

## CHAPTER IV

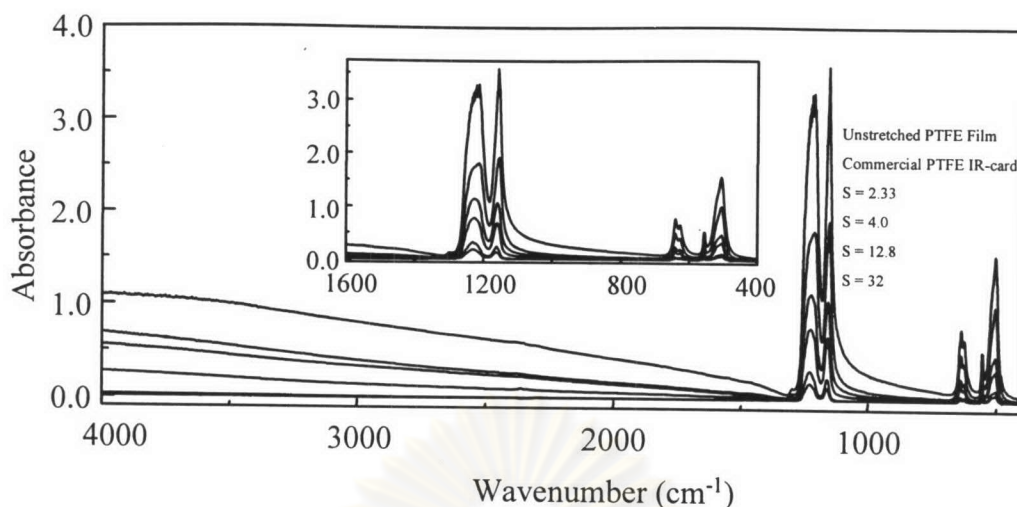
### RESULTS AND DISCUSSION

#### 4.1 Spectroscopic properties of the home-made PTFE IR card from a thin PTFE film

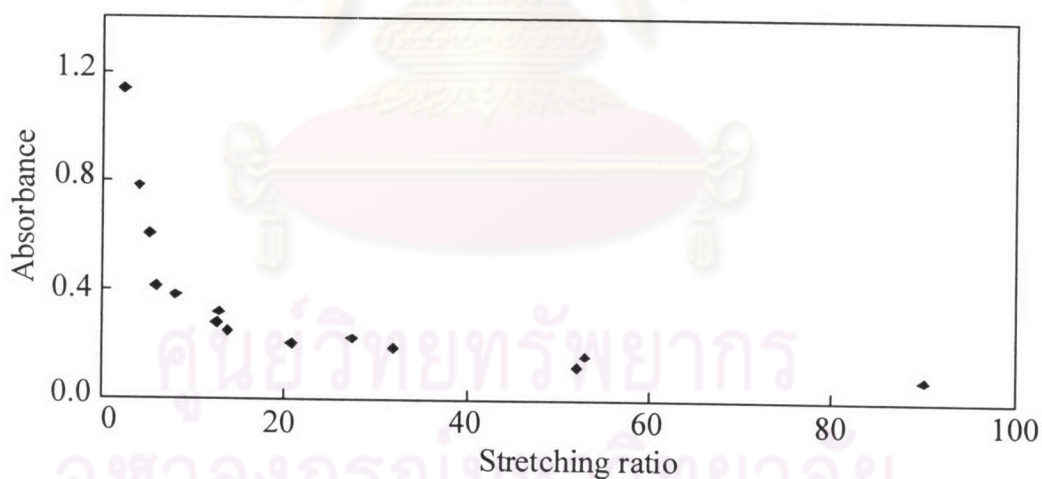
##### 4.1.1 Difference in film thickness

Polytetrafluoroethylene (PTFE or Teflon) film was chosen as the home-made IR cards for analyzing various types of samples. The first attempt at making, the home-made IR card was with a short strip of PTFE tape, cut directly from the roll, and tape to a piece of the circular PVC sheet. The home-made IR card without a sample was placed in the part of the IR beam and the spectrum was collected. Strong scattering was observed in the  $4000\text{-}1600\text{ cm}^{-1}$  region. This scattering of the home-made IR card is similar to that of a commercial PTFE IR card. It was found that the intensity of the scattered light could be reduced by simply stretching the PTFE tape perpendicularly and parallel to its longitudinal direction.

Figure 4.1 shows IR spectra of the PTFE tape with different stretching ratio values and the commercial PTFE IR card. The strong absorption bands at  $1228$  and  $1158\text{ cm}^{-1}$  are due to the C-F stretching; whereas the spectral evidence of C-F bending is presented as weak and medium bands at  $640$  and  $508\text{ cm}^{-1}$ , respectively. As is evident from the figure, the scattering of IR radiation was observed in the unstretched tape and the commercial IR card. The strong scattering at high frequencies results in low energy throughput (very high absorptivity;  $> 1.0$  absorbance unit). Thus, a substantial loss of sensitivity was observed. However, by stretching the PTFE tape, light scattering is significantly reduced, resulting in a much higher energy throughput (low absorptivity). The observed scattering may be caused by the particulate nature of the PTFE tape. By nature, unstretched tape consists of interlinked particles, when the tape was stretched, the particles unravel into fibers of PTFE tape. This unraveling in conjunction with the reduced density of the polymer, lessens the scattering of IR radiation and allows higher energy throughput.



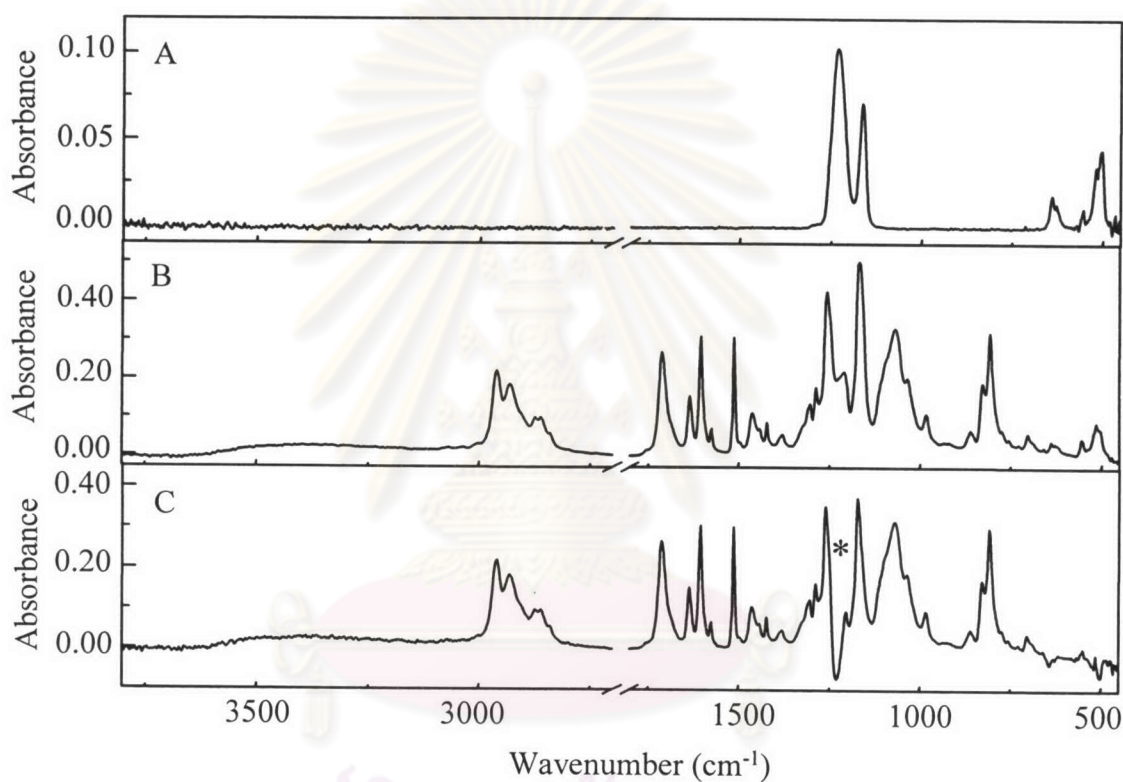
**Figure 4.1** IR spectra of the PTFE (Teflon) tape at different stretching ratios ( $S$ ) and spectrum of the commercial PTFE IR card. From the top to bottom: spectra of unstretched PTFE film, commercial PTFE IR card and the home-made IR card with stretching ratio for 2.33, 4.0, 12.8 and 32, respectively.



**Figure 4.2** Special intensity at  $1228\text{ cm}^{-1}$  of C-F stretching as a function of the stretching ratio.

The peak intensity of C-F stretching observed with a commercial IR card approaches 2.0 in absorbance unit. By comparing the spectral intensity to that of the home-made IR card (*i.e.*,  $S > 10$ ), the intensity of a commercial IR card is significantly higher than the home-made IR card.

The spectral intensity of the home-made IR cards decreased as the stretching ratios increased, as shown in Figure 4.2. The film thickness of the home-made IR card can be roughly determined by absorption magnitude. In this study, PTFE tape from local hardware stores was stretched into thin films with various thicknesses range in absorbance unit as the different stretching ratios. Based on Beer's law,<sup>15</sup> only thin films with absorption intensity less than 0.8 were employed for sample analysis.



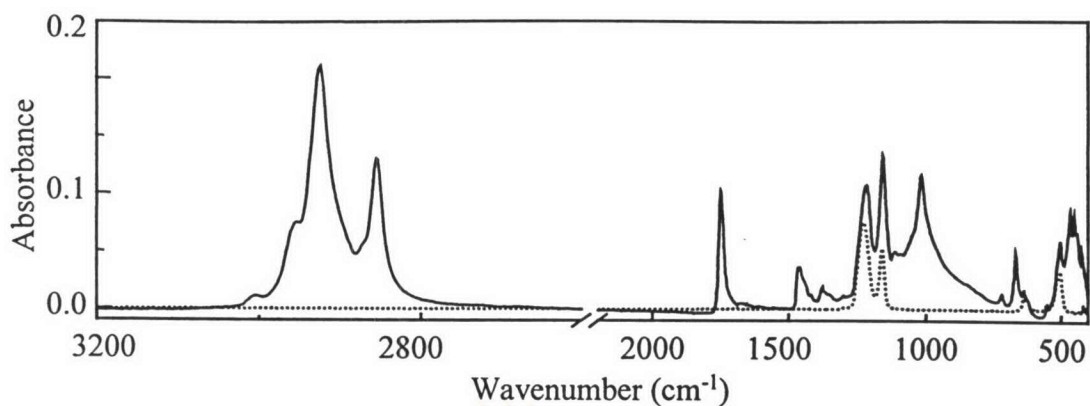
**Figure 4.3** Spectra of a thin PTFE film (A), moisturizing cream (Garnier) on the thin PTFE film (B), the result of subtracting A-B (C). The marked peak in the spectrum C is an unsubtracted PTFE band with a derivative peak shape.

The subtraction process of the sample observed with the home-made IR card is shown in Figure 4.3. The spectra shown in Figure 4.3 are a thin PTFE film (A), the thin PTFE film with sample (B), and finally the subtraction result (C). There are bands around 3000-2800 and 1700-400  $\text{cm}^{-1}$  that belong to the sample. However, PTFE exhibits bands in the range of 1700-400  $\text{cm}^{-1}$ , but these bands can be removed

in order to achieve the spectrum of pure sample used for further identification without interference of PTFE peaks. After subtraction process, peaks at 1228, 1158, 640 and 508  $\text{cm}^{-1}$  are cancelled out, and only spectral characteristic of the moisturizing cream is present. The peak marked with an asterisk in the spectrum C is an unsubtracted PTFE band. The process of subtraction might not be necessary for the sample determination in case that the PTFE spectrum was primarily obtained with good accuracy. The above observation shows a significantly thin PTFE film as a home-made IR card being applied for sample analysis.

#### 4.1.2 Sensitivity determination of the home-made PTFE IR card

The sensitivity of the home-made IR card from a thin PTFE film was investigated with thin-film and low-concentration samples. A thin PTFE film is attached onto the sample molecules. In this observation, the molecules deposited on the human face were chosen as a thin-film sample. After a thin PTFE film is attached to the human face, it was then placed against the IR beam inside the sample compartment for spectral collection. The observed spectrum presented in Figure 4.4 exhibits bands at 2920 and 2848  $\text{cm}^{-1}$  assigned for C-H stretching of hydrocarbons and a strong band at 1700  $\text{cm}^{-1}$  for the C = O stretching. In addition, the small bands at 1460 and 1378  $\text{cm}^{-1}$  are  $\text{CH}_3$  bending, while the O-C-C stretching can be clarified by the strong band at 1015  $\text{cm}^{-1}$ . Based on the spectral assignment presented herein, the sample was consequently identified as a fatty acid type. This observation indicates that the method of using a thin PTFE film has a potential to identify molecules deposited on the surface without sample destruction. Therefore, the home-made IR card achieves a good sensitivity and substantial efficiency for analyzing thin film and low-concentration samples, which possibly can be a new promising technique for forensic analysis.

