}$$

Where ε is the molar absorptivity and c is the molar concentration. Therefore:

$$f(R_\infty) \ = \ \frac{(1 - R_\infty)^2}{2R_\infty} \ = \ \frac{c}{k'} \tag{2.4}$$

where $k' = s/\ 2.303\ \varepsilon.$ Thus diffuse reflectance spectra of samples dispersed in finely powdered KBr or KCl might be expected to be quited similar to the absorbance spectra of the same samples prepared as a KBr disk.

The best spectra will be obtained if the sample is first ground (10 to 20 μm average particle size is sufficient) and then mixed with the nonabsorbing diluent. This procedure must be followed if the Kubelka-Munk transform is to be carried out/ or if quantitative work is to be attempted. An appropriate concentration of sample in diluent is 1 to 5%. Lower concentrations present no problems but will result in

weaker spectra which may then need to be ordinate expanded. Concentration greater than 5% should be strenuously avoided. High sample concentrations, with their correspondingly larger number of sample particulates in the mixture, will often result in specular contributions in the band shapes.

2.1.4.1 Requirements for Quantitative DRIFTS Analysis

1. Linear Calibration Plot

The major application of DRIFT spectroscpy has been the analysis of powders and the interaction of species on fillers. The Kubelka-Munk theory suggests that a linear relationship should exist between the concentration of the silane coupling agent on the filler and the intensity of the reflectance spectrum for each functional group that absorbs infrared radiation. It is also necessary to determine that the range over which the quantification method is going to be used is linear (i.e., it must exceed the range of interest). The scattering requirements are satisfied by grinding the samples into a fine powder and screening to a constant size range (less than 20 μm in this example). Both the theory and experience show that when the particle size is not held constant, major changes in the DRIFT spectroscopy spectra occur, and reproducible results are not obtained.

2. Reproducibility

A basic requirement for quantitative analysis is that the method must yield reproducible results. A convenient way to determine reproducibility is to determine the precision of the test. It can be checked using the results from three different operators using the same FT-IR spectrometer. Each operator collected one spectrum each day on ten different days. All 30 samples were from the same batch of silane-treated filler. All spectra were collected within a 3-week period of time. The same background KBr spectrum was used for every sample that was collected and was stored on disk for easy retrieval. The standard deviation was found to be about 1.5%, which is excellent for any FT-IR sampling technique.

3. Internal Reference

Another requirement for a good quantitative test is an Internal Reference Material (IRM) which can be run to control chart of the test method and indicate when the test is out of control and a correction needs to be made. The IRM material cannot change over time. The silane-treated silica batch studied in the nested design was chosen as an IRM for the DRIFT spectroscopy accessory alignment is changed, an IRM spectrum can be collected to determine if further adjustments must be made to continue to obtain valid results [10].

2.2 Photometric Measurement of Absorption

2.2.1 Principles of Measurement

The scanners commercially available today operate on the basis of the optical train illustrated in Figure 2.4. They can be employed to

- detect absorbing substances against a non-fluorescent plate background (Fig. 2.4 A : recording a scanning curve, absorption spectra, quantitative analysis of absorbing substances)

- detect absorptions directly because of luminescence diminishing. However, it is necessary to introduce a cut-off filter before the detector to absorb the shortwave excitation radiation (Fig. 2.4 B)

- detect and analyze quantitatively fluorescent substances against a non-fluorescent background without spectral analysis of the fluorescent light (Fig.2.4 B)

On emitting phases it is not possible to determine directly (in situ) the fluorescence and absorption spectra of compounds that absorb in the excitation range of luminescence indicators without distorting the measurement signal.

(A)

(B)
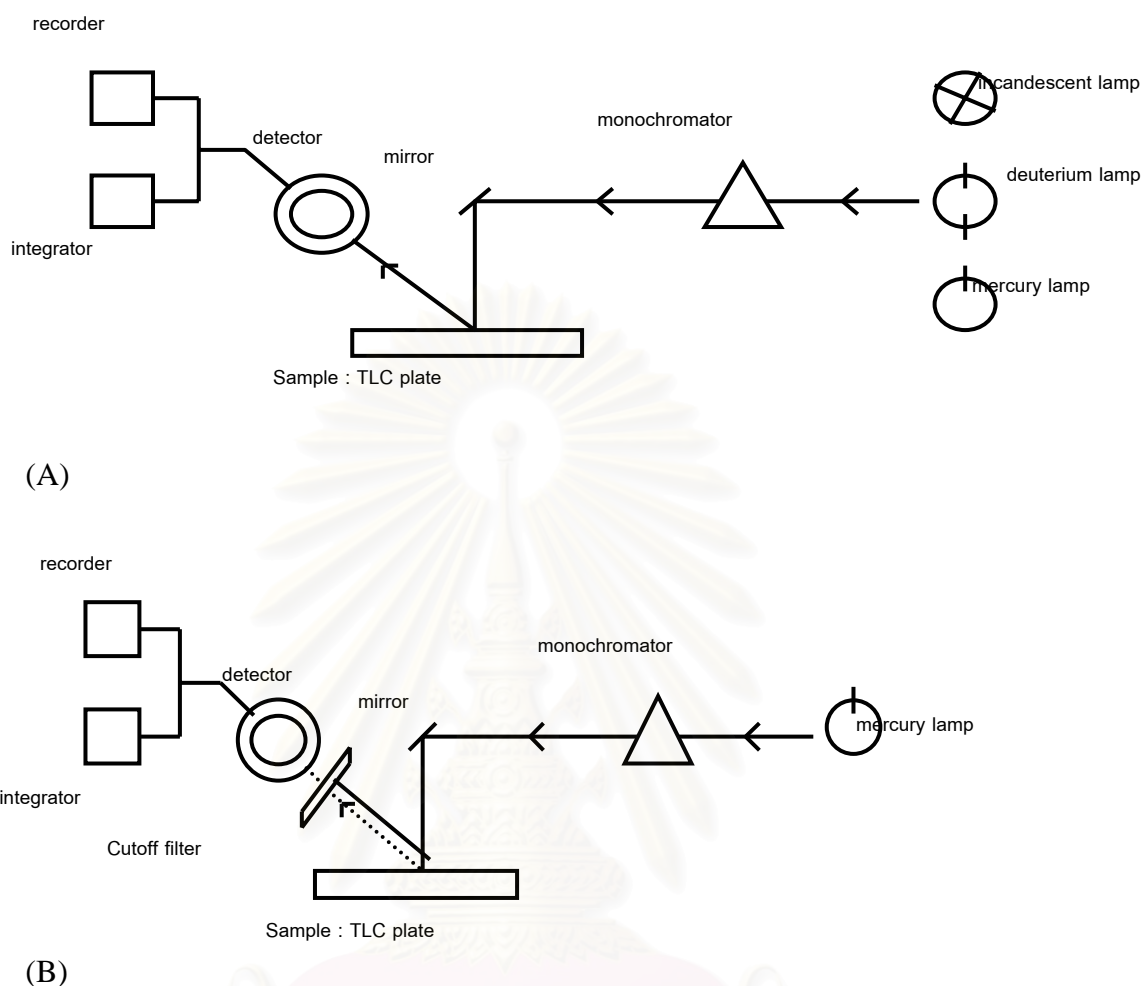
Figure 2.4   Optical trains of the commercially available scanners. (A) absorption,
              (B) fluorescence quenching and true fluorescence

2.2.2 Direct Determination of Absorbance

Determination of absorption spectra in reflection, if there is no luminescence radiation, absorption spectra can be determined using the light path sketched in Figure 2.4 A. If absorbing substances, for example, dyestuffs, caffein or PHB esters are determined spectrophotometically after chromatography, then, depending on the wavelength, these components absorb a proportion (I_{abs}) of the light irradiating them (I_0). The chromatographic zone remits a lower light intensity (I_{ref}) than the environment around it.

$$I_0 - I_{abs} = I_{ref} \tag{2.5}$$

Therefore it is possible to determine absorption spectra directly on the TLC plate by comparison with a substance-free portion of the layer. The wavelengths usually correspond to the spectra of the same substances in solution. However, adsorbents (silanols, amino and polyamide groups) and solvent traces (pH differences) can cause either bathochromic (ketones, aldehydes, dyestuffs) or hypsochromic phenols, aniline derivatives shifts.

However, these absorption spectra can be employed as an aid to characterization, particularly when authentic reference substances are chromatographed on a neighboring track. The use of differential spectrometry yields additional information. Quantitative analysis is usually performed by scanning at the wavelength of greatest absorbance (λ_{max}). However, determinations at other wavelengths can sometimes be advantageous, e.g. when the result is a better baseline. An example is the determination of scopolamine at $\lambda = 220$ nm instead of at $\lambda_{max} = 205$ nm or of the fungicide vinclozolin at $\lambda = 245$ nm instead of at $\lambda_{max} = 220$ nm.

Absorbance (reflectance) scanning: the positions of the chromatographically separated substances are generally determined at λ_{max}. As the chromatogram is scanned the voltage differences produced at the detector are plotted as a function of position of measurement to yield an absorption scan (Figure 2.5). Conclusions concerning the amount of substance chromatographed can be drawn from the areas or heights of the peaks.
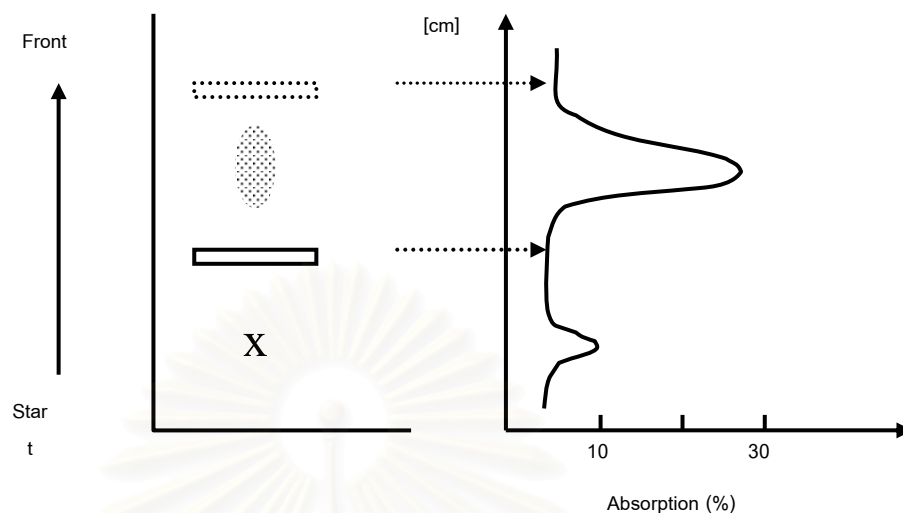
Figure 2.5   Schematic representation of the recording of an absorbance scan.

2.2.3 Quantitative analysis

The determination of the spectrum reveals wavelength that is suitable for quantitative analysis. The wavelength of maximum absorption is normally chosen, because the difference from the background blank is greatest here. In this type of analysis the analyst "sacrifices" all the substance-characterizing information in the spectrum in favor of a single wavelength. When the chromatogram is scanned photometrically at this wavelength a plot is obtained of absorption versus position on chromatogram (Fig.2.5); the peak heights and areas a function of the amount of substance applied. The limiting law is the Kubelka-Munk function.

$$\frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty} \qquad (2.6)$$

Where

k =   absorption coefficient

s =   coefficient of scattering of the stationary phase

R_∞ =   absolute reflectance

According to the BEER-LAMBERT law

$$\frac{I}{I_0} = e^{-kd} \tag{2.7}$$

The coefficient of absorption k can be defined as

$$k = 2.303\ \mathcal{E}\ c \tag{2.8}$$

When

$\mathcal{E}$ = molar extinction coefficient

c = concentration of substance, in the present case the amount of substance applied.