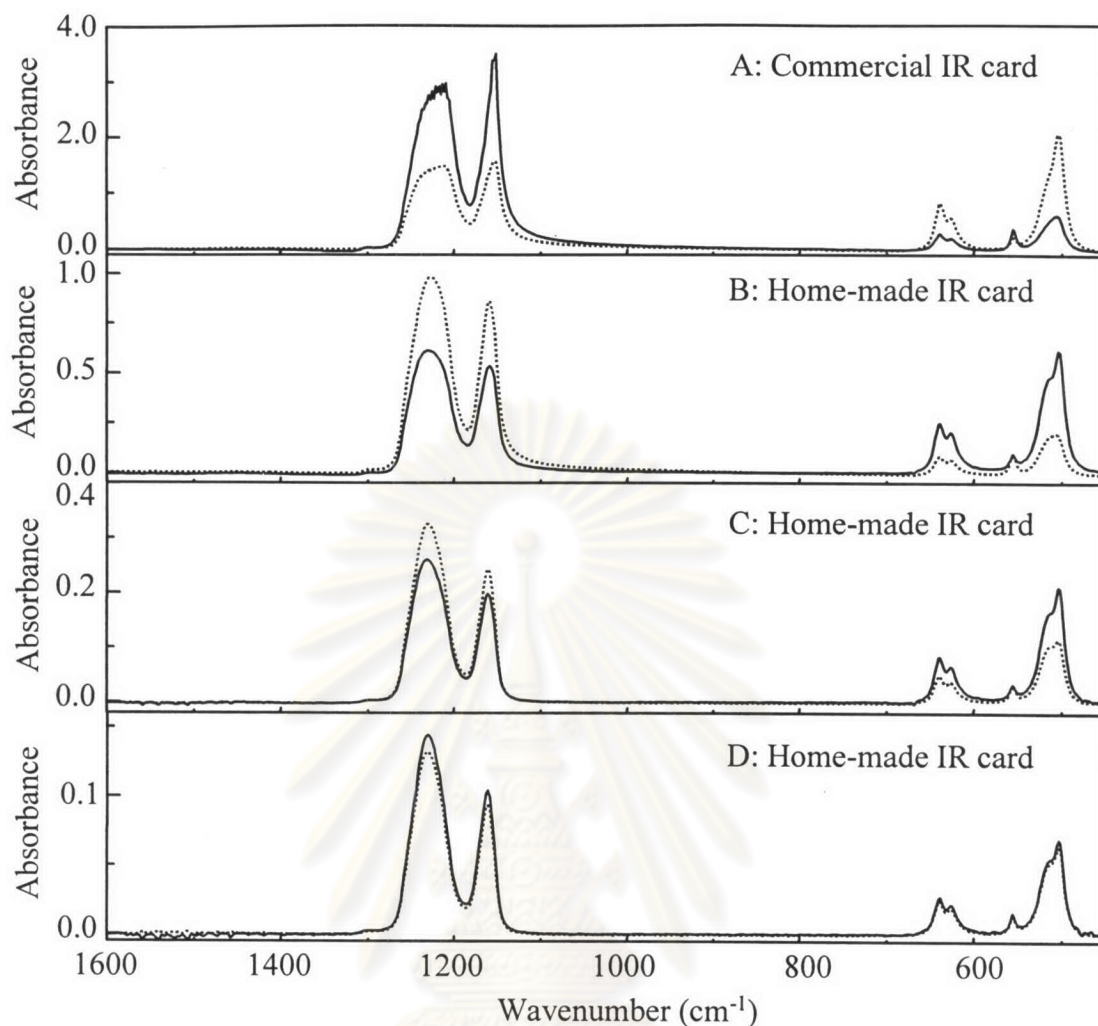


**Figure 4.4** The obtained IR spectrum of deposited molecules on the human face on a thin PTFE film (—) and the original PTFE film (.....).

#### 4.1.3 Orientation of polymer chain

In this section, the home-made IR card was achieved by tetra-axially drawn PTFE film. A drier was used for applying heat onto a thick PTFE film during drawing process in order to acquire a uniformly thin film with less stretching force. Stretching and heating produced different kinds of chain orientation in a polymer film. Therefore, the orientation of the home-made IR card is of interest for further investigation, which can be accomplished by using the polarized IR radiation. Infrared linear dichroism (IRLD) is a well-suited technique to characterize the molecular orientation in an oriented polymer<sup>19</sup>. Since it can provide information on the orientation of different chemical groups of polymers in terms of the dichroic ratio, i.e.,  $R = (A_{\parallel}) / (A_{\perp})$ <sup>19</sup>.

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**Figure 4.5** Different dichroic spectra of PTFE film obtained from the commercial (A) and the home-made IR cards (B-D) with different film thicknesses with parallel (—) and perpendicular (.....) polarized light.

Figure 4.5 shows polarized spectra of PTFE film of the commercial and the home-made IR cards. As seen in the figure, the spectral intensity of the home-made IR card is observed with insignificantly different perpendicular and parallel polarized light, the dichroic ratios of the home-made IR cards decreased as the PTFE film thicknesses decreased. This result shows only a slight orientation of thin PTFE film in consistent with the stretching process of polymer.<sup>20</sup> In the stretched specimen, a particular crystallographic axis consequently aligned along the stretching direction, and the orientations of the polymer chain in the crystal on this axis might be the same. In case of the commercial IR card, the spectral intensity with perpendicular polarized light is substantially weaker than that with parallel polarized light. The difference in

spectral intensity clearly demonstrates that the commercial IR card produces a preferential orientation of fluorine groups parallel to the reference polarization direction, in agreement with the rolling polymer process.<sup>20</sup> For the rolled specimens, double orientation is produced due to the axis aligning with the rolling direction as well as the crystallographic plane, which orient parallel to the plane of the film.

## **4.2 Efficiency of the home-made IR card for sample analysis**

### **4.2.1 Solids**

#### **4.2.1.1 Preparation of solid samples for home-made IR card**

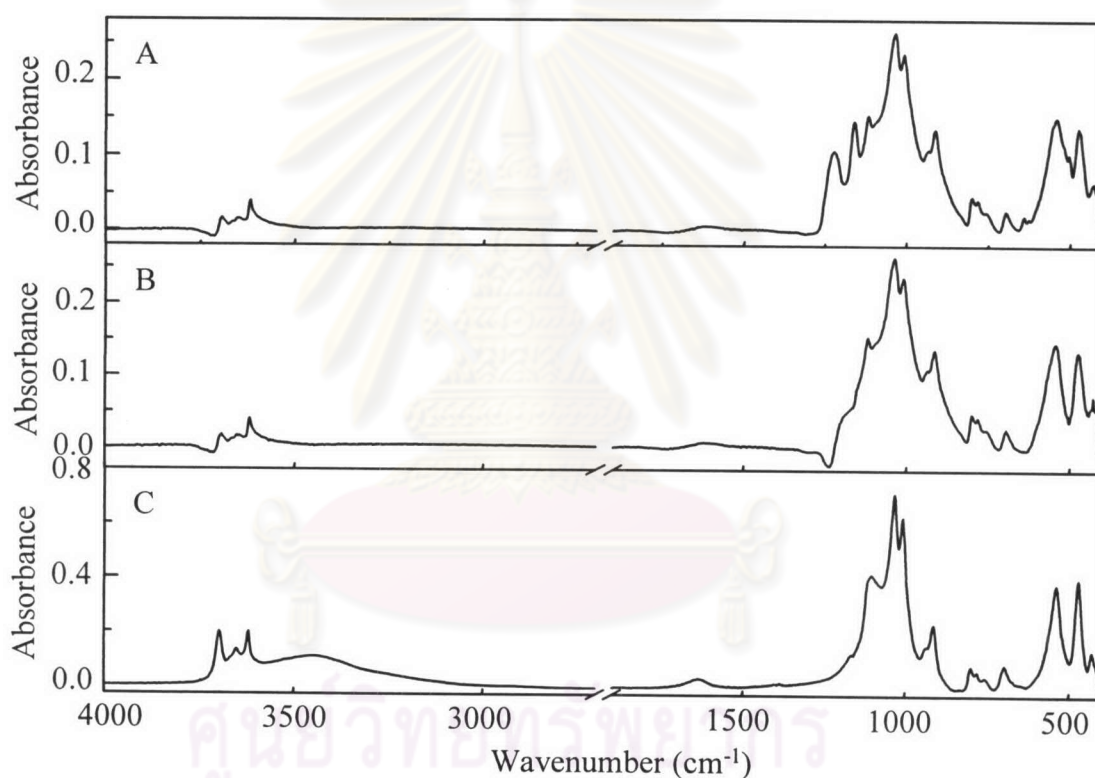
The commercial disposable IR cards are suitable to use for qualitative IR transmission analysis of various types of samples: liquids, materials soluble in organic solvent, semi-solids and pastes. Samples are simply dropped onto the surface of the substrate, and the solvent allowed to completely evaporate. The card is then mounted in the sample slide holder of the instrument, and a spectrum is collected. In this thesis, the home-made IR cards from thin PTFE film were used for solid sample analysis. Two sample preparation methods for solids were operated: (i) grinding in powder form and (ii) dissolving in organic solvent. The resulting spectra of solids were compared between using the home-made IR cards and potassium bromide (KBr) pellets.

##### **4.2.1.1.1 Grinding in powder form**

KBr pellets are popularly used to obtain the IR spectra of solids. Generation of a pellet involves the grinding of the sample with KBr and pressing the prepared mixture with a hydraulic or hand press to form a transparent pellet. A major advantage of this method is that KBr has no absorption bands in the IR above 250  $\text{cm}^{-1}$  region, an unimpeded spectrum of the compound is obtained. Therefore, preparation as halide disks loses less information. However, there are some problems of this method. For coordination compound that is  $\text{Br}^-$  from the KBr can often replace ligands in the compound whose spectrum is desired, misinterpretation of the spectrum will result. In some cases structural changes that caused by high pressure applied to the sample/KBr mixture. In addition, KBr is a very hygroscopic material, it will

adsorb water directly from the atmosphere. It is common to observe absorbances of moisture when using KBr disks.

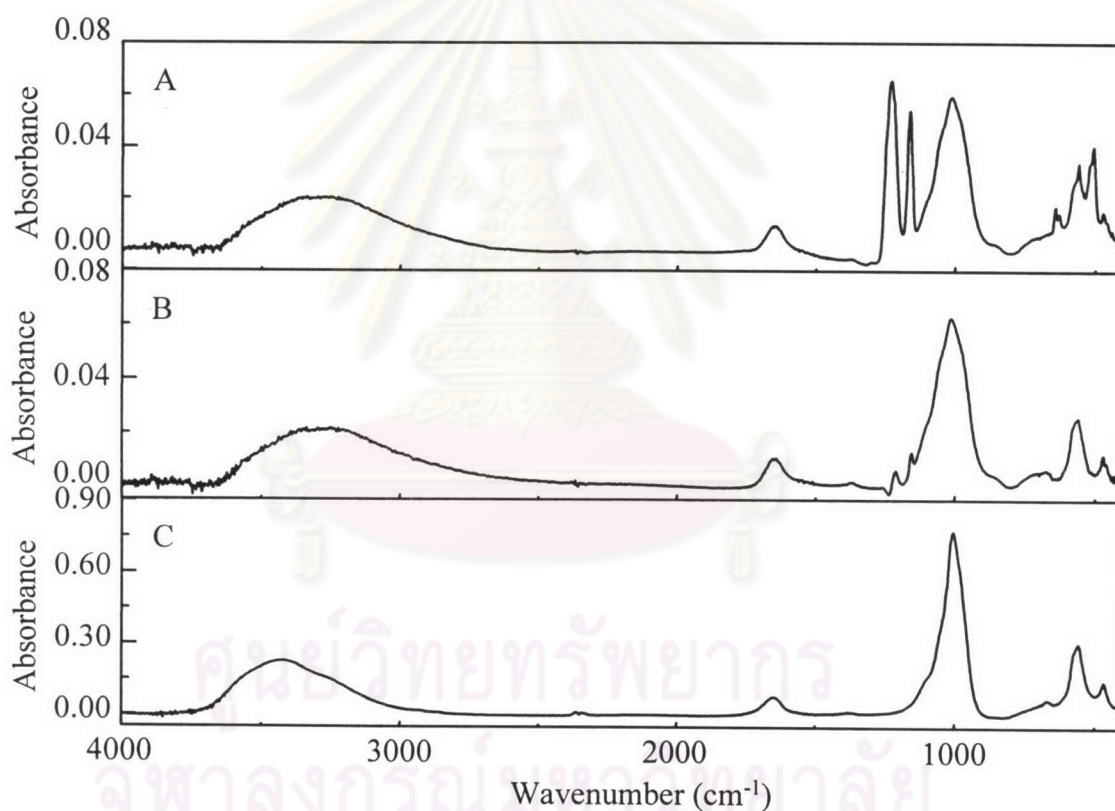
Alternatively, in an attempt to reduce these problems, the solid samples studied here were ground as finely as possible without mixing with KBr. The samples were ground in an agate mortar and then placed onto the home-made IR cards. Clay, zeolite Y and chromium benzoate were chosen as the solid samples for analyzing with this method. Figures 4.6-4.8 show IR spectra of clay, zeolite Y and chromium benzoate, respectively.



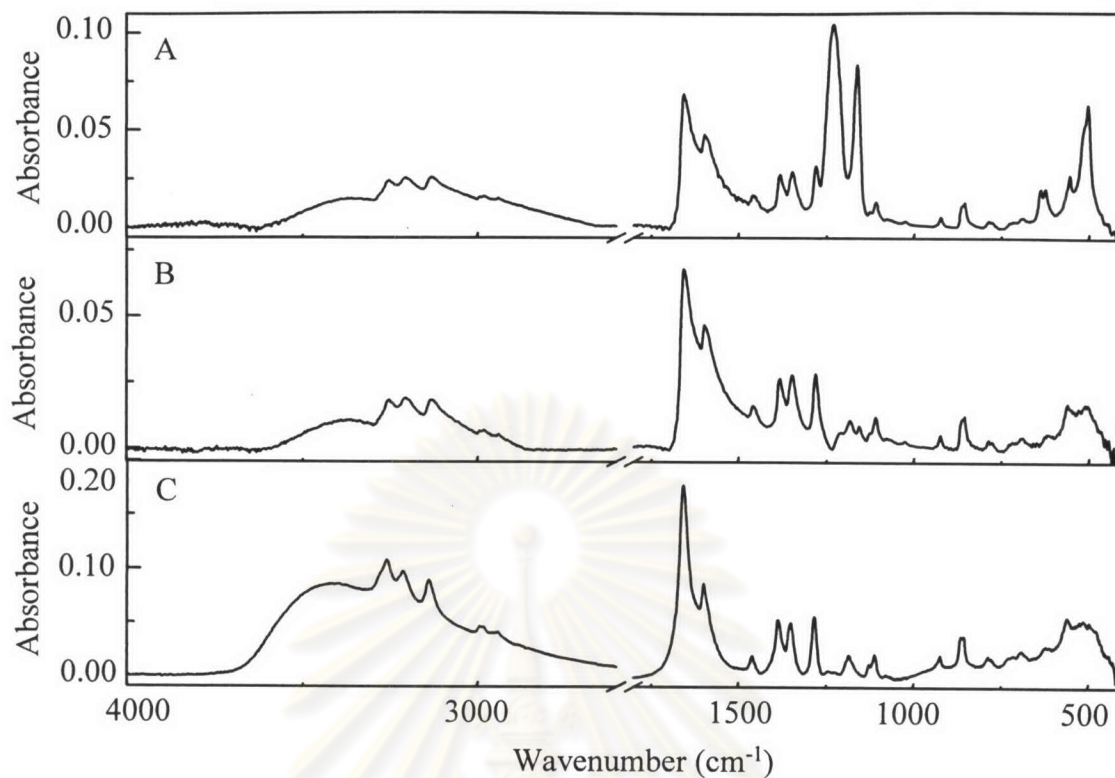
**Figure 4.6** Comparison of IR spectra of clay obtained on PTFE film (A), pure clay after spectral subtraction of PTFE (B) and on KBr pellet (C).



Regarding to Figures 4.6-4.8, the obtained spectra of clay, zeolite-Y and chromium benzoate (after absorption peaks of PTFE were subtracted) from the home-made IR cards are similar to those obtained from KBr pellets. The obtained spectra from the home-made IR cards do not have a broad band at  $\sim 3500\text{ cm}^{-1}$  as the KBr pellet spectra. The broad band at  $\sim 3500\text{ cm}^{-1}$  in the KBr pellet spectrum was most likely an artifact due to adsorbed water, making interpretation is difficult to identify that it is of the sample or KBr disk. In the case of the home-made IR card, it is well known that the PTFE is a non-hygroscopic substrate. Therefore, the presence of water peak in the spectrum of sample from using a home-made IR card can be identified to that of the sample.



**Figure 4.7** Comparison of IR spectra of zeolite Y obtained on PTFE film (A), pure zeolite Y after spectral subtraction of PTFE (B) and on KBr pellet (C).



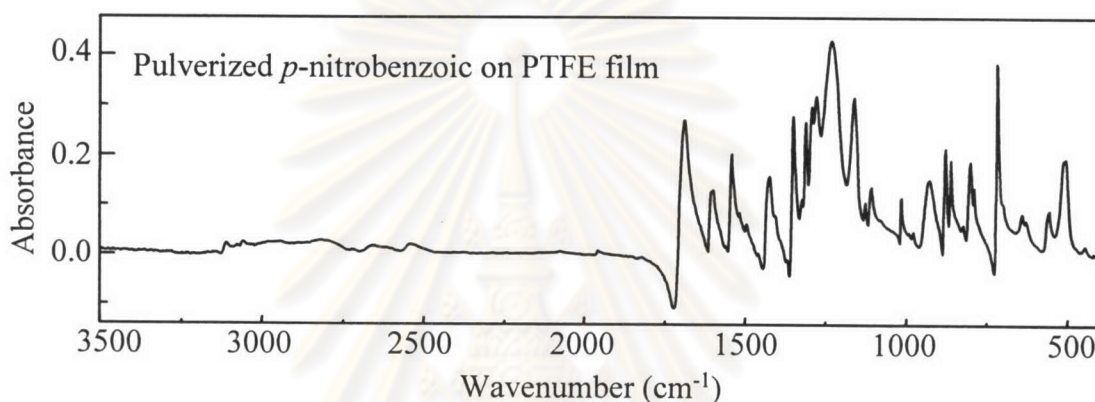
**Figure 4.8** Comparison of IR spectra of chromium benzoate obtained on PTFE film (A), pure chromium benzoate after spectral subtraction of PTFE (B) and on KBr pellet (C).

As seen evidently in Figure 4.7C, the broad band of water at  $\sim 3500$  and  $1650\text{ cm}^{-1}$  in the spectrum can be identified as water in the porous of zeolite Y. The spectrum of clay (Figure 4.6C) obtained by KBr pellet has the broad bands of water. On the other hand, the spectrum of clay on the home-made IR card do not have broad bands of water. It is clearly illustrated that the clay does not have a trace of moisture in the molecules. The broad band at  $3500\text{ cm}^{-1}$  in the spectrum of chromium benzoate (Figure 4.8) was observed too, it would also be identified as the moisture of chromium benzoate.

This observation illustrates that the home-made IR card can eliminate the adsorbed water problem. This home-made IR card technique is certainly adequate for qualitative solid analysis. In addition, sample preparation is easier and faster than the KBr pellet.

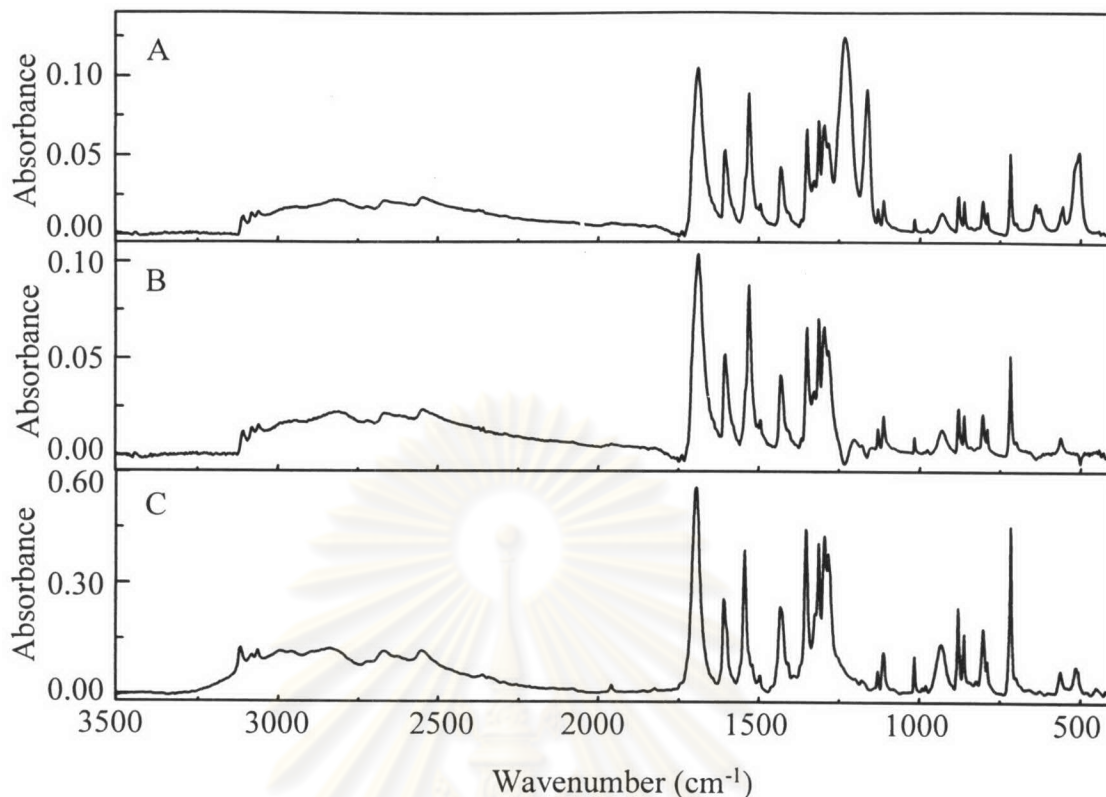
#### 4.2.1.1.2 Dissolving in organic solvent

In some cases grinding solid sample for the home-made IR card technique achieved a poor spectrum, as shown in Figure 4.9. The first derivative peaks in the spectrum of *p*-nitrobenzoic acid were observed. This result may be caused by not grinding finely enough or nature (highly crystalline) of *p*-nitrobenzoic acid particles. Theoretically,<sup>2</sup> the particle size with diameter bigger than 2 microns in diameter will scatter the IR beam and cause a sloping baseline.



**Figure 4.9** IR spectrum of pulverized *p*-nitrobenzoic acid on PTFE film.

An alternative preparation method for *p*-nitrobenzoic acid involved dissolving in organic solvent. The disposable IR card can be used to take an IR spectrum of a soluble solid. A disposable IR card works the same way as the material window (*i.e.*, KBr window) for liquid sample. The major problem of dissolved solid is choosing a solvent to dissolve the sample. Since no solvent is perfect for all solid samples. However, if some information about the sample is known, then a solvent can be chosen accordingly. In general, the common solvents for dissolving the solid samples are the rapid volatile organic solvents, such as carbon tetrachloride, carbon disulfide, cyclohexane, acetone, methanol, ethanol and chloroform.



**Figure 4.10** Comparison of IR spectra of *p*-nitrobenzoic acid obtained on PTFE film (A), pure *p*-nitrobenzoic acid after spectral subtraction of PTFE (B) and on KBr pellet (C). A drop of solution of *p*-nitrobenzoic acid in methanol was applied on the PTFE film and the solvent was allowed to completely evaporate before the spectrum was collected.

In this section, *p*-nitrobenzoic acid was dissolved in methanol. A drop of *p*-nitrobenzoic acid solution was dropped onto the home-made IR card, methanol was allowed to completely evaporate and then analyzed. Subsequently, the feature of spectrum of *p*-nitrobenzoic acid was observed. A comparison of the IR spectra of *p*-nitrobenzoic acid from the home-made IR card and KBr pellet is shown in Figure 4.10. The features of absorption peaks of both spectra are mostly similar, except in the 1200-1000  $\text{cm}^{-1}$  and 650-500  $\text{cm}^{-1}$  regions were PTFE absorbed. Other than the absorption bands from PTFE at 1228, 1158, 640 and 508  $\text{cm}^{-1}$  that were subtracted, are of comparable quality. No first derivative peak appears in the spectrum of *p*-nitrobenzoic acid solution. It indicates that the preparation of solid compounds with appropriate solvent can reduce the undesirable scattering. Nevertheless, in order to avoid overloading or crystallization on the PTFE film, the sample concentration

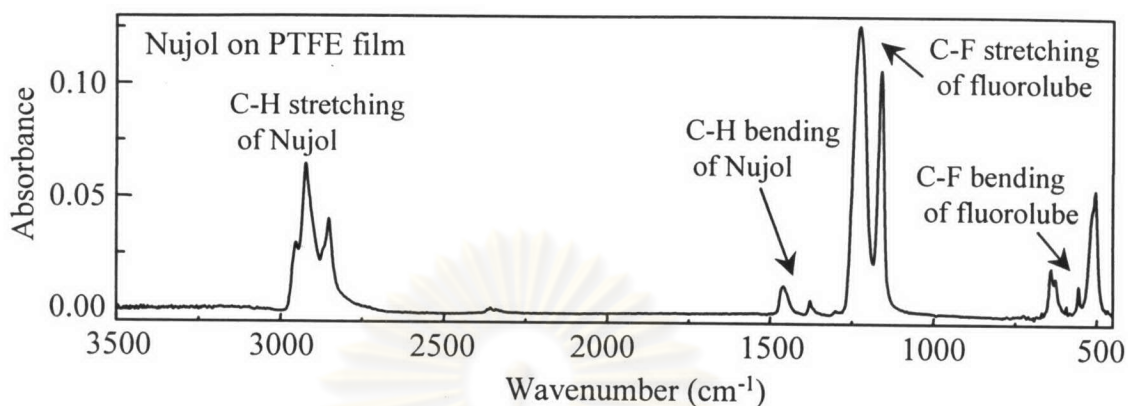
should be far below saturation, because the solute will not precipitate until very late in the drying process. This allows the sample to penetrate into the polymer fiber, rather than to be deposited on the surface of the PTFE film.

#### **4.2.1.2 Effect of the high molecular weight paraffinic hydrocarbon liquids**

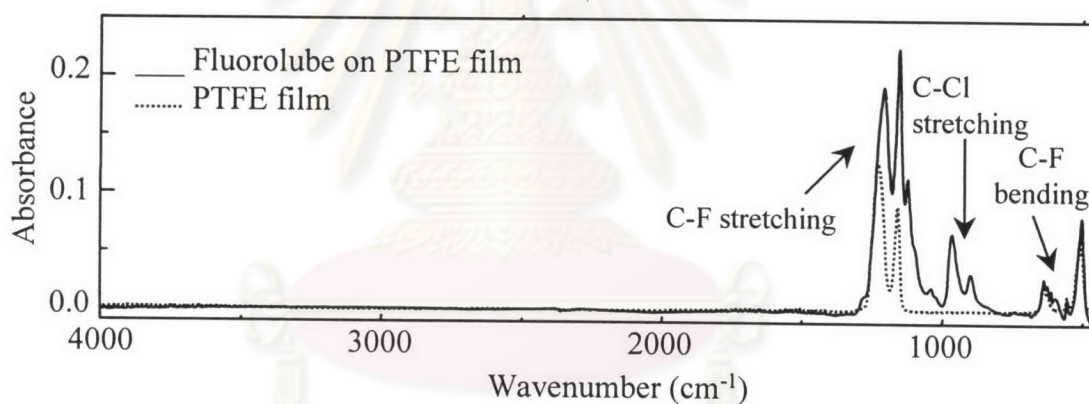
Generally, solid samples consist of multiple components. The preparation of these solids by dissolving in organic solvent is often difficult due to the chosen solvent may react with some components in the solid. The obtained spectrum may be that of product of this reaction rather than of original sample. When the KBr pellet is used, the broad band of water due to KBr disk is usually observed. In addition to using the home-made IR card with some finely powdered solids provided a poor spectrum. Since some solids are highly crystalline and cannot be dispersed properly, causing bands to appear as a first derivative spectrum, as presented in above results. As a consequence, we established the new experimental system for analyzing solid samples based on the mull technique. A new system was relatively about the coating high molecular weight liquid onto the surface of PTFE film of the home-made IR card. A high molecular weight paraffinic hydrocarbon liquid was employed because it has a low volatility, a higher refractive index than the lighter paraffins, and a usefully high viscosity, thereby aiding the coating process. Nujol and Fluorolube were employed for coating process. The home-made IR cards were coated slightly with Nujol and Fluorolube. Subsequently, the finely powdered solid samples were smeared onto the coated PTFE films. It is expected that the intensity of scattered light could be reduced when using a coated PTFE film substrate determined a fine powder.

Figures 4.11 and 4.12 show IR spectra of Nujol and Fluorolube on the home-made IR cards, respectively. As seen in Figure 4.11, except in the 1200-1000 and 600-400  $\text{cm}^{-1}$  regions where PTFE absorbs, the spectrum of Nujol exhibits C-H stretching frequencies in the region of 3000 to 2800  $\text{cm}^{-1}$  and deformations at 1460 and 1375  $\text{cm}^{-1}$ . These bands will overlap any corresponding carbon-hydrogen frequencies in the sample. As can be observed in Figure 4.12, Fluorolube has no bands at high wavenumber, but many bands below 1300  $\text{cm}^{-1}$  due to C-F and C-Cl stretching and bending vibrations were observed. The PTFE also has absorption bands

in this region. Therefore the coated PTFE film with Fluorolube was selected as a substrate for solid analysis.