Strictly speaking the Kubelka-Munk function is only applicable under the following conditions:

- The irradiation of the sample must be diffused.
- Monochromatic radiation must be employed for the analysis, so that the diffraction and refraction phenomena in the layer shall be as uniform as possible. This also means that the radiation reaching the detector in reflectance retains its "color value" and only changes in its intensity. This would not be the case for polychromatic light; since a certain proportion of the light is absorbed during the determination the composition of the light would change and would, amongst other things, alter the sensitivity of the photomultiplier to the remaining light.
- Mirror reflection must not occur.
- The layer thickness must be large in comparison with the wavelength employed so that no radiation can penetrate right through the layer and escape measurement.
- The particles must be randomly distributed in the layer to avoid interference effects.
- The particles making up the adsorbent must be very much smaller in size than the thickness of the chromatographic layer.

CHAPTER 3

EXPERIMENT

3.1 Studying of Silica gel

3.1.1 Materials and Equipments

1. Commercial TLC sheet (Merck, model 60 F_{254}, thickness 0.2 mm)
2. Potassium bromide (Merck)
3. Diffuse reflectance infrared Fourier transform accessory (Spectra Tech, USA)
4. Bruker Vector 33 FT-IR spectrometer
5. UV lamp

3.1.2 FT-IR Spectrometer Operating Conditions

Bruker Vector 33 FT-IR Spectrometer
Experimental Setup

Mode	Diffuse Reflectance
Resolution	4.0 cm^{-1}
Number of Scans	16
Signal Gain	2
Energy Throughput	16000
Result Spectrum	Kubelka-Munk unit

Optic Parameters

Source Setting	Globar (MIR)
Detector Setting	DTGS
Beam Splitter Setting	KBr

3.1.3 Factors that Influence the Spectral Intensity

3.1.3.1 Particle size

1. KBr powder was ground to small particle size in order to use entirely in this experiment.

2. Silica gel was diluted to 2 wt.% in ground KBr, by varying particle size, then the spectra of silica gel were obtained.

3. Diffuse reflectance spectra of silica gel were collected under the following conditions:

Uniform packing, by pressing each mixture identically, the spectra of uniform packing were obtained. These spectra were acquired with different particle size.

3.1.3.2 Packing density

1. Silica gel was diluted to 2 wt.% in ground KBr, by varying packing pressure, then the spectra of silica gel were obtained.

2. Diffuse reflectance spectra of silica gel were collected under the following conditions:

Uniform particle size, by using same particle size for each mixture, the spectra of uniform particle size were obtained. These spectra were acquired with different packing press.

3.1.4 Studying the Spectra of Silica gel Coated on TLC Sheet Between the Surface and Bottom area

1. Silica gel coated on TLC sheet at the surface and bottom area was abraded in order to use as a test material.

2. Each silica gel area was diluted in ground KBr, the spectra of each area of silica gel were obtained.

3. Diffuse reflectance spectra of silica gel were collected under the following conditions:

3.1   Uniform packing density

By pressing each mixture identically, the spectra of uniform packing density were obtained. These spectra were acquired with different area between the surface and bottom position on TLC sheet.

3.2   Uniform particle size

By using the same lot of ground KBr, because the scattering effects can occur differently on different particle size so that these spectra were acquired with different area between the surface and bottom position on TLC sheet.

3.1.5   Studying the Spectra of Silica Gel in Potassium Bromide at Various Concentrations

1.   Silica gel coated on TLC sheet was abraded in order to use as a test material for all spectral acquisitions.

2.   Spectra of silica gel were collected by diluted in ground KBr at various percent weight concentrations as shown in Table 3.1

3.   Diffuse reflectance spectra of silica gel were collected under the following conditions:

3.1   Uniform particle size

By using the same lot of ground KBr, because the scattering effects can occur differently on different particle size so that these spectra were acquired with different percent weight concentration.

3.2   Uniform packing density

By pressing each mixture identically, the spectra of uniform packing were obtained. These spectra were acquired with different percent weight concentration.

4.   Calibration curve of silica gel spectra were constructed between the spectral intensity and percent weight concentration. The calibrated frequency of silica gel is 810 cm^{-1}. The maximum capacity of silica gel obtained in the mixture must be in the linear range.

Table 3.1   Concentration of silica gel in KBr employed for calibration.

Silica gel (g)	Potassium Bromide (g)	Total weight (g)	Concentration (wt.%)
0.0000	0.0110	0.0110	0
0.0002	0.0108	0.0110	2
0.0004	0.0106	0.0110	4
0.0007	0.0103	0.0110	6
0.0009	0.0101	0.0110	8
0.0011	0.0099	0.0110	10

3.2   Determination of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) using Densitiometer

3.2.1   Materials and Equipments

1. Commercial TLC sheet (Merck, model 60 F_{254}, thickness 0.2 mm)
2. 4, 4´-methylenebis (2, 6-di-tert-butylphenol) (Commercial grade)
3. Cyclohexane (Merck)
4. Densitiometer (CAMAG TLC Scanner II)
5. Recorder Model 56 (Perkin-Elmer)

3.2.2   Densitiometer Operating Conditions

Experimental Setup

Light source	Deutorium
Number of scan	1
Track space	10.0 mm
Wavelength	400 nm
Sensitivity	245
Span	20
Offset	5

3.2.3 Studying Chromatographic Sheets of Standard solution of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at various concentrations

1. Five solutions of different concentrations of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) were dissolved in cyclohexane ranging from 3.16 to 16.12 g/L as shown in Table 3.2. Each solution was spotted on the TLC sheet for 3 spots as shown in the Fig. 3.1 and each spot was contained for 1 μL by microsyringe

2. Unknown concentration sample of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) was also spotted on the TLC sheet for 3 spots and each spot was contained for 1 μL.

3. After spotting, the sheets were radiated with UV lamp for 5 minutes, then each spot on the TLC sheets was scanned and recorded as absorbance scan.

4. Calibration curve of each concentration of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) was constructed between the height of absorbance scan and percent concentration of each solution.

5. Unknown percent weight concentration of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) solution can be obtained from the calibration curve of standard 4, 4´-methylenebis (2, 6-di-tert-butylphenol).

Table 3.2 Concentration of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) dissolved in cyclohexane employed for calibration.

4, 4´-methylenebis (2,6-di-tertbutylphenol) (g)	Cyclohexane (g)	Total weight (g)	Concentration (wt.%)
0.0157	3.9000	3.9157	0.4
0.0314	3.9000	3.9314	0.8
0.0474	3.9000	3.9474	1.2
0.0634	3.9000	3.9634	1.6
0.0796	3.9000	3.9796	2.0
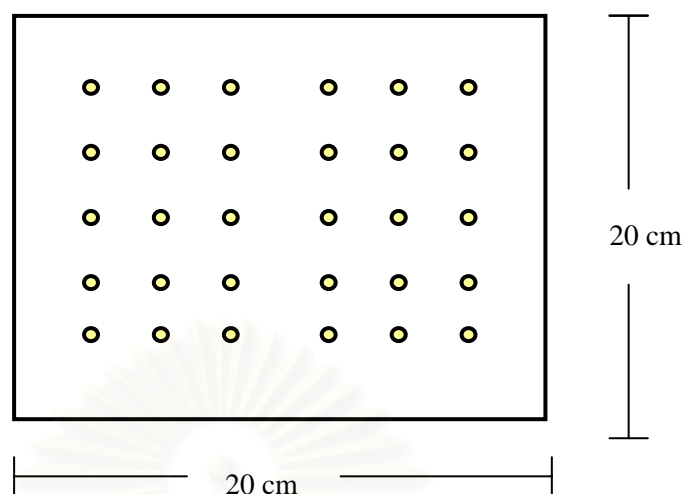
Figure 3.1   Schematic of TLC sheet of standard solution of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at the various concentrations.

3.3   Determination of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) using Diffuse Reflectance Infrared Fourier Transform Spectroscopy

3.3.1   Materials and Equipments

1. Commercial TLC sheet (Merck, model 60 F_{254}, thickness 0.2 mm)
2. Potassium bromide (Merck)
3. 4, 4´-methylenebis (2, 6-di-tert-butylphenol) (Commercial grade)
4. Cyclohexane (Merck)
5. Diffuse reflectance infrared Fourier transform accessory (Spectra Tech, USA)
6. Bruker Vector 33 FT-IR spectrometer
7. UV lamp

3.3.2   FT-IR Spectrometer Operating Conditions

Bruker Vector 33 FT-IR Spectrometer

Experimental Setup

Mode	Diffuse Reflectance
Resolution	4.0 cm^{-1}
Number of Scans	16
Signal Gain	2
Energy Throughput	16000
Result Spectrum	Kubelka-Munk unit

Optic Parameters

Source Setting	Globar (MIR)
Detector Setting	DTGS
Beam Splitter Setting	KBr

3.3.3   Studying the Spectra from spotted TLC Sheet of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at Various Concentrations

1.   Use the TLC sheets in the section 3.2 as the studying material in this section.

2.   Determine the position of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) on each spot of TLC sheets that yellow spot was appeared after radiated with UV light. Then each area of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) on each sheet was abraded in the same quantity in order to study and use as a test material for all spectral acquisitions. The spectra were obtained under the following conditions:

2.1   Uniform percent weight concentration

Each concentration of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) that abraded from TLC sheet was diluted to 5 wt.% in ground KBr, the spectra of uniform percent weight concentration were obtained. These spectra were acquired with different concentrations of 4, 4´-methylenebis (2, 6-di-tert-butylphenol).

2.2   Uniform particle size

By using the same lot of ground KBr, because the scattering effects can be occurred differently on different particle size so that these spectra were acquired with different percent weight concentration.

2.3   Uniform packing density

By pressing each mixture identically, the spectra of uniform packing were obtained. These spectra were acquired with difference percent weight concentration.

3.   Each spectrum of each concentration of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) was subtracted with water spectrum in order to obtain only spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) coated on silica gel.

4.   Each spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) was performed with the normalization process in order to adjust and compare in the same condition.

5.   The calibrated frequency of each concentration of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) is 2967 cm^{-1} so that the calibration curve was constructed between the spectral area in the range 2995.442 to 2850.781 cm^{-1} and percent concentration.

6.   Unknown percent weight concentration of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) solution can be obtained from the calibration curve of standard 4, 4´-methylenebis (2, 6-di-tert-butylphenol).

CHAPTER 4

RESULT AND DISCUSSION

4.1   Introduction of Silica Gel

Silica gel is the most popular adsorbent and it is prepared by the hydrolysis of sodium silicate followed by condensation and polymerization. The structure of silica gel is shown in Figure 4.1.
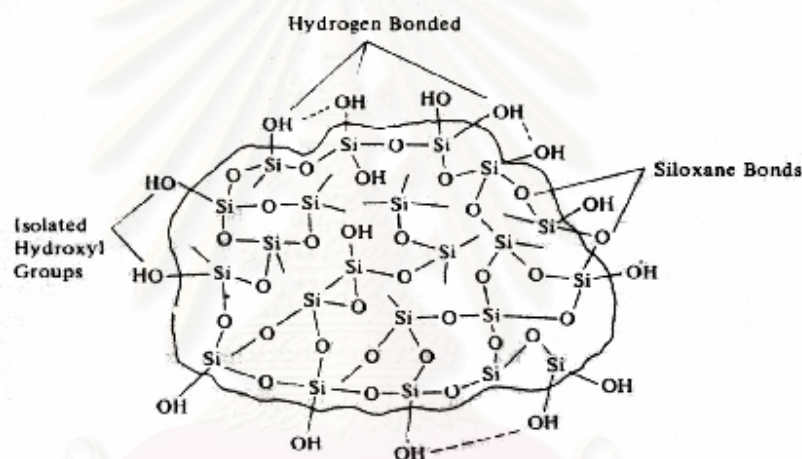
Figure 4.1   Structure of silica gel [11].