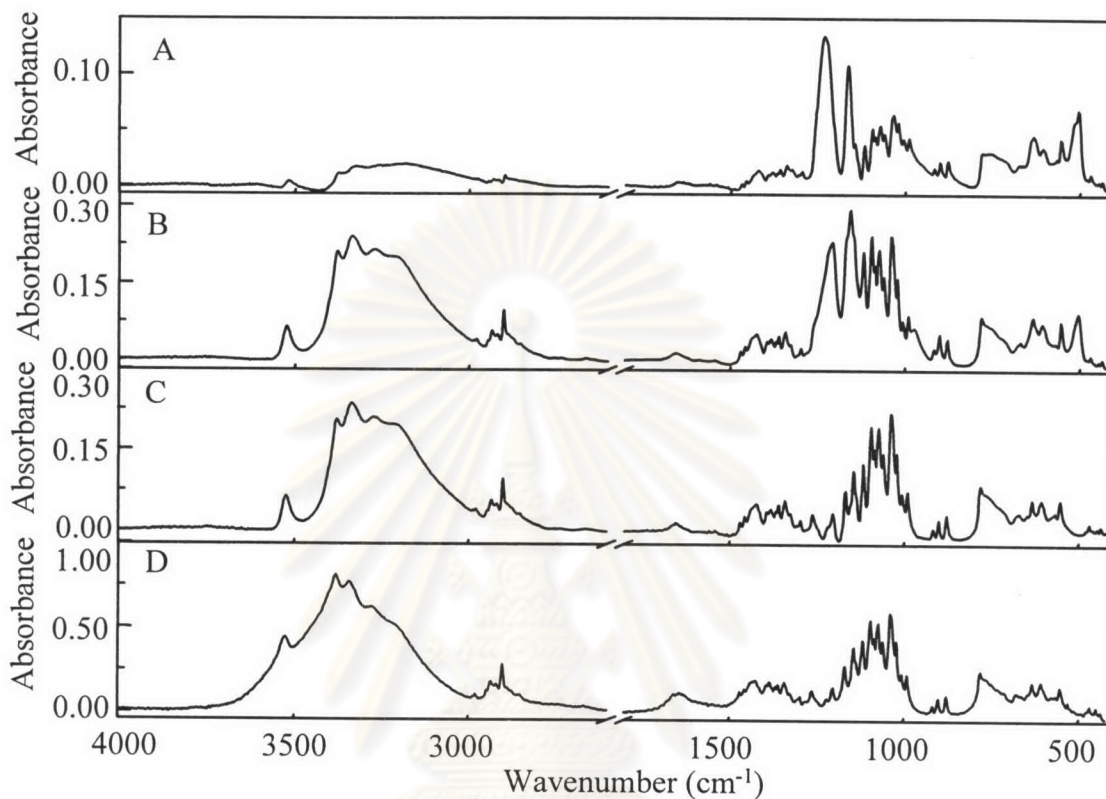
**Figure 4.11** IR spectrum of Nujol on a PTFE film.



**Figure 4.12** IR spectrum of Fluorolube on a PTFE film.

In order to investigate the efficiency of Fluorolube coated on the surface of PTFE film, paracetamol and chlorphenylamine hydrochloride tablets were employed as solid samples. A drop of Fluorolube was dropped on the first glass slide, a second glass slide was squeezed against the first to make as possible thin film of Fluorolube, and then separated the glass slides together. The home-made IR card was attached to this glass slide and then slightly pulled off. The obtained home-made IR card was ready to use. Subsequently, small amounts of finely powdered paracetamol and chlorphenylamine hydrochloride were smeared on the coated PTFE films. The feature of spectrum of paracetamol and chlorphenylamine hydrochloride were

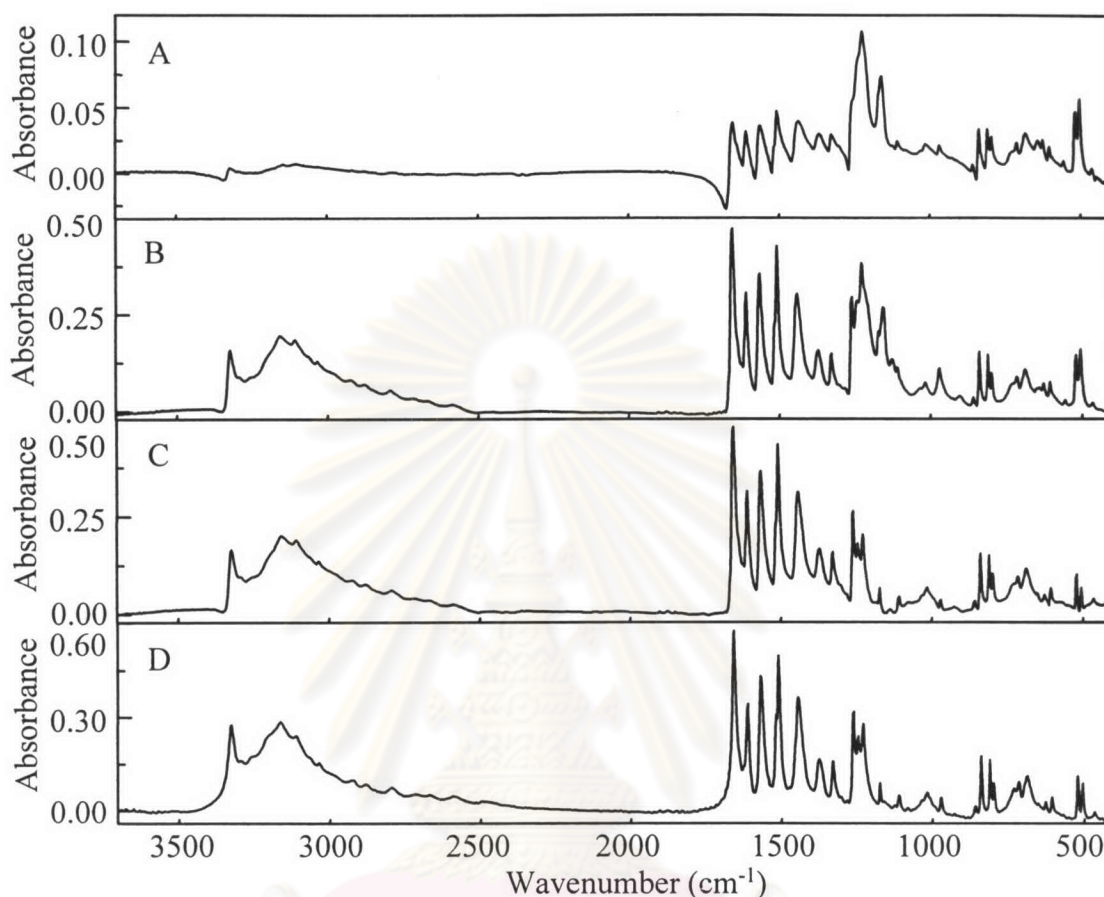
observed and compared with three preparation methods: (i) KBr pellet, (ii) smearing finely powdered sample onto PTFE film with coating and (iii) smearing finely powdered sample onto PTFE film without coating.



**Figure 4.13** Comparison of IR spectra of chlorphenylamine hydrochloride obtained on PTFE film (A), on coated PTFE film with Fluorolube (B), pure chlorphenylamine hydrochloride after spectral subtraction of Fluorolube and PTFE (C) and on KBr pellet (D).

Figure 4.13 shows the obtained spectra of chlorphenylamine hydrochloride on the home-made IR card and by KBr pellet. The absorption intensity of spectrum of chlorphenylamine hydrochloride on the PTFE film with coating was more evident than that of PTFE film without coating. When the absorption bands of PTFE film and Fluorolube were subtracted, the obtained spectrum of a pure chlorphenylamine hydrochloride is similar to those obtained by KBr pellet. As seen in Figure 4.14, on a PTFE film without coating, the presence of the first derivative peaks of paracetamol spectrum was significantly observed. On the other hand, in the case of PTFE film with coating, no first derivative peak appeared in the spectrum and

absorption intensity to be evident. The spectrum of paracetamol after subtracting of absorption bands of PTFE and Fluorolube is identical to those obtained by KBr pellet.



**Figure 4.14** Comparison of IR spectra of paracetamol obtained on PTFE film (A), on coated PTFE film with Fluorolube (B), pure paracetamol after spectral subtraction of Fluorolube and PTFE (C) and on KBr pellet (D).

In case of the use of a PTFE film without coating, quality of the spectra were rather poor due to scattering and reflection loss. The scattering and reflection might be caused by a poorly dispersed paracetamol on the surface of PTFE film. When the beam of IR radiation pass through the home-made IR card with paracetamol, most of the radiation will pass into powdered paracetamol and PTFE film, some will be absorbed, and the remainder transmitted. In addition, a fraction of IR radiation will be reflected from the surface of powdered paracetamol and PTFE film and be lost. The size of this fraction depends on the difference in refractive index between paracetamol/air and PTFE film/air (which, in the case of air, is a very close



approximation to 1.0, PTFE is 1.35 and 1.5 is to be figure fairly representative of many organic compounds).<sup>21,22</sup> On a contrary, there is no scattering occur when a PTFE film with coating was used to analyze paracetamol. Since Fluorolube coated on a surface of PTFE film work as a matrix material similar to KBr in KBr pellet. A refractive index of Fluorolube is very close to paracetamol. It is assumed that refractive index of paracetamol and Fluorolube is a single value. Therefore, when paracetamol was surrounded with a Fluorolube, it would approach continuity and as a result the scattering would be much less than that from a dry powder. This observation presents an efficiency of the coating PTFE film with Fluorolube for solid analysis, especially for highly crystalline particles. The advantages of coating PTFE film over KBr pellet is that coated PTFE film is easier and faster to make since there is no time consuming pellet squeezing involved, Fluorolube also protected the sample from water vapor in the atmosphere since it is hydrophobic.

From the above observations, the preparations of the solid samples in order to determine by using the home-made IR cards are important to achieve the good quality transmission spectra. The grinding in order to obtain the finely powdered particles is easier and faster than dissolving in organic solvents. If the solid sample is a pure and soluble compound, it should be dissolved in an appropriate organic solvent. However, when these approaches are not applicable because of sample insolubility or too crystallinity and it is necessary to examine samples in powder form, by smearing them onto the coated PTFE films is an alternative way to take quality spectra.

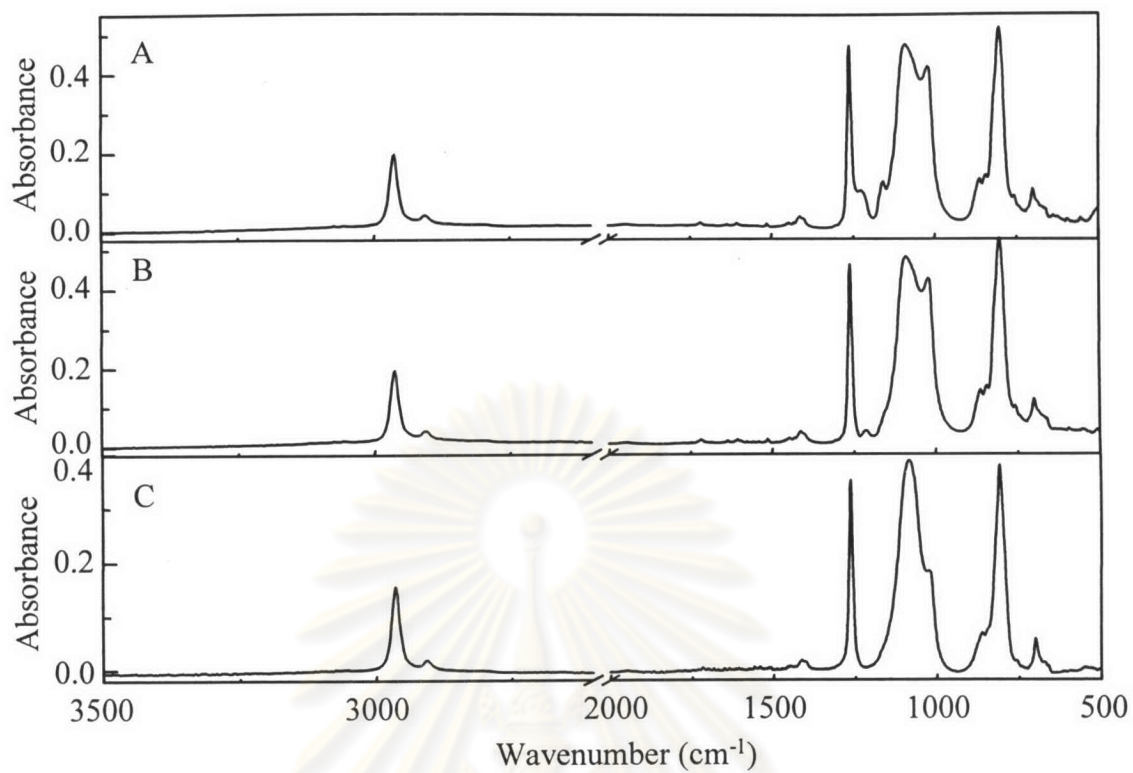
#### 4.2.2 Viscous liquids

The accessories often used to obtain spectra of viscous liquid and solutions are demountable cells and seal cells. These cells consist of a pair of infrared transmitting windows with a spacer placed between them to establish sample thickness. A lot of window materials are available for sample analysis, such as potassium bromide (KBr), potassium chloride (KCl), sodium chloride (NaCl), calcium fluoride (CaF<sub>2</sub>), barium fluoride (BaF<sub>2</sub>), zinc sulfide (ZnS) and zinc selenide (ZnSe). Samples were dropped or smeared onto the windows and then fast and easily analyzed. There are some restrictions in using this technique for sample analysis. When a window is employed, it became fogged or it would chemically react with the

sample. If the sample reacts with the window material, the damage is permanent. If the sample is very viscous, the window is difficult to clean. Therefore, care must be taken when handling the window. In addition, water soluble window materials (*i.e.*, KBr, KCl and NaCl) should not be used with sample contained traces of moisture. The moisture will cause the windows to fog and will result in spectra with sloping baselines. Alternatively, wet samples can be analyzed by using water insoluble windows (*i.e.*, ZnS, ZnSe, BaF<sub>2</sub> and CaF<sub>2</sub>). Unfortunately, they tend to be more expensive and usually have shorted transmission ranges. Thus, important major factors in selecting a window material are cost, reactivity with the sample and transmission range.