According to Figure 4.1, the OH groups attached to the silicon atoms are reactive and solely responsed to the absorptive properties of silica gel. Its activity is due to the Si-OH (silanol) groups on the surface. There are several different types of active sites, each varying in strength of adsorption. Substances are adsorbed on silica via H-bonding, and the surface hydroxyls serve as hydrogen donors. The Si-O-Si stretching frequencies of siloxanes are characterized by the very strong IR absorption band in the region 1100-1000 cm^{-1}. The Si-O-H group has a strong IR band involving Si-O stretching at 920-830 cm^{-1}. The OH stretching band is the same as that in alcohols, 3700-3200 cm^{-1}, for free and hydrogen-bonded OH [12].

4.1.1 Spectra of Silica Gel

Spectra of silica gel acquired via diffuse reflectance and transmission modes are shown in Figures 4.2 and 4.3, respectively. Both have the same features that are broad bands in the 3800 and 3000 cm^{-1} region due to OH stretching of hydrogen-bonded OH. The strong bands at 1100, 810, and 470 cm^{-1} are Si-O-Si stretching bands that are the characteristic of siloxane group. The difference between the spectrum of silica gel achieved via diffuse reflectance and transmission modes is the baseline of the spectrum. It can be seen that the baseline via diffuse reflectance mode is more linear than that obtained via transmission mode because DRIFT spectroscopy can minimize the specular reflection more than transmission mode. The reflection spectra do not come from the front surface alone, but the radiation that penetrates into the materials can reappear after scattering or reflection at a second surface so that the incident beam will be traversed throughout almost area in the materials. In addition, the preparation of the samples for DRIFT studies are fast including the quantity of sample spending which is not limited as transmission mode. In transmission mode, the incedent beam of infrared will be transmitted directly to the surface of KBr pellet only the more the sample, the more absorption. Beyond this in transmission mode, it must be careful for over absorption phenomenon that can be occurred easily.

The restriction for the spectral analysis using a self-supporting TLC sheet is limited between 4000 to 1300 cm^{-1} region owing to the strong Si-O-Si stretching modes, which occur below 1300 cm^{-1}. Furthermore, silica gel is strong infrared scatterer, and adsorbed molecule leads to change in the spectral artifacts in the region containing the bulk modes. These artifacts dominate and mask out the much weaker bands due to adsorbed species. However the strong bands can still be detected by DRIFT spectroscopy so that the optimization of spectral features made it possible to obtain semi-quantitative analysis. However, qualitative analysis can also be achieved by this technique.
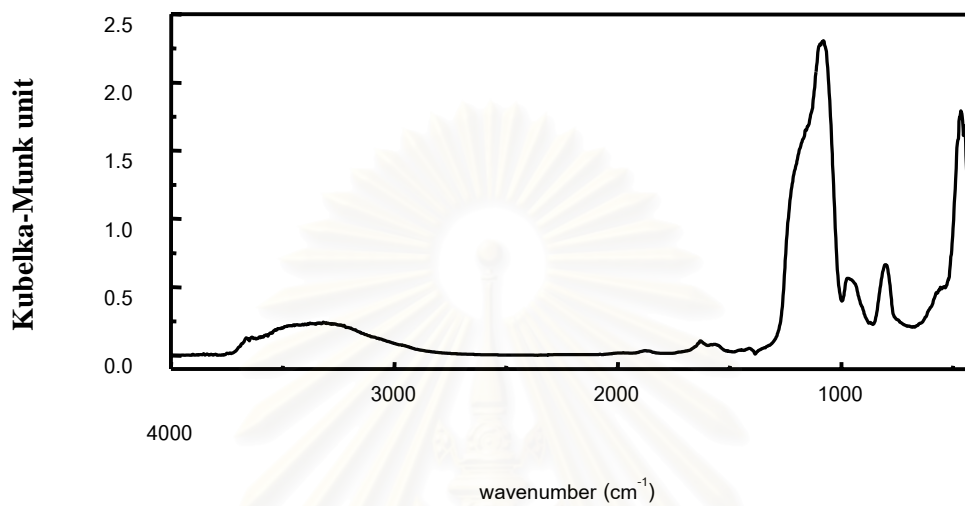
4.1.1.1 Diffuse Reflectance Spectrum

Figure 4.2   Diffuse reflectance spectrum of silica gel at 5 wt.% in KBr.

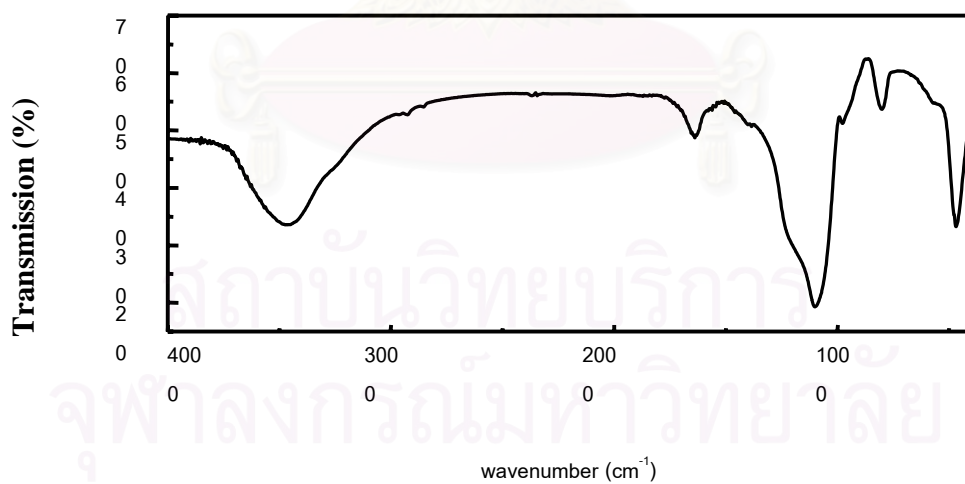**4.1.1.2 Transmission Spectrum**

Figure 4.3   Transmission spectrum of silica gel at 1 wt.% in KBr.

4.1.1.3 Reference Spectrum of Silica gel

Silica is a generic term to describe a variety of silicon oxides from low-surface area materials (e.g., glass plates, the oxide layer on silicon) to high-surface area materials such as silica gel and fumed silica. Thus, the spectrum of silicon (IV) oxide in Figure 4.4 can be used as reference spectrum for silica gel coated on TLC sheet. Moreover, it also used to compare the features of silica gel spectra achieved via diffuse reflectance and transmission mode as shown in Figures 4.2 and 4.3, respectively.

To compare with reference spectrum, the strong bands at 1100, 810, and 470 cm^{-1} were appeared in the same shape and frequency similar in both spectra via diffuse reflectance and transmission modes. But there are the weak features located between 2000 and 1300 cm^{-1} is different, by spectrum of silicon (IV) oxide has no weak features located between 2000 and 1300 cm^{-1} and broad bands between 3800 and 3000 cm^{-1}. It can be explained that silicon (IV) oxide, (- SiO_2 -) has no free or hydrogen-bonded OH to show broad bands between 3800 and 3000 cm^{-1}. The weak features between 2000 and 1300 cm^{-1} can be assigned to the absorption of fluorescent substance (F_{254}) that has been added to the commercial TLC sheet.
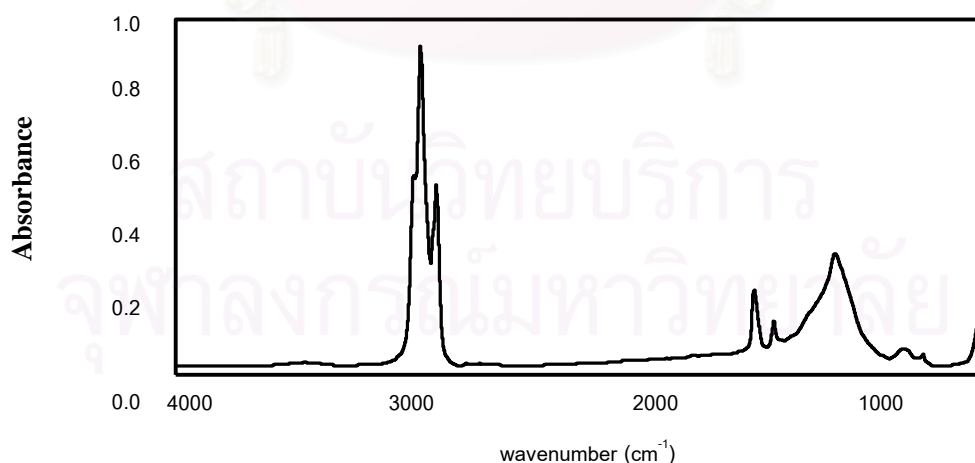
Figure 4.4   Reference spectrum of silicon (IV) oxide [11].

4.1.2 Factors that influence to Spectral Intensity

4.1.2.1 Particle Size

It is usually said that quantitative analysis using DRIFT spectroscopy is possible only if both particle size distribution and sample density are perfectly controlled. In this work, the particle size and packing density effects are studied. Figure 4.5 illustrates the effect of particle size on the diffuse reflectance spectra of silica gel in KBr. Intensities, bandwidths, and baselines of the spectra decrease substantially as the particle diameter is reduced. It is noted that the intensity of certain bands appears to dramatically change with particle size. This effect is particularly noticeable for the silica gel bands at 1100 cm^{-1}. This is due to scattering effects in bigger particle diameter can occur more than smaller one that means the absorption in rough particle size is also less than fine one owing to low spectral intensity.
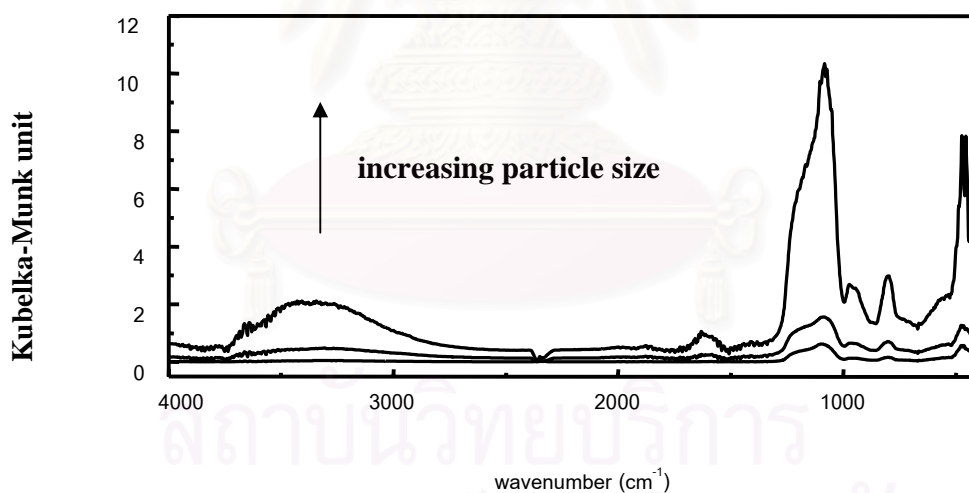
Figure 4.5   Diffuse reflectance spectra of silica gel in KBr at various particle sizes.

4.1.2.2 Packing density

Figure 4.6 illustrates the effect of packing density on the diffuse reflectance spectra of silica gel in KBr. The greater the packing intensity is, the stronger the absorbance will be. It can be explained that the particles in higher packing density are closed to each other, therefore the radiation that penetrates into the material can reappear after scattering or reflection many times so when this radiation emerges it will have experienced more absorption. On the other hand, the particles in lower packing density were not approached therefore the radiation that penetrates into the material can reappear after scattering or reflection for less time. So when this radiation emerges, it will be experienced small absorption.
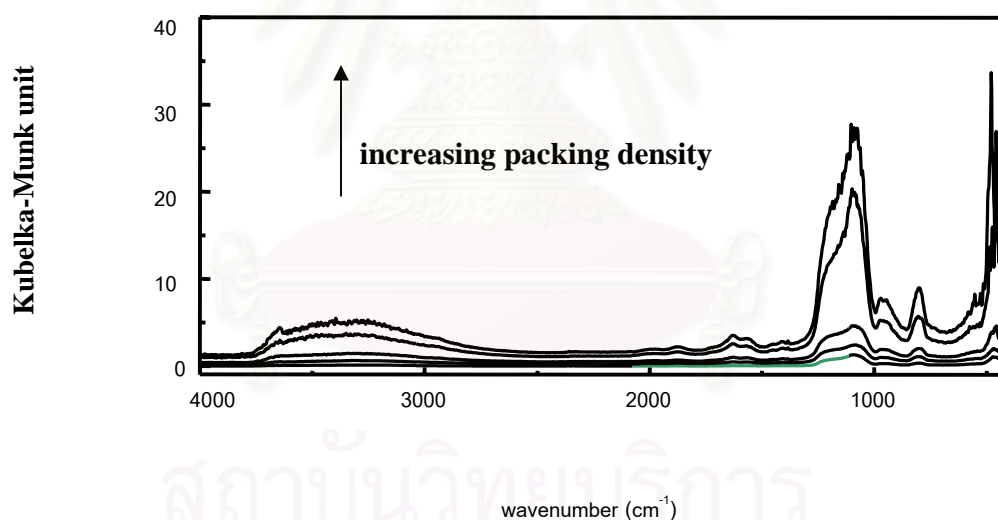

Figure 4.6   Diffuse reflectance spectra of silica gel in KBr at various packing densities.

4.1.3 Spectra of Silica gel Coated on TLC sheet

In this work, a sample must be applied on commercial TLC sheet coated with silica gel using TLC technique. The sample was developed in the suitable solvent then components of the sample are separated and distributed throughout the entire area of commercial TLC sheet in both surface and bottom area. So all areas of TLC sheet must be studied in order to inspect that there are different features between them or not. Because the separated component of sample must be abraded all over its area in order to continue quantitative analysis by DRIFT spectroscopy so it should have no effect from the position and level of abrading. From the Figure 4.7, it can be shown that all features in both surface and bottom areas of silica gel are similar by having the broad bands of OH stretching mode in the region of 3800 to 3000 cm^{-1}, and the strong bands at 1100, 810, and 470 cm^{-1} are Si-O-Si stretching modes that shown the characteristic of siloxane group. By that means, each component separated on TLC sheet can be abraded all over levels and areas of each position and can be studied by have no effect from other features.
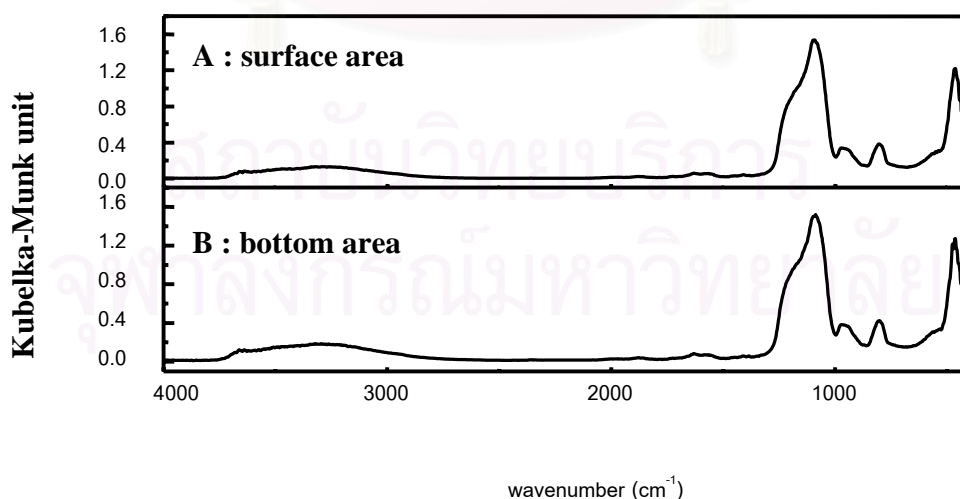
Figure 4.7   Diffuse reflectance spectra of silica gel in KBr between surface (A) and bottom area (B).

4.1.4 Silica gel in Potassium Bromide at Various Concentrations

Since this research is concerning the quantitative measurements, the relationship between sample concentration and spectral intensity must be studied. In this work, the sample concentration is related to silica gel coated on TLC sheet. Furthermore, silica gel is strong infrared scatterer and adsorbed molecule leads to change in the spectral artifacts in the region containing the bulk modes. However the strong bands of sample can be achieved by DRIFT spectroscopy in the condition that the quantity of silica gel in the sample must be controlled in order to obtain the spectral intensity of sample that can overcome the absorption of silica gel. Beyond this the scattering effects can be reduced by dispersing silica gel in KBr. The relationship between the quantity of silica gel and spectral intensity was studied as illustrated in Figures 4.8 and 4.11. It has been shown that the spectral intensity of the broad bands in the region 3800 to 3000 cm^{-1} including the strong bands at 1100, 810, and 470 cm^{-1} increase substantially with the quantity of silica gel. Figure 4.11, shows linear relationship between the spectral intensities and concentrations of silica gel in KBr. The quantitative analysis can be achieved via diffuse reflectance mode. It was found that the maximum range of silica gel can be dispersed in the sample should not be more than 5 % by weight. If more than this, over absorption is observed. The characteristic of over absorption can be noticed from blunt and broken peak (as illustrated in Figure 4.8) or using single channel beam as shown in Figures 4.9 and 4.10. In Figure 4.9 was the single channel beam of KBr that used as reference background and in Figure 4.10 has been shown the single channel beam at various concentrations of silica gel in KBr. It can be seen that the greater the concentration is, the closer to zero the signal will be at the frequency 1100 cm^{-1}. This phenomenon called over absorption.
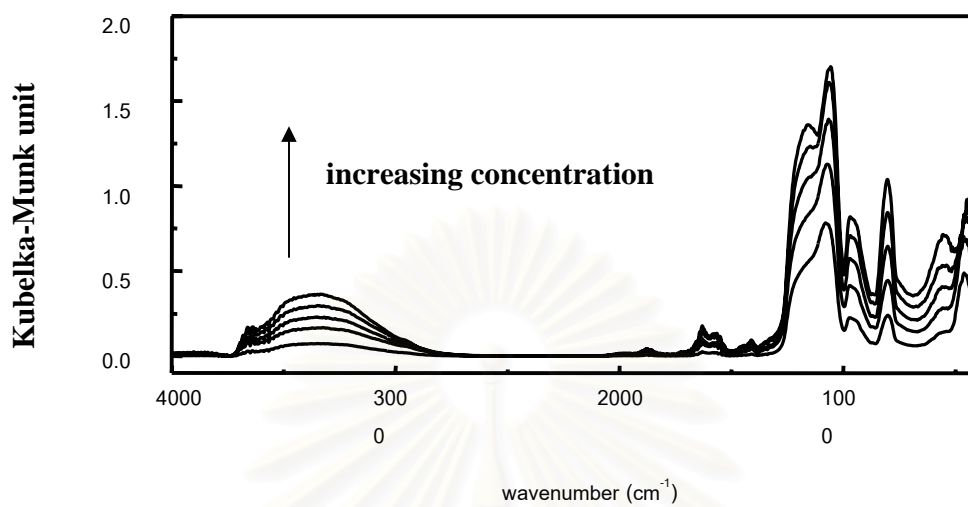
Figure 4.8   Diffuse reflectance spectra of silica gel in KBr at various concentrations
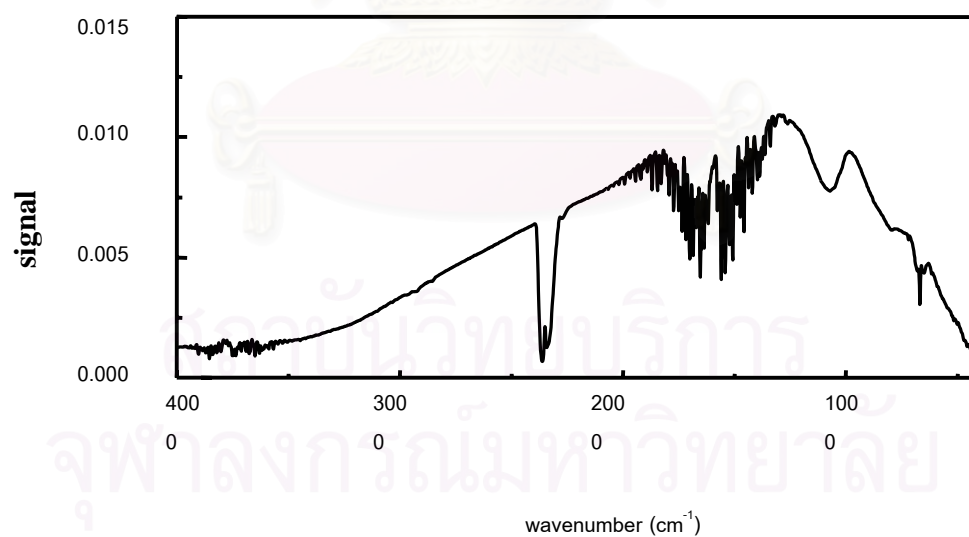(From 2, 4,…, to 10 wt.%).

Figure 4.9   Single channel beam of Potassium bromide.

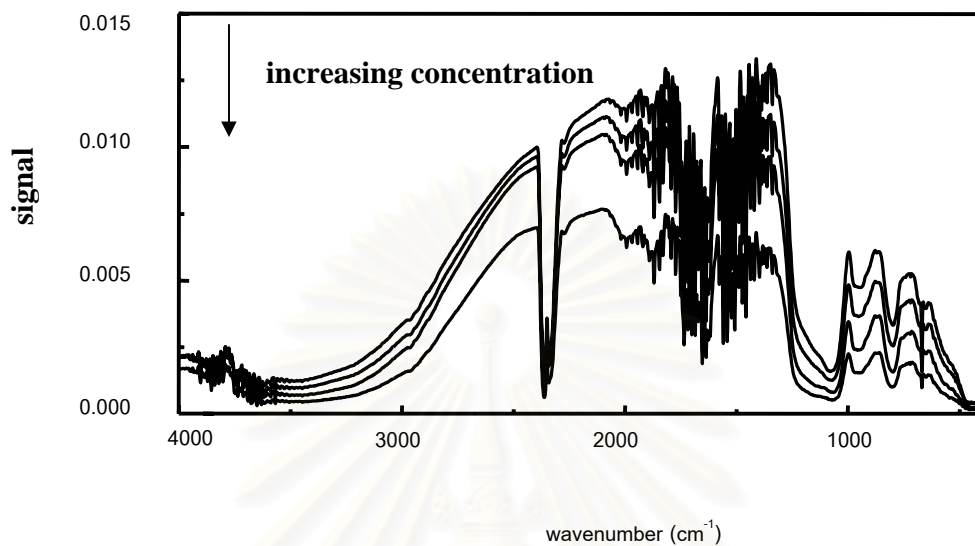Figure 4.10   Single channel beam of silica gel in KBr at various concentrations
(From 2, 4,…, to 10 wt.%).

concentration of silica gel (wt.%)
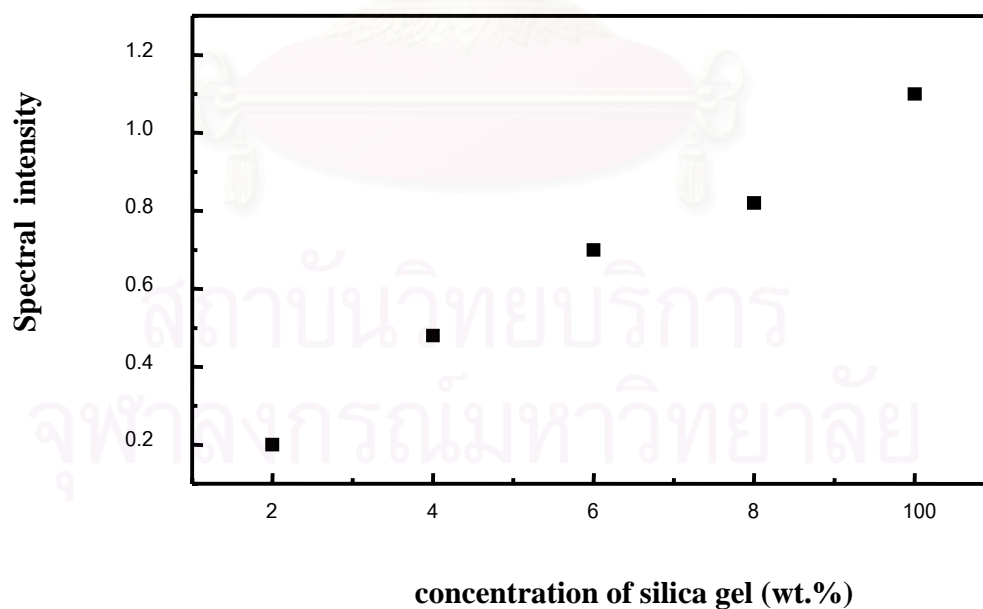
Figure 4.11   Relationship between the spectral intensity (at 810 cm^{-1}) and concentration
of silica gel in KBr.