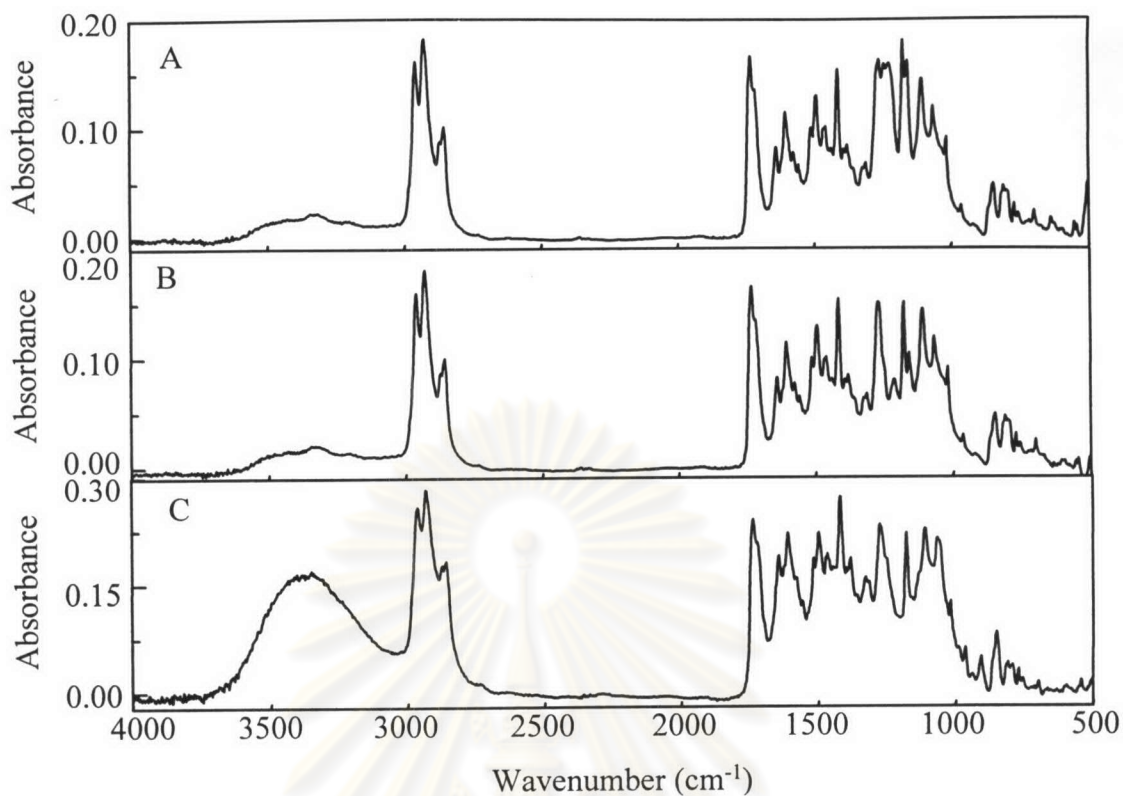
Disposable IR card is developed in order to minimize the restrictions of using windows for sample analysis. In this section, the home-made IR card from thin PTFE film was used as a window for viscous liquid sample analysis. Hair treatment (Oriental Princess), gel (Eucerin) and cream (La Roche) were used as representative viscous liquid samples. A small amount of three samples were directly smeared onto the home-made IR cards. These IR sample cards were then placed into the sample compartment of FT-IR spectrometer and collected spectra. IR spectra of hair treatment, gel and cream on home-made IR cards and ZnSe windows are shown in Figures 4.15, 4.16, 4.17, respectively.

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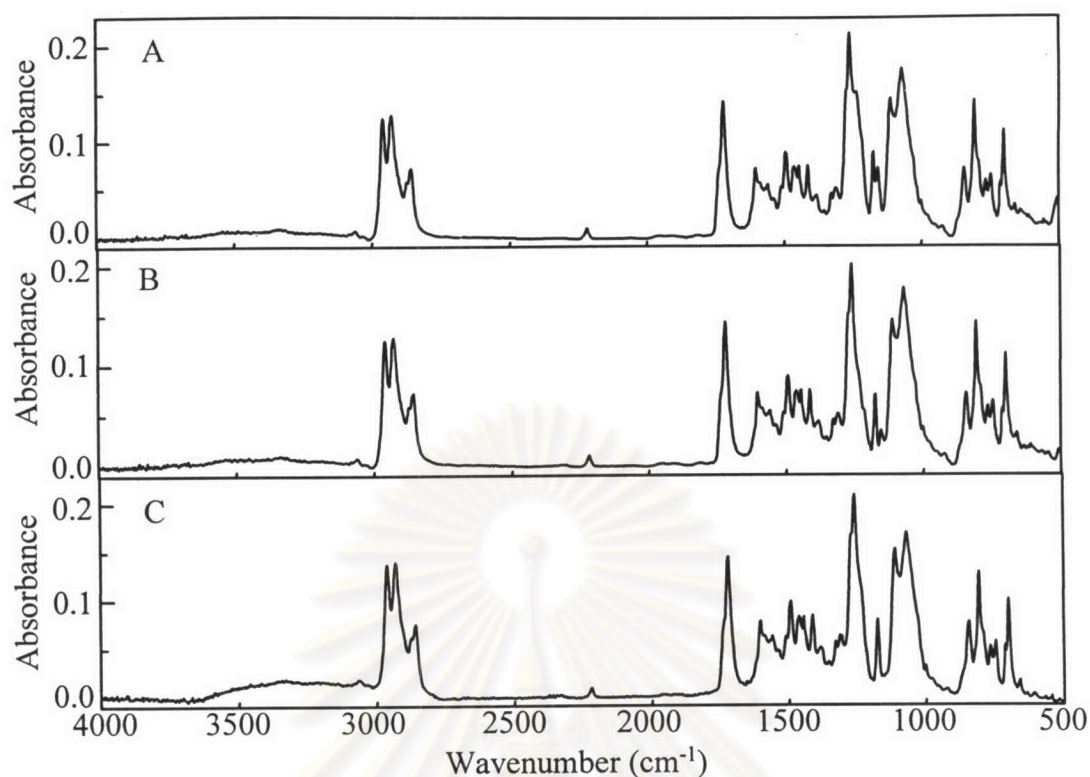
**Figure 4.15** IR spectra of hair treatment (Oriental Princess) acquired by using PTFE film (A), ZnSe window (C) and subtracting spectrum of PTFE film from a two-phase system of hair treatment/PTFE film (B).

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**Figure 4.16** IR spectra of gel (Eucerin) acquired by using PTFE film (A), ZnSe window (C) and subtracting spectrum of PTFE film from a two-phase system of gel/PTFE film (B).

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**Figure 4.17** IR spectra of cream (La Roche) acquired by using PTFE film (A), ZnSe window (C) and subtracting spectrum of PTFE film from a two-phase system of cream/PTFE film (B).

The comparison of the IR spectra of three sample types was obtained with the home-made IR cards and the spectra from ZnSe windows, the home-made IR cards can produce spectra almost identical to those produced by ZnSe windows. Use of subtracting process of PTFE bands from the spectrum of sample with PTFE will reduce the intensity of the absorption inherent to PTFE card. Although, spectral subtraction process of PTFE spectrum does not achieve completely, the unsubtracted PTFE bands still remained and have a little effect on absorption bands of sample, but it was ignored when interpreting the sample spectrum.

As the above results illustrate, the capability of rapid adjustment of the sample preparation on the home-made IR card obtains the quality of the spectrum. More samples can quickly be added or smeared to the cards. The cards can easily be used and no additional accessories are required. The home-made IR card does not need cleaning after using because it is a disposable card. In addition, most of viscous liquid samples were analyzed by the home-made IR card, the moisture in samples

does not affect to PTFE film. The home-made IR card is appropriate to routine procedure.

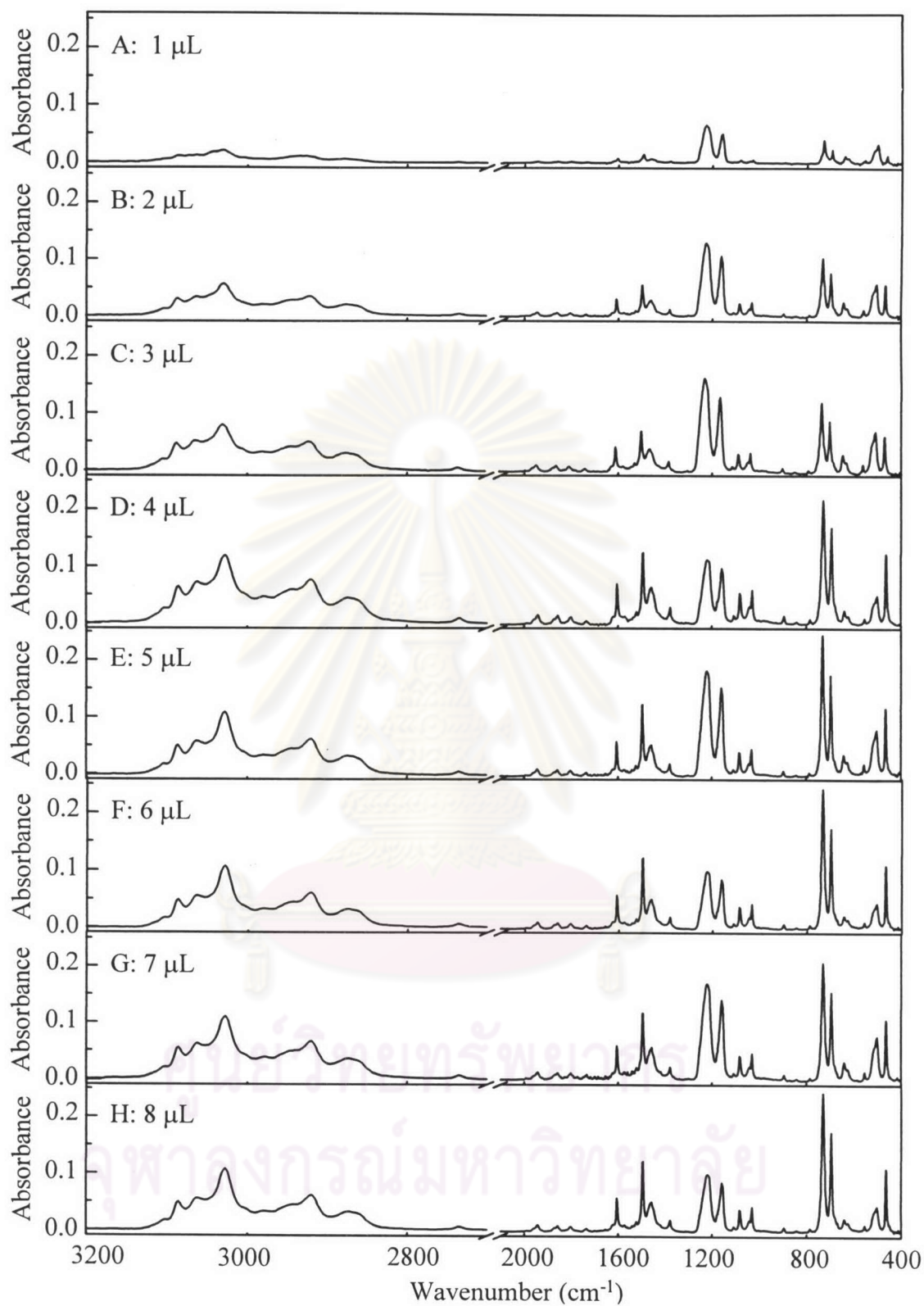
### 4.2.3 Volatile liquids

#### 4.2.3.1 Effect of sample volume

Two thin PTFE films were employed as a window material for holding volatile liquid samples, with the aid of capillary force which helps firmly holding both windows together. In this work, the home-made IR card shows possibility of being a powerful analytical method for volatile liquid samples.

In order to investigate the suitable volume of volatile liquid that analyzed by the IR card window, toluene was used as volume-test analyte. The toluene was dropped onto the first IR card before being covered with another IR card. Then IR spectrum was collected with 16 scans. Figure 4.18 shows IR spectra of toluene with increasing volumes of 1, 2, 3, 4, 5, 6, 7 and 8  $\mu\text{L}$ , respectively. A characteristic absorption band was observed in all spectra with different volumes. It is clearly seen that with increasing amount of toluene volume, the band intensity becomes higher. The absorbance starts to be saturated when the volume reaches 5  $\mu\text{L}$ . The bands observed with sample volume in the range of 1-3  $\mu\text{L}$  cannot be identified due to their low signal. The absorption intensity of > 5  $\mu\text{L}$  volume toluene shows no intensity increase, but feature characteristic is clearly observed. Therefore volume of toluene sample was chosen to be 5  $\mu\text{L}$  for further investigation described later on.

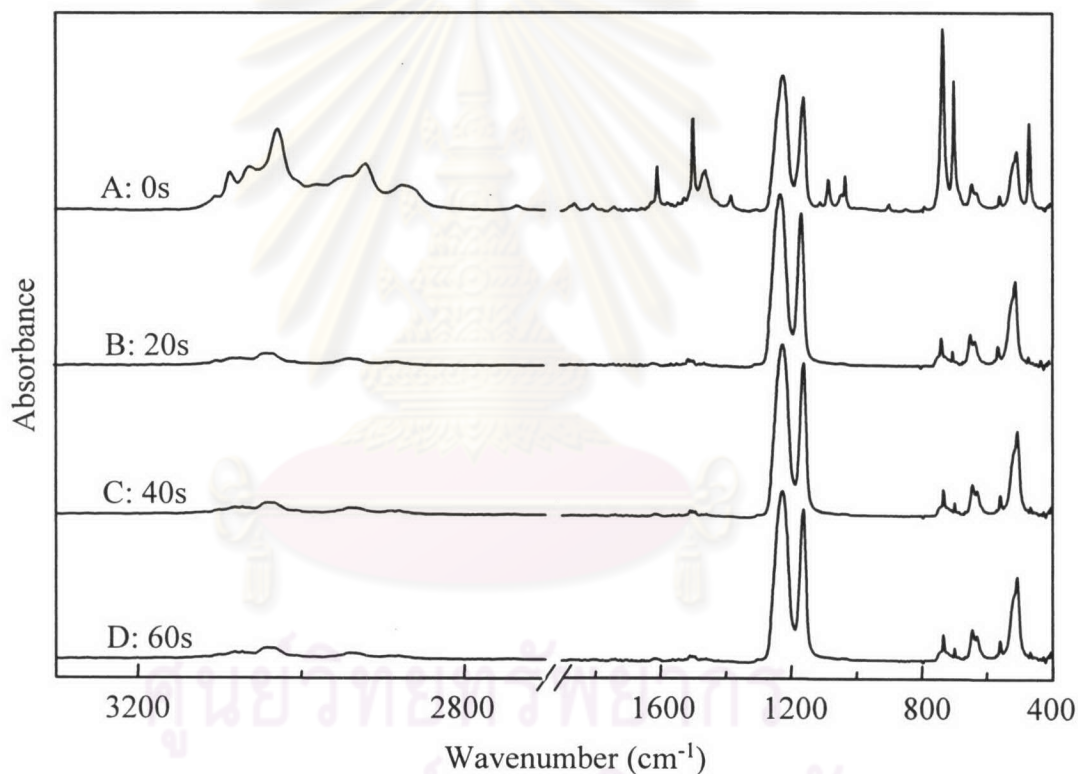
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**Figure 4.18** IR spectra of toluene with increasing volume of 1 (A), 2 (B), 3 (C), 4 (D), 5 (E), 6 (F), 7 (G), and 8  $\mu\text{L}$  (H), respectively.

#### 4.2.3.2 Time-dependent phenomena

The above observation indicates the presence of the capillary-thin-film phenomena of home-made IR card cell with liquid sample. Subsequently, the time-dependent effect on the capillary-thin-film was investigated by means of changes in spectral feature, in order to determine the efficiency of the home-made IR card. A 5 $\mu$ L toluene was used for data collection automated by Macro-Nicolet program. Each spectrum in the series was taken as a function of time with 16 scans (*i.e.*,  $\sim$ 19s) until completing 1 minute. The observed IR spectra of toluene were demonstrated in Figure 4.19.



**Figure 4.19** IR spectra of toluene with increasing time: initial time (A), 20s (B), 40s (C), and 60s (D).

The characteristic absorption bands of toluene rapidly decrease with increasing time. After 20 seconds, the acquired spectra present no evidence of the toluene left in the cell. However, the spectral feature of the initial data collection clearly displayed strong characteristic bands of the toluene sample. This spectral series indicate that the capillary-thin-film can exist in between the card cell within a



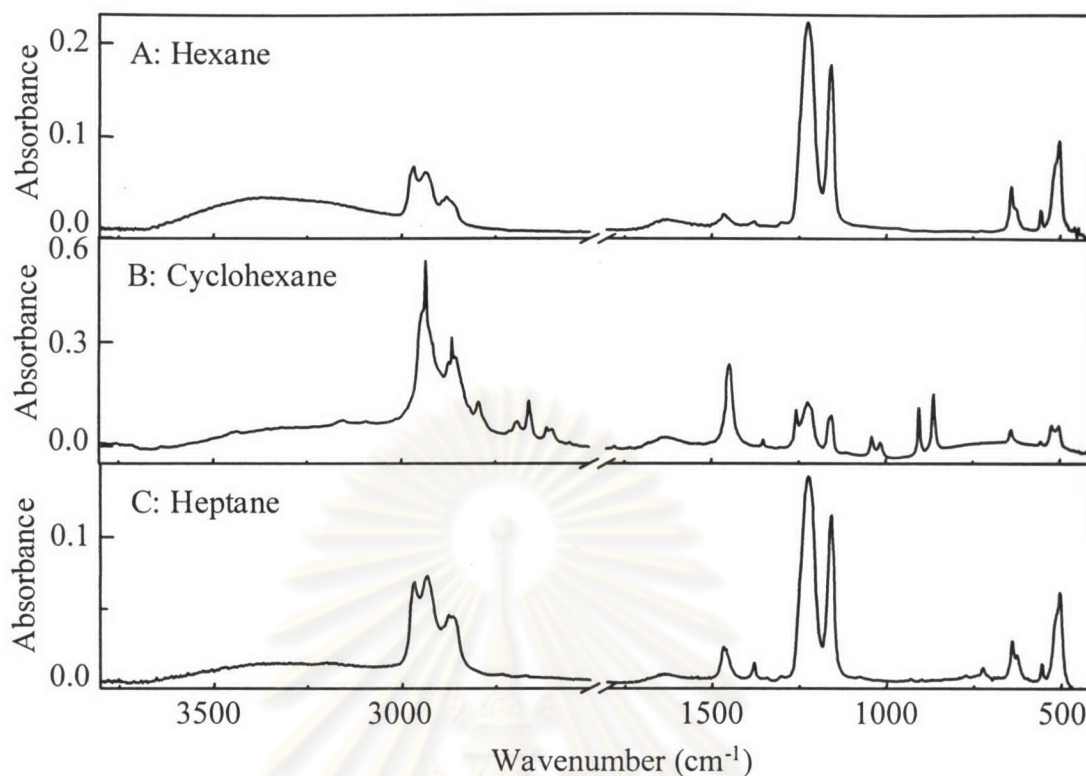
short period of time (*i.e.*, ~20s). When the home-made IR card was used as a liquid cell, the exact thickness of a capillary-film-film cannot be controlled. This is probably due to changes in morphology of the thin PTFE film as a result of heating and stretching process. As a consequence, the uniform thickness and a smooth surface of a thin film can hardly be prepared. In addition, toluene may partially evaporate during process of spectral collection. Sample evaporation of the capillary thin film can particularly cause problems for quantitative analysis. However, the home-made IR card exhibits an excellent potential for qualitative analysis of volatile liquids.

#### 4.2.3.3 Effect of polarity of volatile liquids

Since the home-made IR card has an ability for spectroscopically identifying volatile liquid compounds within a short time, it was additionally applied for different types of liquid samples in order to determine its relative efficiency. Four types of volatile liquids were used (i) non polarity (*i.e.*, hexane, cyclohexane and heptane), (ii) low polarity (*i.e.*, benzene, toluene, and *p*-xylene), (iii) moderate polarity (*i.e.*, ethanol, isopropanol and acetone) and (iv) high polarity (*i.e.*, methanol and diethylene glycol). The data for each of the volatile liquids were achieved individually with the same scanning time (16 scans), by dropping 5  $\mu$ L of the volatile liquid onto the thin PTFE film. The analyte enrichment depends on how good the analyte can attach and spread onto the surface of the thin film PTFE, with regard to their chemical properties. Figures 4.20-4.23 show IR spectra of these volatile liquid compounds.

##### 4.2.3.3.1 Non-polar volatile liquids

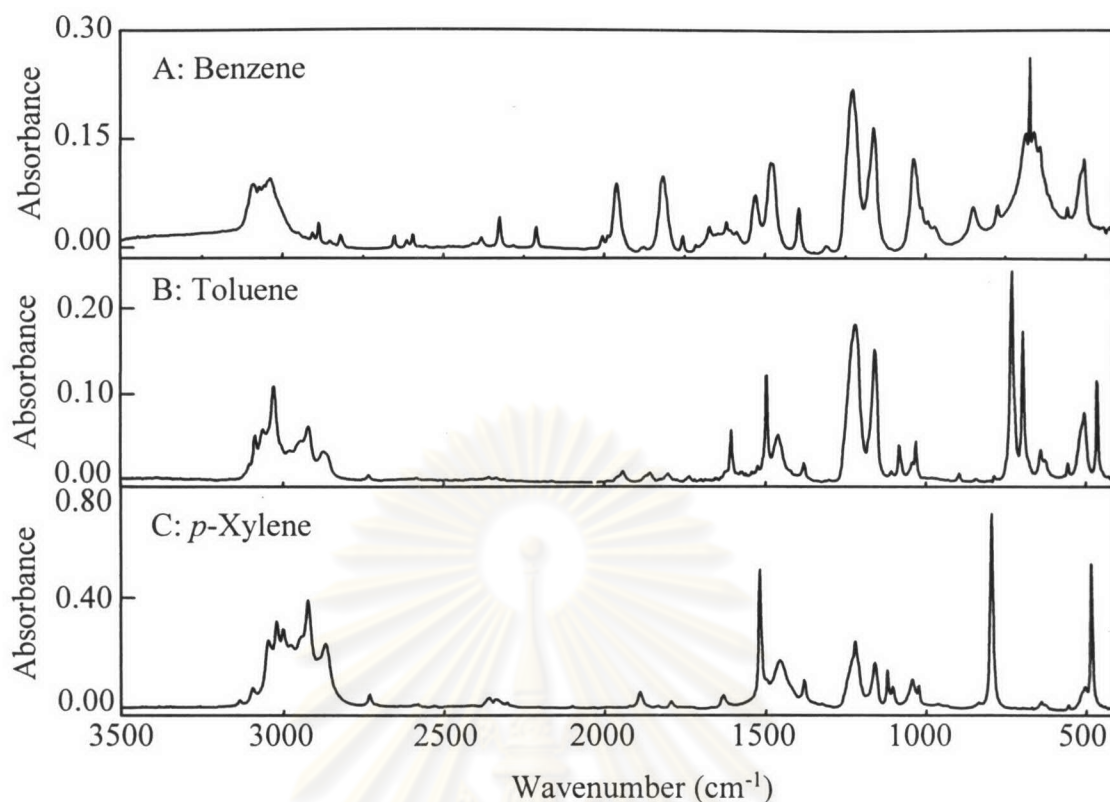
Non-polar volatile liquids can be detected by using the home-made IR card. Figure 4.20 shows IR spectra of hexane (A), cyclohexane (B) and heptane (C). These spectra have broad bands of vapor water. This is due to partial evaporation of these volatile liquids while the data collection was under the process. However, the absorption bands of vapor water does not affect those characteristic bands of the liquid samples investigated.



**Figure 4.20** IR spectra of non-polar volatile liquids: hexane (A), cyclohexane (B) and heptane (C).

#### 4.2.3.3.2 Low-polar volatile liquids

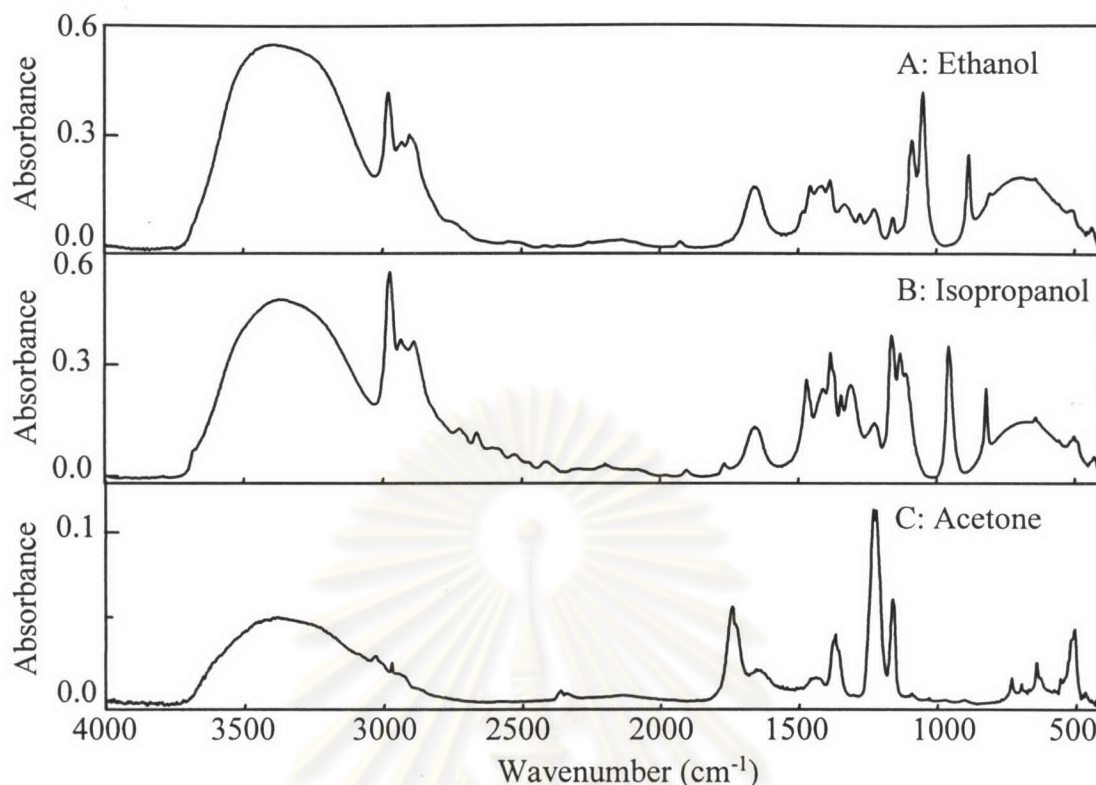
Figure 4.21 shows the IR spectra of low-polar volatile liquids (*i.e.*, benzene, toluene and *p*-xylene, respectively). In particular the acquired spectra show overall absorption peaks with sufficient intensity for identifying all kinds of liquids.



**Figure 4.21** IR spectra of low-polar volatile liquids: benzene (A), toluene (B), and *p*-xylene (C).

#### 4.2.3.3.3 Moderate-polar volatile liquids

Some moderate-polar volatile liquids were further investigated as shown in Figure 4.22. Every spectrum clearly exhibits a characteristic of O-H stretching, a strong broad band centered near  $3400\text{ cm}^{-1}$  and a sharp peak at  $1600\text{ cm}^{-1}$ . In case of ethanol and isopropanol, the broad band near  $3400\text{ cm}^{-1}$  caused by water molecule appear coincidentally to the O-H stretching of the alcohol group. The result of water peaks in acetone spectrum may occur by the presence of air gap in the IR card cell. Because acetone has a low boiling point ( $56^\circ\text{C}$ ),<sup>23</sup> its evaporation will be affected. Then it was left to expose to the environment. In any case, the strong peaks of vapor water did not cause the problem to peak assignment.