4.2 Determination of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) using Densitiometer

4.2.1 Densitiometer Operating Conditions

CAMAG TLC Scanner II

Experimental Setup

Light source	Deutorium
Number of scan	1
Track space	10.0 mm
Wavelength	400 nm
Sensitivity	245
Span	20
Offset	5

Table 4.1 Peak height of absorbance scan of standard solution of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at various concentrations and standard deviation.

Concentration (wt%)	Peak height (cm)			Average	Standard Deviation
	No.1	No.2	No.3		
0.4075	3.2	3.7	3.5	3.47	0.2517
0.8017	7.3	6.5	6.7	6.83	0.4164
1.2110	8.9	8.9	8.8	8.83	0.0731
Unknown	*10.1*	*10.6*	*10.2*	*10.3*	*0.2958*
1.6091	11.9	12.5	12.75	12.38	0.4369
2.0427	16.4	15.9	16.3	16.2	0.2646

From peak height data of standard solution and unknown concentration sample in Table 4.1, the calibration curve was constructed shown in Figures 4.12 and 4.13. An unknown concentration sample can be obtained. Considering the conditions of measurement, the correlation coefficient of calibration curve is 0.9958, standard deviation was 0.5204 and the obtained result of the unknown concentration sample is 1.31 wt.%. To be compared the obtained result with the actual value that is 1.35 wt.%, therefore the error was 3.0 %. From this result, it will be used to confirm that the unknown concentration can be achieved via DRIFT spectroscopy also as the results shown in the section 4.3.

Although densitiometer is so convenient to acquire the results but this technique also has the limitation in concentration range of sample. Because the principle of this technique is photometric measurement of absorption so the concentration must be controlled in the suitable range in order to be measured by have no over absorption.

In this research, the detection range of measurement was 0.40 to 2.0 wt.%. Actually the concentration can be measured to 0.08 wt.% by densitiometer but from the reason that TLC sheets that used to be measured in this section must be abraded and measured again by DRIFT spectroscopy so the range of concentration must be high enough to obtain the spectrum of sample.
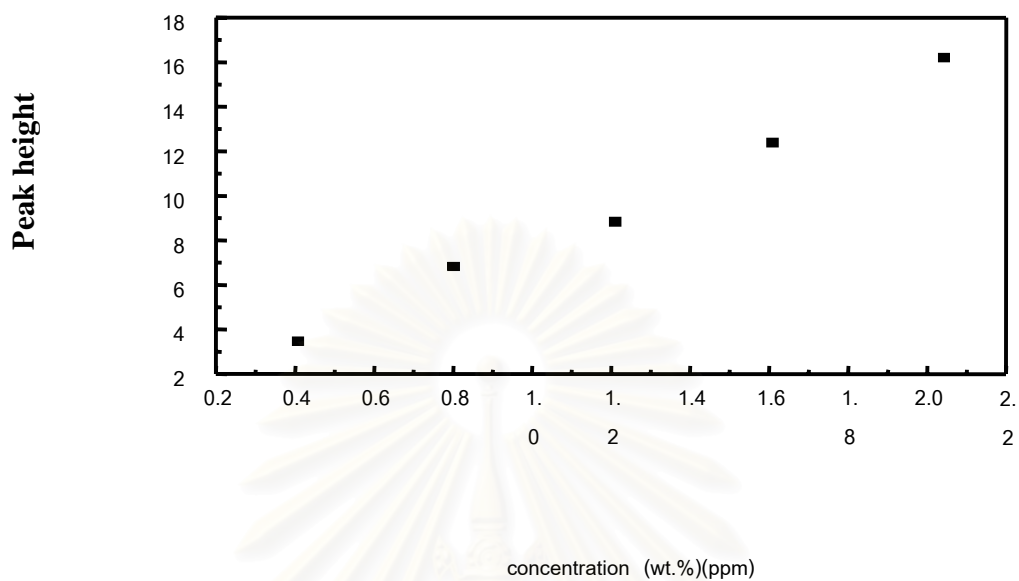
Figure 4.12   Calibration curves between peak height and various concentrations of
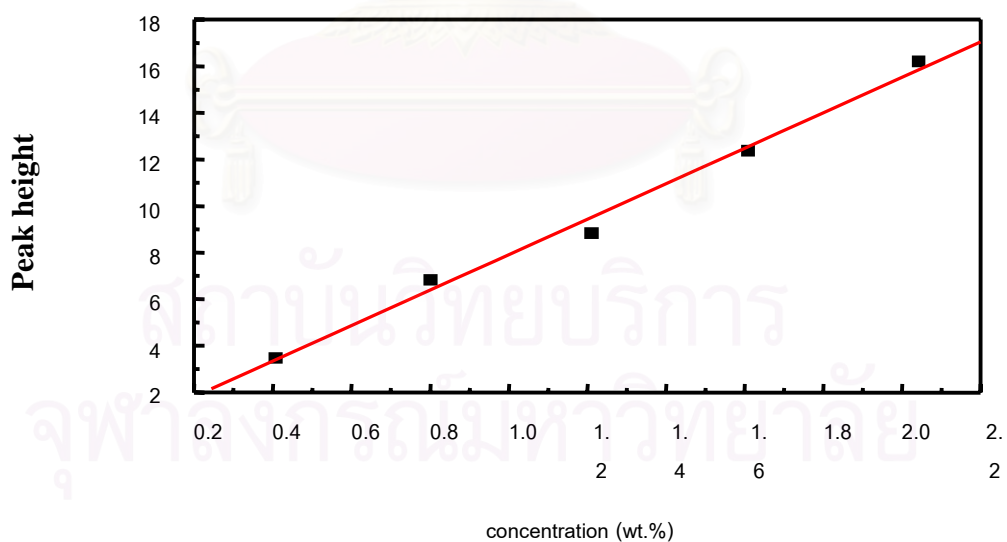4, 4´- methylenebis (2, 6-di-tert-butylphenol)

Figure 4.13   Linear least-squares fit of calibration curves shown in Fig. 4.12

4.3   Introduction of Lubricant Additives

Modern Lubricants are formulated from a range of base fluids and chemical additives. The base fluid has several functions but primary it is the lubricant, providing a fluid layer separating moving surfaces or removing heat and wear particles while keeping friction at a minimum. Many of the properties of the lubricant are enhanced or created by the addition of special chemical additives to the base fluid. For example, stability to oxidation and degradation in an engine oil can be improved by the addition of antioxidants while extreme pressure anti-wear properties needed in gear lubricant are created by the addition of special additives [13].

Therefore, the quantity of lubricant addives is very important to concern in order to adjust for acquired lubricant. In this work, 4, 4´-methylenebis (2, 6-di-tert-butylphenol) is one of phenolic antioxidant added to the lubricant. The structure is shown in Figure 4.14.
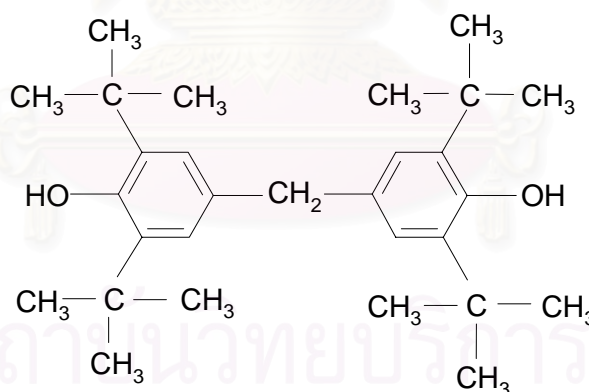
Figure 4.14   Structure of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) [14].

4.3.1 Spectra of 4, 4´-methylenebis (2, 6-di-tert-butylphenol)

Spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) acquired via diffuse reflectance and transmission mode are shown in Figures 4.15 and 4.16, respectively. It has been shown that all features in both spectra are similar by having strong band of OH stretching at the frequency 3610 cm^{-1}, the strong band of CH_3 asymmetric stretching at the frequency 2960 cm^{-1}, the strong band of CH_3 asymmetric bending at the frequency 1435 cm^{-1} and another one at the frequency 1250 cm^{-1} (skeletal vibration). The difference between the spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) achieved via diffuse reflectance and transmission mode is baseline. It can be seen that the baseline via diffuse reflectance mode is more linear than that via transmission mode. Because the scattering of light does not affect so much the baseline via diffuse reflectance mode, which moreover DRIFT spectroscopy can minimize the specular reflection more than transmission mode because the reflection spectra do not come from the front surface alone, but the radiation will be penetrated into the materials and reappeared after scattering or reflection at a second surface so that the incident beam will be traversed throughout almost area in the materials. In addition, the preparation of the samples for DRIFT studies are fast including the quantity of sample spending is not limited as that in transmission mode. In transmission mode, the incedent beam of infrared will be transmitted directly to the surface of KBr pellet only so the more the sample is, the more absorption will be. Beyond this in transmission mode, it must be careful for over absorption phenomenon that can be occurred easily.

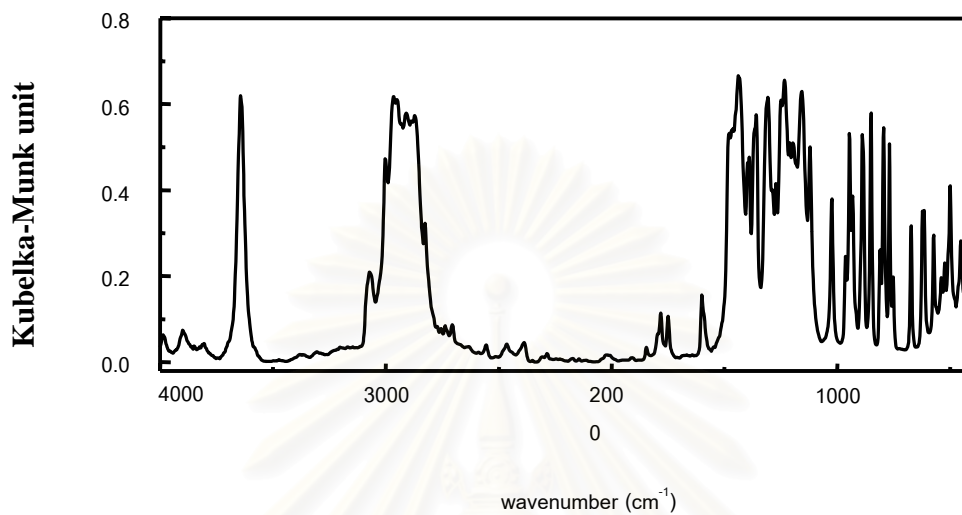### 4.3.1.1 Diffuse reflectance Spectrum

Figure 4.15   Diffuse reflectance spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at 5 wt.% in KBr

4.3.1.2 Transmission spectrum
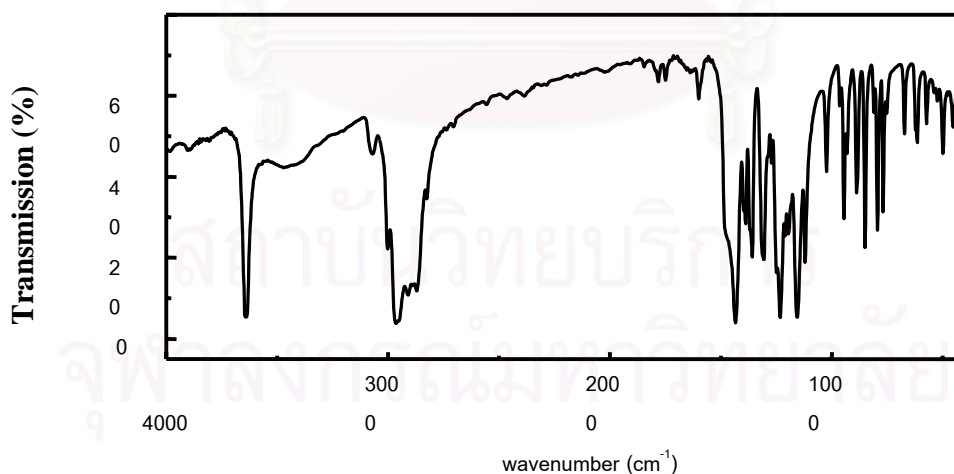
Figure 4.16   Transmission spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at 2 wt.% in KBr.