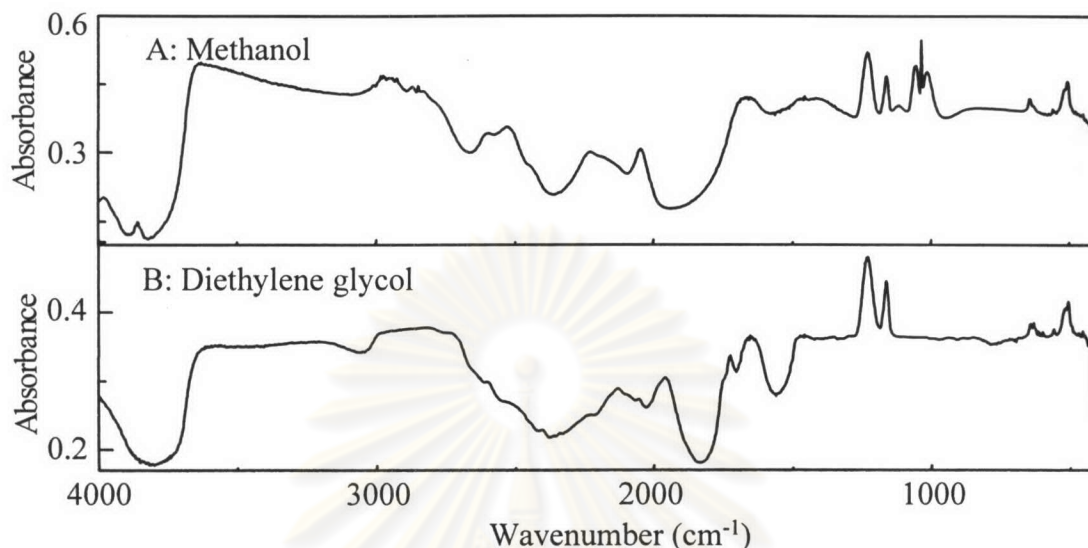


**Figure 4.22** IR spectra of moderate-polar volatile liquids, ethanol (A), isopropanol (B) and acetone (C).

#### 4.2.3.3.4 High-polar volatile liquids

According to Figure 4.23, the broad bands between 3600 and 3200  $\text{cm}^{-1}$  and the strong bands near 1600  $\text{cm}^{-1}$  provide the presence of the molecular water. These bands obscure the significant features, which would give a guide of identifying the present species. Therefore, the characteristic peaks of methanol and diethylene glycol, shown in spectra A and B respectively, become indistinguishable. As a result, it suggests that the large air gap appeared at the interface of volatile liquid (methanol and diethylene glycol) and thin PTFE film. The appearance of an air gap can explain the repelling behavior of sample molecule away from fluorine atoms of PTFE. Based on repelling behavior, fluorine atoms of PTFE prefer the same kind of molecules while repel the others kind of molecules. Since methanol and diethylene glycol have high polarity (0.762 and 0.713, respectively),<sup>23</sup> they cannot spread throughout over the surface of a thin PTFE film. On the other hand, a drop of the

volatile liquid was formed on the thin PTFE film, leading a difficulty to apply the home-made IR card for analyzing the high-polar volatile liquids.



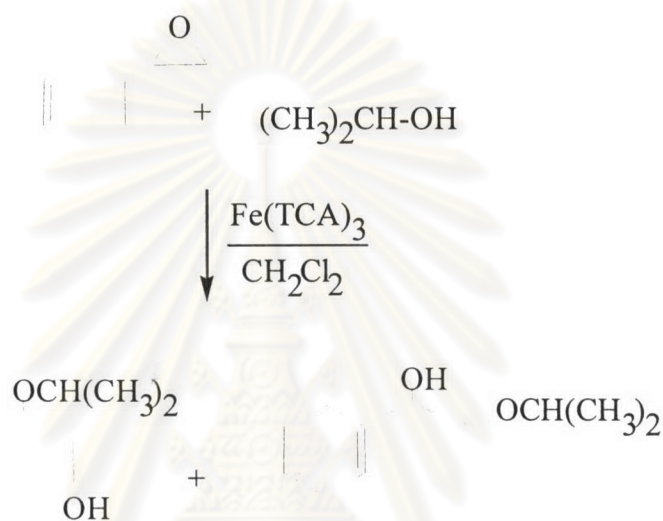
**Figure 4.23** IR spectra of high-polar volatile liquids: methanol (A) and diethylene glycol (B).

In conclusion, the efficiency of the home-made IR-card cell depends on morphology of the thin PTFE film and types of volatile liquids used as the sample of interest. According to this observation, the home-made IR card shows an excellent potential to analyze low-polar volatile liquids, and a substantial efficiency with non-polar and moderate-polar liquids. In contrast, the PTFE IR card cannot acquire the sufficiency useful information for high-polar volatile liquid samples.

#### 4.2.3.4 Application of the home-made IR card with liquid mixture

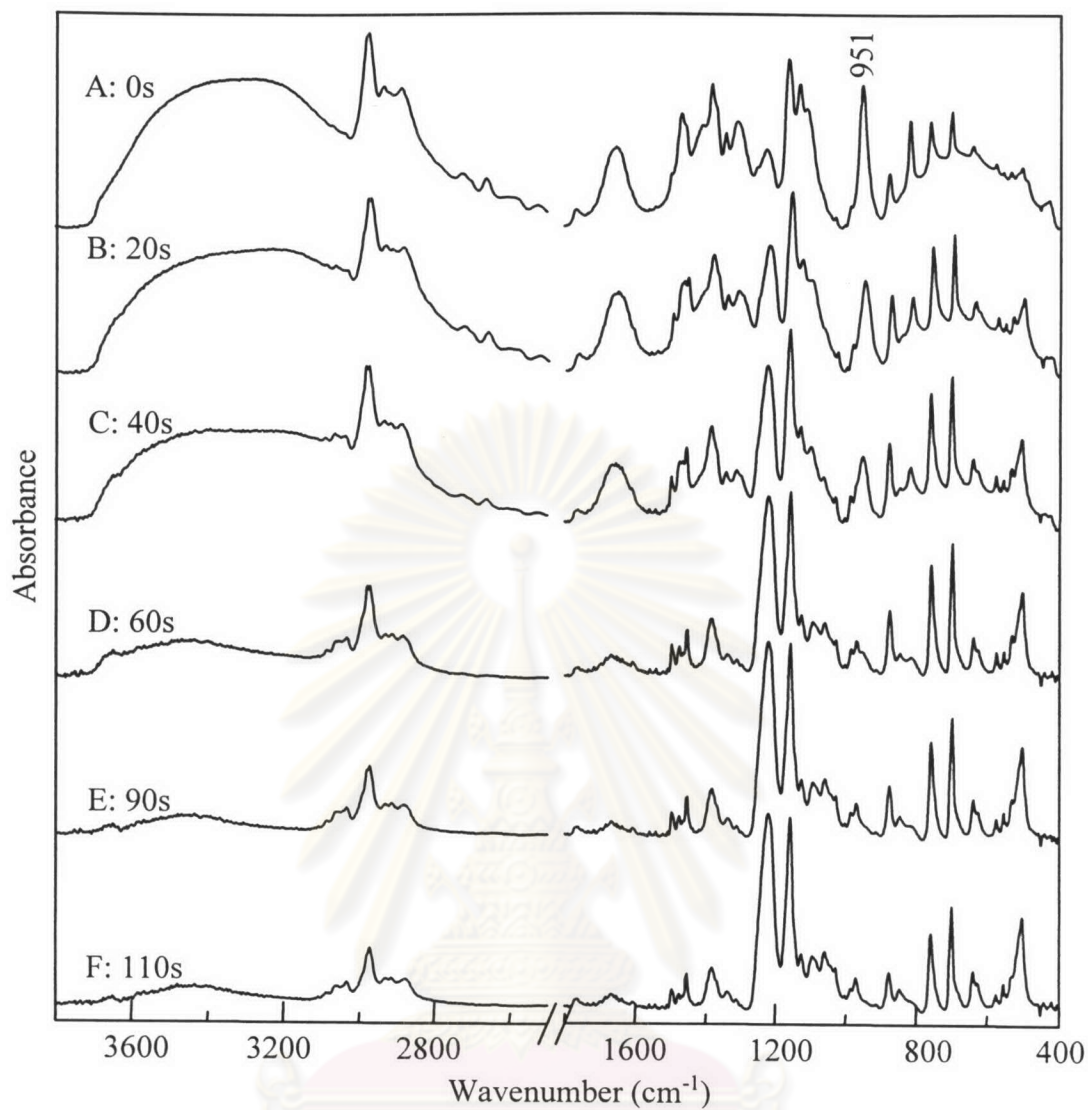
The application of the home-made IR card for analyzing a mixture of volatile liquids was observed. The ring-opening reaction at 2 hours of styrene oxide was examined. Figure 4.24 schematically represents the ring-opening reaction of styrene oxide with an existence of isopropanol and iron (III) trichloroacetate ( $\text{Fe}(\text{TCA})_3$ ) used as catalysts. The peak assignment of these spectra is as described in Table 4.1.

The ring-opening reaction of styrene oxide was initially induced by  $\text{Fe(TCA)}_3$  catalyst with exceed isopropanol in the solution of dichloromethane. The spectra were taken within the first 2 minutes in order to investigate spectral changes as a function of time. The spectra obtained were then interpreted to predict the organic species present in the system.



**Figure 4.24** Ring-opening reaction of styrene oxide with isopropanol.

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**Figure 4.25** IR spectra observed for the ring-opening reaction of styrene oxide with increasing time: initial time (A), 20s (B), 40s (C), 60s (D), 90s (E) and 110s (F), respectively.

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**Table 4.1** Frequencies ( $\text{cm}^{-1}$ ) of absorption bands attributed to organic species in ring-opening reaction of styrene oxide

Initial time	Wavenumber ( $\text{cm}^{-1}$ )					Assignment
	20 seconds	40 seconds	60 seconds	90 seconds	110 seconds	
3400 vs	3400 vs	3400 vs	3400 w	3400 w	3400 w	H <sub>2</sub> O
-	-	3088 vw	3088 vw	3088 vw	3088 vw	} $\nu_{\text{CH}}$ of aromatic ring
-	-	3063 vw	3063 vw	3063 vw	3063 vw	
-	-	3035 vw	3035 vw	3035 vw	3035 vw	
2947 s	2947 s	2947 s	2947 s	2947 s	2947 s	} $\nu_{\text{CH}}$ of aromatic ring
2932 vw	2932 vw	2932 vw	2932 vw	2932 vw	2932 vw	
2889 vw	2889 vw	2889 vw	2889 vw	2889 vw	2889 vw	
1760 vw	1760 vw	1760 vw	1760 vw	1760 vw	1760 vw	C=O stretching
1650 vs	1650 vs	1650 vs	1650 w	1650 w	1650 w	H <sub>2</sub> O
1499 sh	1499 w	1499 w	1499 m	1499 m	1499 m	Ring mode of aromatic
-	-	1473 vw	1473 w	1473 w	1473 w	Ring mode of aromatic
1465 m	1465 sh	1465 vw	-	-	-	CH <sub>3</sub> bending
-	1451 sh	1451 w	1451 m	1451 m	1451 m	Ring mode of aromatic
1383 s	1383 s	1383 s	1383 m	1383 m	1383 m	CH <sub>3</sub> umbrella mode
1360 sh	1360 sh	-	-	-	-	CH <sub>3</sub> umbrella mode
1308 m	1308 w	1308 w	1308 vw	1308 vw	1308 vw	In-plane-of OH bending
1123 sh	1123 w	1123 w	1123 w	1123 vw	1123 vw	C-C-O asymmetric stretching
1095 sh	1095 sh	1095 sh	1095 w	1095 w	1095 w	O-C-C stretching
-	-	1029 sh	1029 sh	1029 sh	1029 sh	O-C-C stretching
951 vs	951 s	951 m	951 w	951 w	951 w	CH <sub>3</sub> -C-CH <sub>3</sub> stretching
874 m	874 s	874 s	874 s	874 m	874 w	C-Cl stretching
818 s	818 m	818 w	-	-	-	C-C-O symmetric
755 m	755 s	755 vs	755 vs	755 vs	755 vs	Out-of-plane of CH bending of aromatic
697 m	697 s	697 vs	697 vs	697 vs	697 vs	C-C bending of aromatic

Note: vw = very weak, sh = shoulder, vs = very strong, s = strong

m = medium, w = weak

$\nu$  = stretching vibration



As seen in Figure 4.25, there are spectral changes. Spectra A to C show a strong broad band at  $3600\text{-}3000\text{ cm}^{-1}$  and a sharp band at  $1600\text{ cm}^{-1}$ , which are characteristic peaks of OH stretching vibration. These peaks significantly decrease with the increasing time. The broad bands at  $3600\text{-}3000\text{ cm}^{-1}$  interfere the C-H stretching band of an aromatic ring generally present in the frequency range of  $3100\text{-}3000\text{ cm}^{-1}$ . According to the spectrum C, the triplet peaks at  $3000\text{ cm}^{-1}$  assigned for benzene ring can be distinguished after 40 seconds as well as that of the ring mode at  $1500\text{-}1350\text{ cm}^{-1}$ . In addition, two intense bands centered at  $755$  and  $697\text{ cm}^{-1}$ , assigned as the out-of-plane of C-H bending and the ring bending of a benzene ring, can be clearly recognized with significantly high intensities. These bands confirm the unsaturation of a benzene ring. On the other hand, the band at  $697\text{ cm}^{-1}$  with the evidence of the C-H bending represents a mono-substituted benzene ring. In contrast, the C-Cl stretching, occurring at  $874\text{ cm}^{-1}$  indicates the presence of dichloromethane and  $(\text{Fe}(\text{TCA})_3)$ .

The prominent spectral feature in spectrum A displayed three absorption ranges: (i)  $3600\text{-}2850\text{ cm}^{-1}$ , (ii)  $1470\text{-}1300\text{ cm}^{-1}$  and (iii)  $1100\text{-}820\text{ cm}^{-1}$ , which are easily identified as a result of isopropanol. Evaporation of isopropanol leaves liquid mixture giving rise to the moderately intense bands of ring mode of benzene (at  $1470\text{-}1300\text{ cm}^{-1}$ ) and weak bands of ester (at  $1095$  and  $1029\text{ cm}^{-1}$ ). The C=O stretching band presented at  $1760\text{ cm}^{-1}$  for every spectrum in the series confirm an occurrence of ester which could be a result of  $(\text{Fe}(\text{TCA})_3)$ .