4.3.1.3 Reference spectrum of 4, 4´-methylenebis (2, 6- di-tert-butylphenol)

Reference spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) in Figure 4.17 has been shown the strong band of OH stretching at the frequency 3610 cm^{-1}, the strong band of CH$_3$ asymmetry stretching at 2960 cm^{-1} and the strong band of CH$_3$ asymmetric bending at the frequency 1435 cm^{-1} and another one at the frequency 1250 cm^{-1} (skeletal vibration). To be compared with the spectra via diffuse reflectance and transmission mode, it can be seen that both of them were appeared in the same shape and frequency as the reference spectrum.
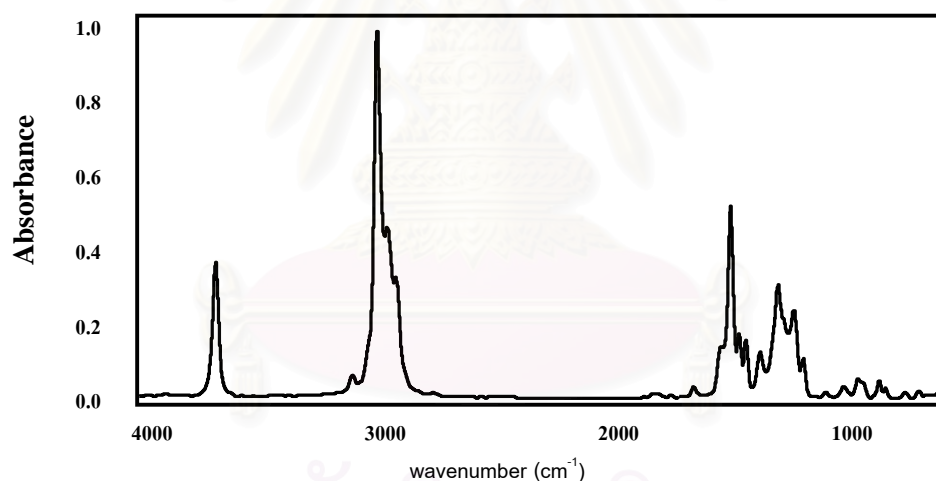

Figure 4.17   Reference spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) [14].

4.3.2 Diffuse Reflectance Spectra of 4, 4´-methylenebis (2, 6- di-tert-butylphenol) Achieved via TLC sheet

From Figure 4.18, it was shown peaks of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) compared with peaks of silica gel. The dominant peaks that expected to see if they can overcome the absorption of silica gel are the strong band of OH stretching at the frequency 3610 cm^{-1} and the strong band of CH$_3$ asymmetric stretching at the frequency 2967 cm^{-1}. In the Figure 4.19, there are two peaks of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) that can be seen. One is the strong band of CH$_3$ asymmetric stretching at the frequency 2967 cm^{-1} as shown in Figure 4.20 and another is the band of CH$_3$ asymmetric bending at the frequency 1435 cm^{-1} as shown in the Figure 4.21.

The quantitative analysis of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) treated on silica gel using TLC technique can be achieved by using the spectral intensity or peak area at the frequency 2967 cm^{-1} or another one at the frequency 1435 cm^{-1} that varied with the concentrations of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) treated on TLC sheet.

In this work, the calibration curve was constructed using all peak areas obtained from five concentrations (0, 0.4, 0.8,…, and 2.0 wt.%) of solution of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) as shown in the Figure 4.22. Background scans were obtained with the use of potassium bromide powder.

Very occasionally, it was found that this procedure did not permit exact compensation of the interfering bands, the most trouble some feature was the water band at 1640 cm^{-1}. In this case, additional digital methods were used to eliminate these features.

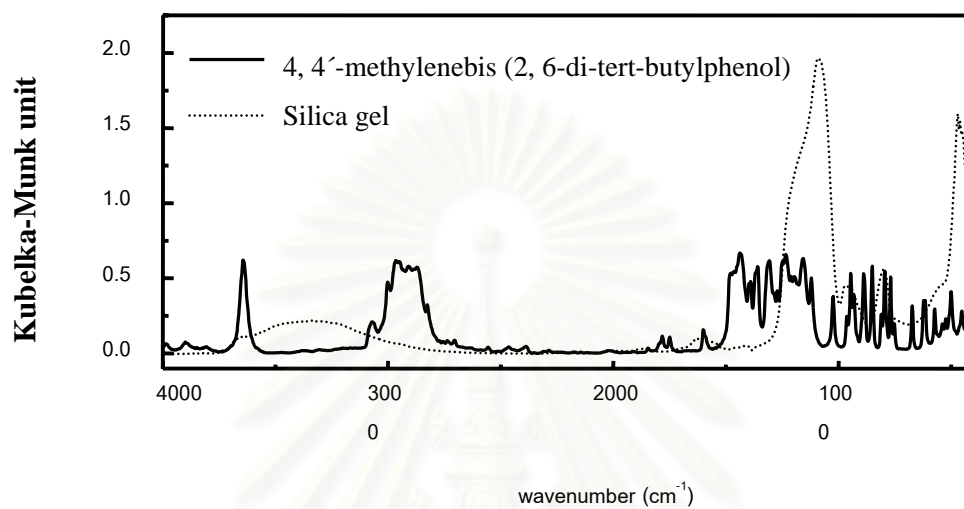Figure 4.18   Diffuse reflectance spectra of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) compared with silica gel in KBr.
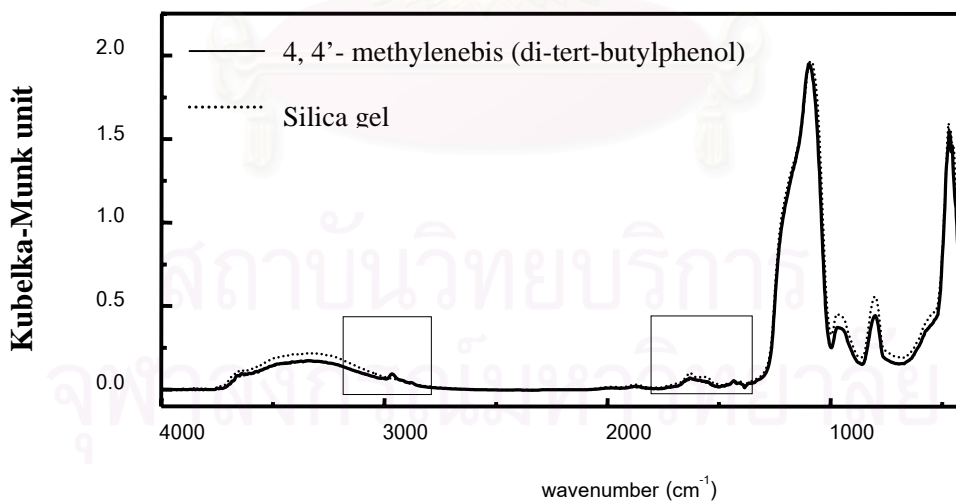

Figure 4.19   Diffuse reflectance spectra of 20 wt.% conc. of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) achieved via TLC sheet at 5 wt.% in KBr compared with silica gel at 5 wt.% in KBr.
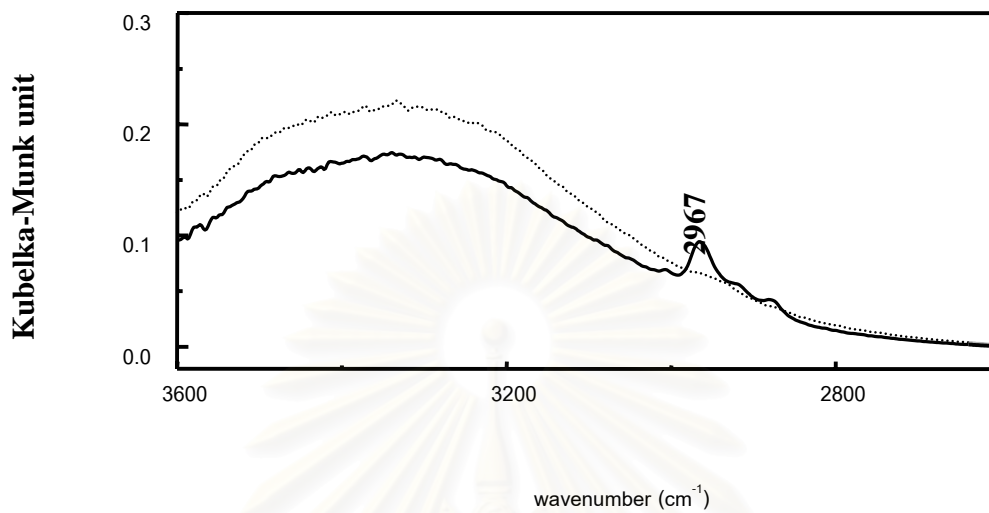
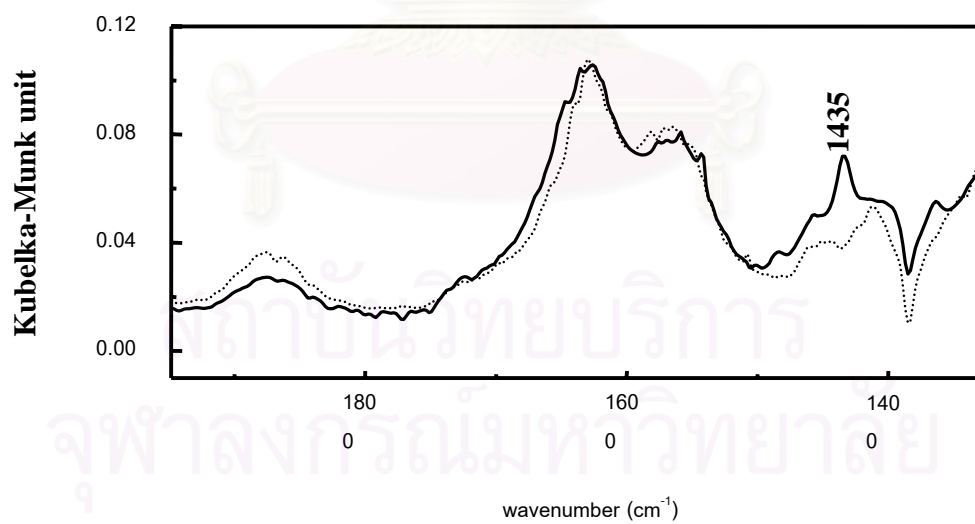Figure 4.20   Expanded spectrum of Figure 4.19 inset.

Figure 4.21   Expanded spectrum of Figure 4.19 inset.

4.3.3 Diffuse Reflectance Spectra of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at Various Concentrations

The fringe-eliminated spectra as shown in the Figure 4.22 were then used to construct calibration curve between the peak areas at the frequency 2967 cm^{-1} and concentrations. It shows superimposed spectral plots of the five concentration of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) over a concentration range of 0-2.0wt.%. It is clear that the relative concentrations, which differ by only 0.4%, are internally accurate. The signal-to-noise ratio (S/N) is high, and the overall reproducibility of this single measurement is good, at least on a semi-quantitative basis. To further quantitative analysis in this system, data after normalizing the peak height $f(R_\infty)$ of each concentration at the analytical frequency 2967 cm^{-1} and peak areas were obtained in the range 2995.442 to 2850.781 cm^{-1} as shown in Table 4.2. Calibration curve and a linear least-squares fit were constructed as shown in the Figures 4.23 and 4.24, respectively. The curve was later used to find out concentration of unknown concentration sample. Considering the conditions of measurement, the correlation coefficient of calibration curve is 0.9934 and the obtained result from the calibration curve is 1.41 wt.% compared with the actual value that is 1.35 wt%. Therefore the error is 4.4%. It can be shown that the unknown concentration can be obtained via this applied technique.

However this applied technique also has the limitation in measurement about detection range of sample that treated on TLC sheet. Because silica gel that coated on TLC sheets can absorb infrared beam in the same frequency of the sample so the detection range of solution must be high enough to overcome the absorption of silica gel. In this research the detection range was 0.40 to 2.0 wt.%. Actually the concentration of sample can be higher than 2.0 wt.% but treated TLC sheets must be analyzed in both densitiometer and DRIFT spectroscopy. Therefore, the detection range should be suitable to measure in both methods.
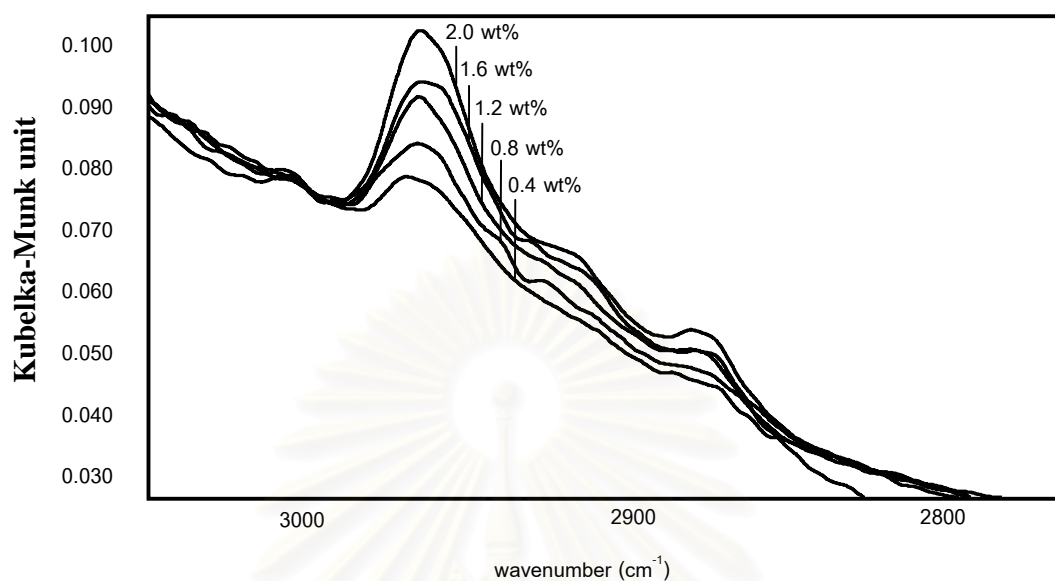
Figure 4.22   Diffuse reflectance spectra of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at various concentrations at the frequency 2967 cm^{-1}.

Table 4.2   Actual concentration and peak areas   (in the range 2995.442 to 2850.781cm^{-1}) of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) treated on TLC sheet.

Concentration	Peak area			Avearage	Standard
(wt%)	No.1	No.2	No.3		Deviation
0	0	0	0	0	0
0.4075	0.533	0.520	0.534	0.529	0.0078
0.8017	1.648	1.680	1.634	1.654	0.0236
1.2110	2.575	2.291	2.514	2.460	0.1493
Unknown	3.191	3.133	3.246	3.190	0.0565
1.6091	3.892	3.862	4.003	3.919	0.0743
2.0427	4.717	4.734	4.784	4.745	0.0348

Figure 4.23   Calibration curves between peak areas at frequency 2967 cm^{-1} and various concentrations of 4, 4´-methylenebis (2, 6-di-tert-butylphenol)

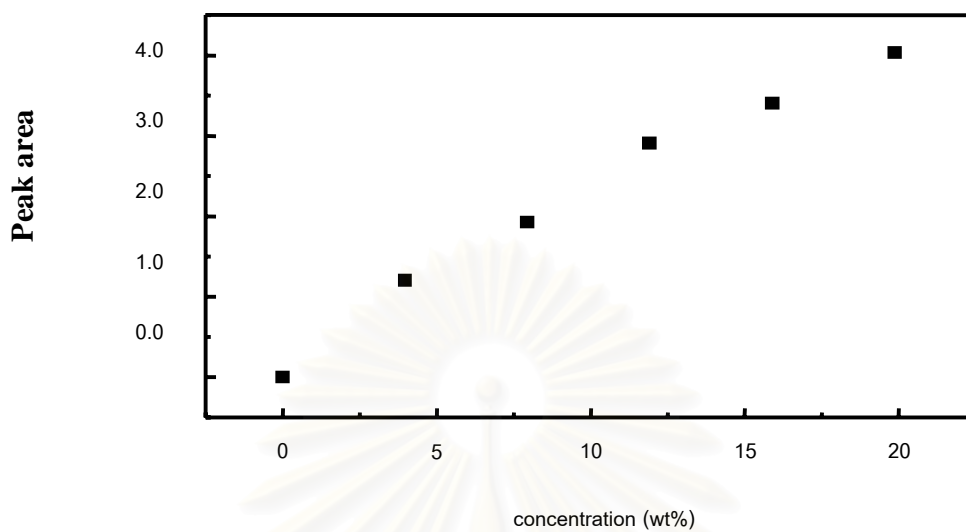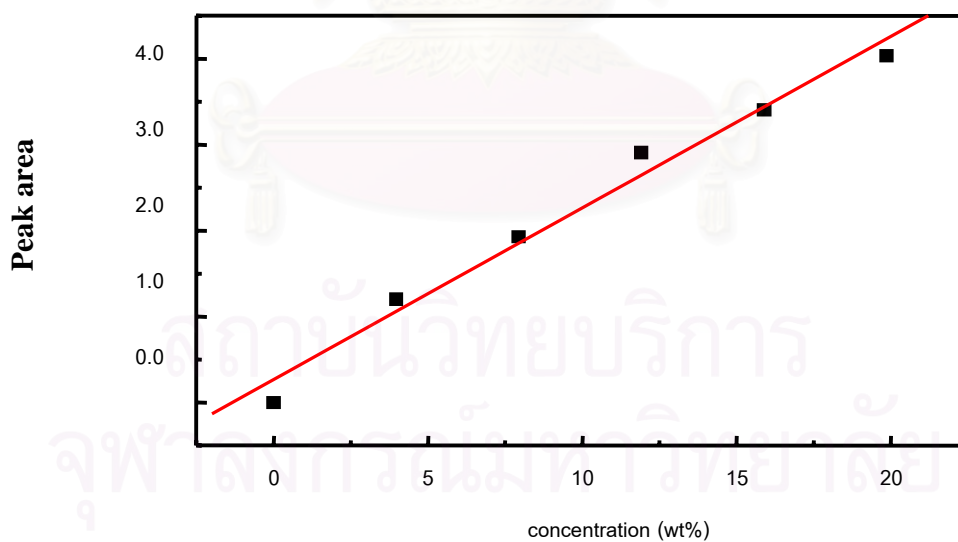Figure 4.24   Linear least-squares fit of calibration curves shown in Fig. 4.23

Because this measurement is TLC technique coupled with DRIFT spectroscopy so that the detection range must be covered in both techniques. The detection limit of 1 microliter of sample size that analyzed using this applied technique is 0.4 wt.%. This is the minimum concentration of sample treated on TLC sheet that can be detected and shown the diffuse reflectance spectrum using DRIFT spectroscopy. It can be found by varying concentrations and testing with densitiometer coupled with DRIFT spectroscopy. Figure 4.25 shows diffuse reflectance spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at 0.4 wt.% concentration and Figure 4.26 shows diffuse reflectance spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at 0.1 wt.% concentration that have no peak of sample to be appeared.
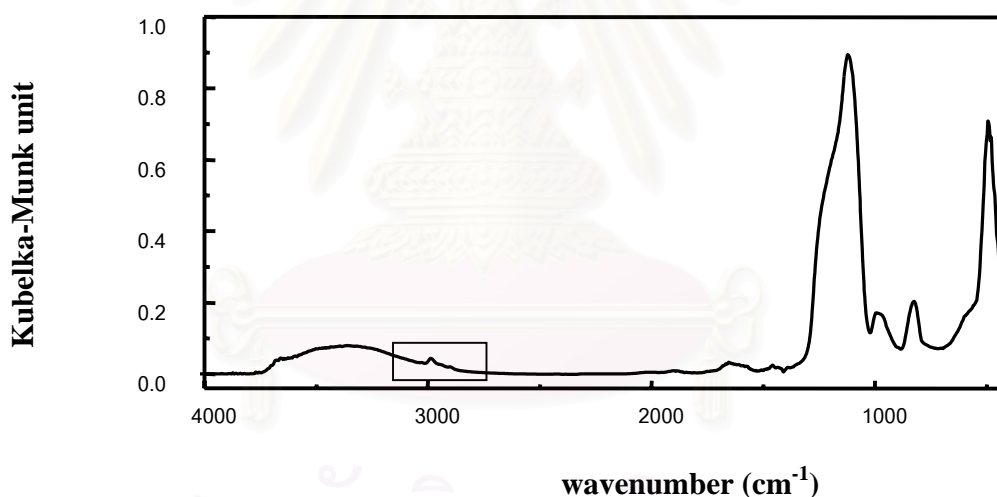

Figure 4.25   Diffuse reflectance spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at 0.4 wt.% concentration.
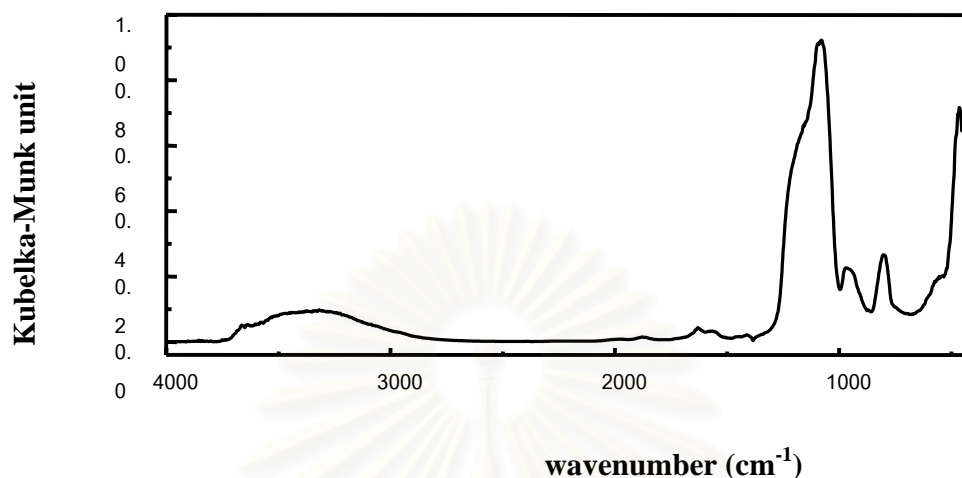
Figure 4.26   Diffuse reflectance spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) at 0.1 wt.% concentration.

Generally, Infrared (IR) spectrum of an organic substance has often been called its "fingerprint." Since the spectrum of each molecular species is unique, IR is a powerful tool for the identification of organic compounds. In this work, the obtained spectrum via DRIFT spectroscopy can be analyzed to identify organic compounds also.

As the result of subtracting the $f(R_\infty)$ spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) treated on silica gel and silica gel was shown in Figure 4.25. It was shown peak of CH_3 asymmetric stretching at the frequency 2960 cm^{-1} and peak of CH_3 asymmetric bending at the frequency 1435 cm^{-1} also. Although there are less peaks to show but at least this spectrum can be known that CH_3 asymmetric stretching and CH_3 asymmetric bending are two characteristic peaks of this substance. All the positive bands are due to peak of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) that can be shown that diffuse reflectance spectrometry may prove to be a very useful technique for quality assurance. Although conventional transmission spectroscopy can be capable to analyze for qualitative applications but it seems hardly to prepare the sample in the step called the KBr mulls or pressed-pellet technique [15]. Considerable difficulty is likely to be encountered in controlling for the same condition in every pellet such as pressing the powder in a die to form a transparent or translucent pellet, thickness of pellet, dispersion

of the sample etc. Moreover, conventional transmission spectroscopy can be made difficult because of morphological changes occurring as a result of the grinding or hot compression molding procedures adopted in the preparation of samples.   In the other hand, the sample is ground more gently, and pressing is not involved at all, polymeric changes induced by sample preparation are very unlikely in DRIFT spectroscopy.
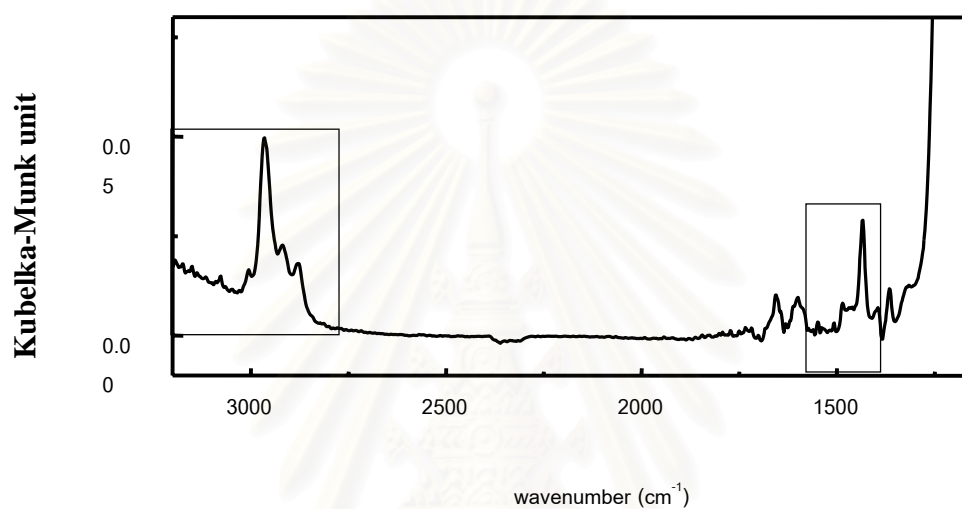

Figure 4.27   Subtracting spectrum of 4, 4´-methylenebis (2, 6-di-tert-butylphenol) treated on silica gel and silica gel.
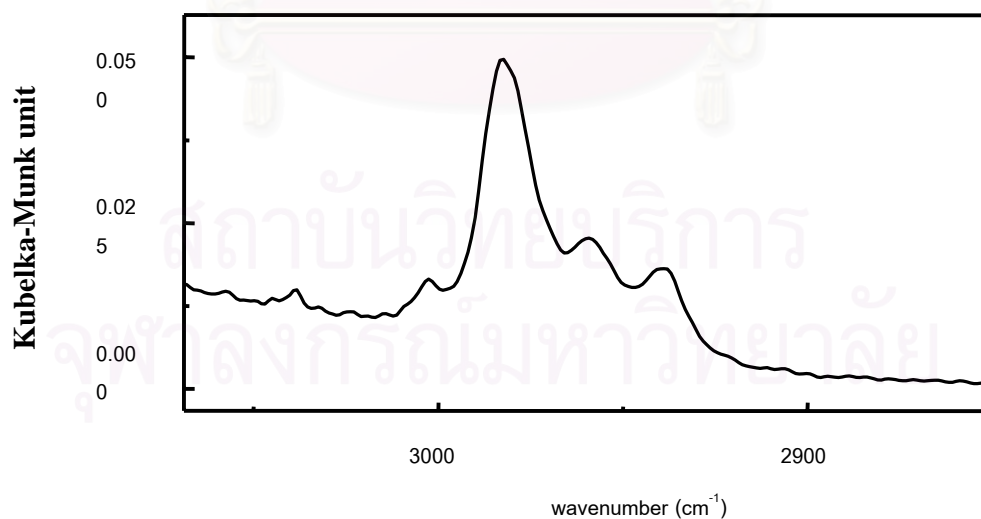

Figure 4.28   Expanded spectrum of Figure 4.25 in the region 3000 – 2900 cm^{-1}.

CHAPTER 5

CONCLUSION

5.1   Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy

Measuring the infrared spectrum of TLC spots using a TLC technique coupled with DRIFT spectroscopy is certainly quicker than methods reported in the past that used column chromatography. It can be seen that the spectra obtained via DRIFT spectroscopy are similar to the spectra obtained via transmission method. The advantages of DRIFT spectroscopy include ease sample preparation, less time for sample preparation and measurement and less chemicals used. Beyond this DRIFT spectroscopy also has the linear baseline. The classic transmission method, on the other hand, always has the scattering problems that produce non-linear baseline.

5.2   Quantitative Analysis Using DRIFT Spectroscopy

The detection limit of the sample size 1 microliter analyzed using this applied technique is 0.4 wt.%. This is the minimum concentration of sample treated on TLC sheet that can be detected and shown the diffuse reflectance spectrum using DRIFT spectroscopy. According to the obtained result of sample with unknown concentration using calibration curves, the concentration of the sample was found to be 1.31 and 1.41 wt.% from densitometer and DRIFT spectroscopy respectively. Actually the concentration of unknown sample is 1.35 wt.% (as shown in table 5.1). It can be seen that the error of obtained results via densitometer is less than that via DRIFT spectroscopy by 3.0 and 4.4%, respectively. However it can be seen that the obtained result via TLC technique coupled with DRIFT spectroscopy is close to that via densitometer so TLC technique can be applied with DRIFT spectroscopy in order to analyze in both qualitative and quantitative analysis.

Table 5.1   Results obtained via densitiometer and DRIFT spectroscopy

Technique	concentration (wt.%)		Error (%)	Standard Deviation
	actual	Obtained via calibration curve		
Densitiometer	1.35	1.31	3.0	0.2958
DRIFT spectroscopy	1.35	1.41	4.4	0.0565

Although TLC technique coupled with DRIFT spectroscopy can be used for qualitative and quantitative analysis but this technique still has limitations such as the concentration of the sample should be high enough to overcome the absorption of silica gel coated on TLC sheet, the condition of experiment such as particle size, packing density, homogeneity and concentration must be controlled in the same manner through the entire measurement.

REFERENCES

1. Coates, J. P., and Setti, L. C. (eds). (1985). <u>Oils, Lubricants, and Petroleum Products Characterization by Infrared Spectra.</u> New York and Basel: Marcel Dekker.

2. Porro, T. J., and Pattacini, S. C. (1990). The Use of Diffuse Reflection FT-IR Spectroscopy for the Quantitative Analysis of a Number of Silanized Kaolin Clays. <u>Appl. Spectrosc. </u>44(7): 1170-1175.

3. Percival, C. J., and Griffiths, P. R. (1975). Direct Measurement of the Infrared Spectra of Compounds Separated by Thin-Layer Chromatography. <u>Anal. Chem</u>. 47(1): 154-156.

4. Chalmers, J. M., and Mackenzie. (1985). Some Industrial Applications of FT-IR Diffuse Reflectance Spectroscopy. <u>Appl. Spectrosc</u>. 39(4): 634-641.

5. Azambre, B., Heintz, O., Schneider, M., Krzton, A., and Weber, J. V. (1999). Optimization of some instrumental factors in diffuse reflectance infrared Fourier transform spectroscopy. <u>Talanta</u>. 50: 359-365.

6. Perkins, W. D. (1993). Sample Handling in Infrared Spectroscopy-An Overview. In Coleman, P. B. (ed.). <u>Practical Sampling Techniques for Infrared Analysis,</u> pp. 11-53. Boca Raton: CRC Press.

7. Fuller, M. P. (1978). Diffuse Reflectance Measurement by Infrared Fourier Transform Spectrometry. <u>Anal. Chem</u>. 50(13): 1906-1910.

8. Spragg, R. (1997). Reflection Spectra. <u>Internet J.Vib.Spect.</u> [www.ijvs.com] 1(4): 14-25.

9. Culler, S. R. (1993). Diffuse Reflectance Infrared Spectroscopy: Sampling Techniques for Qualitative/ Quantitative Analysis of solids. In Coleman, P. B. (ed.). <u>Practical Sampling Techniques for Infrared Analysis.</u> pp. 93-106. Boca Raton: CRC Press.

10. Compton, S. V., and Compton, D. A. C. (1993). Quantitative Analysis-Avoiding Common Pitfalls. In Coleman, P. B. (ed.). <u>Practical Sampling Techniques for Infrared Analysis</u>. pp. 217-254. Boca Raton: CRC Press.

11. Amornsit, M., and Petsom, A. (1992). <u>Principles and Techniques of Instrumental Analysis</u>. Bangkok: Chuanpimm.

12. Lin-Vien, D., Colthup, N. B., Fateley, W. G., and Grasselli, J. G. (1991). <u>The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules</u>. San Diego: Academic Press.

13. Prince, R. J. (1994). Base oils from petroleum. In Mortier, R. M., and Orszulik, S. T. (eds.) <u>Chemistry and Technology of Lubricants</u>. pp. 1-6. London: Chapman & Hall.

14. Pouchert, C. J. (1995). <u>The Aldrich Library of FT-IR Spectra, Edition I.</u>

15. Smith, A. L. (1979). <u>Applied Infrared Spectroscopy; Fundamentals, Techniques, and Analytical Problem-solving</u>. New York: John Wiley&Sons.

16. Jork, H., Funk,W., Fisher, W., and Wimmer, H. (1990). <u>Thin-Layer Chromatography: Reagents and Detection Methods Volume 1a.</u> New York: VCH.

CURRICULUM VITAE

Watcharee   Katinonkul

1973   Born May, 27 in Khon Kaen, Thailand

Father   : Mr. Veera   Katinonkul

Mother : Mrs. Sangeum   Katinonkul

1977   Elementary School (Prakumarnyesoo elementary school)

1979   Primary School (Satit Modindaeng Demonstration School,

Khon Kaen University, Khon Kaen)

1985   High School (Satit Modindaeng Demonstration School, Khon Kaen

University, Khon Kaen)

1991   Bachelor degree of Science (Chemistry),

Khon Kaen University, Khon Kaen

1995   Thai Kansai Paint Co., Ltd (in the position of Chemist)

1998   Department of Science service, Division Of Chemistry

Ministry of Science, Technology and Environment

(in the position of Scientist)

1999   Master degree student at Faculty of Science,

Chulalongkorn University, Bangkok