Theoretically speaking, a product of the ring-opening reaction of styrene oxide is an ether species. Normally, the interpretation of ether is complicated due to their peak positions which are identical to that of hydrocarbon and alcohol. Thus, change in the absorbance band of styrene oxide was observed to indicate 2-(*iso*)-propanoxy-2-phenylethanol occurs in this reaction. In case of styrene oxide, the spectrum exhibits dominant bands: strong absorption bands in the range of  $965\text{-}875$  and  $880\text{-}750\text{ cm}^{-1}$  assigned for the asymmetric- and symmetric-ring deformation, respectively. Isopropanol, dichloromethane and styrene oxide also absorbed strongly in this region. Practically speaking, the strong absorption bands at  $951$  and  $755\text{ cm}^{-1}$  were assigned as the ring deformation of styrene oxide. According to the mechanism of the ring-opening reaction of styrene oxide, the epoxide ring is opened by the

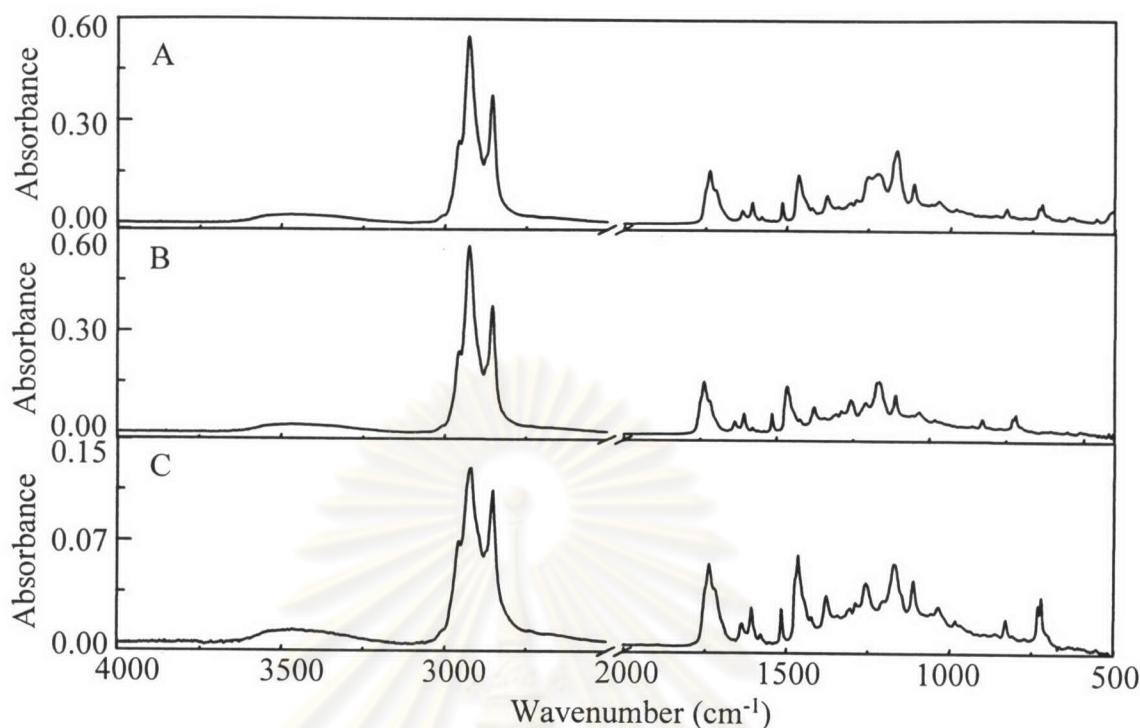
breaking of a C-O bond of epoxide ring with isopropanol. In consequence, the molecule of styrene oxide transforms from a ring structure to linear chain structure (see Figure 4.24). A significant decrease in absorption intensity of epoxide ring with increasing time indicates the complete ring-opening reaction of styrene oxide.

#### 4.2.4 Thin films

A previous sensitivity investigation of the home-made IR cards, it presents evidently that thin PTFE film have a potential to determine the thin film samples. A flexibility of PTFE film increases when it is stretched to make a thin film. When a thin PTFE film was closely attached to the surface of materials, it could be easily distorted along material shape. As a result, no cutting material to piece in order to determine the molecules deposited on the material surface. To confirm a potential and an application of thin PTFE film, four types of samples were examined in the study here: (i) the thin film of lipstick on the glass, (ii) the deposited molecules on the dried fish surface, (iii) the molecules of dust deposited on the glass fiber paper, and (iv) the released organic compounds in the plastic packaging.

##### 4.2.4.1 Determination of the thin film of lipstick on the glass

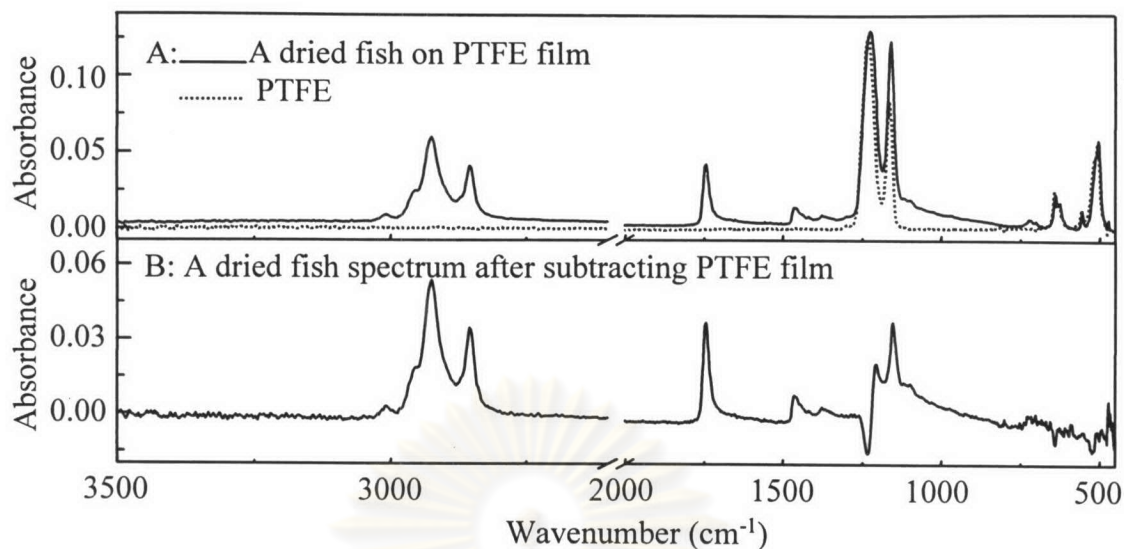
A home-made IR card was attached to the glass surface at deposited lipstick area. The little press was applied in order to attach closely with surface. Subsequently, the home-made IR card was slightly pulled and then was collected. In addition, a thin lipstick film was scraped and smeared to the ZnSe window in order to collect spectrum. The spectrum of lipstick from ZnSe window was compared with its spectrum from the home-made IR card, as shown in Figure 4.26. The feature characteristic of lipstick from the home-made IR card is almost the same as the spectrum from ZnSe window. As a result, it indicates that the home-made IR card can remove deposited molecules on the glass as well. The sampling with the home-made IR card is easier and faster than a ZnSe window. This is because the scraping of thin lipstick film was ignored for a home-made IR card when it was used and no cleaning was required. In contrast to the ZnSe window was absolutely cleaned after using. Care must be taken when using the ZnSe window because it was easily scratched. In addition, the scraping sample might cause the nature destruction of sample.



**Figure 4.26** Comparison of IR spectra of the thin-film lipstick obtained on PTFE film (A), pure thin film lipstick after spectral subtraction of PTFE (B) and on ZnSe window (C).

#### 4.2.4.2 Determination of deposited molecules on the dried fish

In the market, the dried fish can be easily available to buy for cooking. The dried fish may consist of contaminants when it was allowed to encounter the atmosphere without a good store. In some cases, the fishmonger squirted the pesticides at the dried fish in order to protect the insects. Contaminants and pesticides usually affect health of the consumers. Therefore, the qualitative determination of the dried fish is very important to ensure that the integrity and qualitative of the deposited molecules are not compromised. In the previous research work,<sup>24</sup> standard methods such as measurement of gas permeability by mass spectrometer and water vapor permeability by gravimeter, was used to assess the functionality of non-edible coatings. These methods may available to destructively characterize the nature materials. Therefore, this research attempts to characterize deposited molecules on the dried fish surface without the sample destruction.

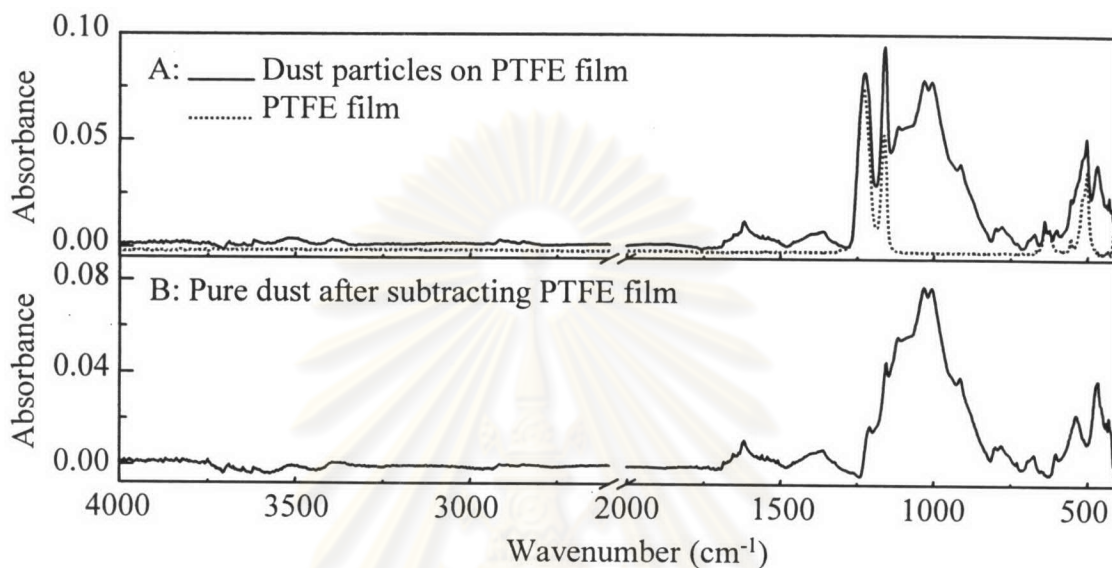


**Figure 4.27** IR spectrum of deposited organic molecules on a dried fish obtained on PTFE film (A) and pure deposited organic molecules after spectral subtraction of PTFE (B).

The home-made IR card was closely attached and slightly pressed on a dried fish surface. Subsequently, it was slowly pulled off and then the spectrum of dried fish was collected. The observed spectrum presented in Figure 4.27, exhibits bands at  $2900\text{--}2700\text{ cm}^{-1}$  assigned for C-H stretching of hydrocarbons, a small band at  $3007\text{ cm}^{-1}$  for C-H stretching of aromatic ring, a sharp band at  $1745\text{ cm}^{-1}$  for C=O stretching, the small bands at  $700\text{--}600\text{ cm}^{-1}$  assigned to out-of-plane of C-H bending and ring-bending of aromatic, the C-Cl stretching is typically this region. The bands at  $1462, 1420, 1373$  and  $1158\text{ cm}^{-1}$  are in the fingerprint region that was often the most complex and confusing region to interpret. In addition, the baseline shift at  $1000\text{--}700\text{ cm}^{-1}$  indicates that the absorption bands of sample even though absorption intensity was not rather clearly observed. This result can predict the deposited molecules observed that should be contaminated rather than the organic compounds in tissue of the dried fish. Because the obtained spectrum consist of absorption bands similar to the absorption bands of pesticides, as evidently seen at C-Cl region. Normally, most pesticides consist of Cl atom in the molecules. In addition, a home-made IR card displays a potential examination of the characteristic of deposited molecules with nondestructive sample. As a result, it will provide valuable information on a dried fish quality. Not only that, a dried fish can be stored to determine the various desirable

further information, for instance, the effect of deposited molecules on a dried fish surface and the diffusion of deposited molecules into a dried fish.

#### 4.2.4.3 Determination of dust particles deposited on the glass fiber paper



**Figure 4.28** IR spectrum of dust particles obtained on a PTFE film (A) and pure dust particles after spectral subtracting of PTFE film (B).

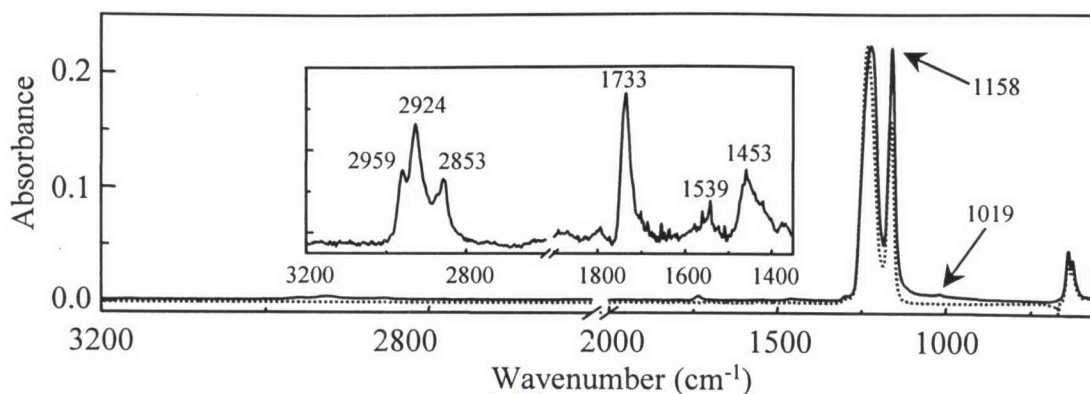
Systematic measurements and analytical determinations of the air and its impurities have been received a lot of attention in recent years.<sup>25</sup> Therefore, the development and improvement of appropriate methods seem to be an important task. The amount of sedimentable dust is usually measured by gravimetric method. But this method can not identify the characteristic of dust sediments. IR spectroscopic method can determine specific components in atmospheric dust are advanced to obtain their spectra. In this section, the atmospheric dust sediments on the glass fiber paper were determined by using the home-made IR card. The home-made IR card was attached onto a glass fiber paper surface with a slight press force and then pulled off carefully. Subsequently, the spectrum of dust particles was collected, the obtained spectrum of dust particles is shown in Figure 4.28.

As seen in Figure 4.28, it indicates that the broad bands in the region between 3400 and 3100 cm<sup>-1</sup>, which is caused by hydrogen-bonded hydroxyl groups,

crystal water and interaction of adsorbed water molecules. Ammonium ions could also contribute to this band but are obscured. In addition to the water vibrations appearing at 3514, 3394  $\text{cm}^{-1}$  and the small band at 1615  $\text{cm}^{-1}$  are unique for gypsum. There is no doubt to ascribe the bands at 2914 and 2842  $\text{cm}^{-1}$  to aliphatic CH groups, it shows the appearance of content of organic molecules in a sample. The feature absorption bands in the 1200-400  $\text{cm}^{-1}$  region was significantly observed, it was attributed to the position bands of quartz, clay, feldspar, gypsum, nitrate, sulfate and carbonate (which their characteristics were determined and described in the literatures for more than a year).<sup>26-30</sup> From this observation, the infrared spectrum of dust deposited on a glass fiber paper can be obtained in a simple way by the home-made IR card from thin PTFE film. The dust particles can be coarsely characterized to be inorganic substances, a complex of organic substances and adsorbed water.

#### **4.2.4.4 Determination of released organic compounds in the plastic packaging**

Additives play an important role on the properties of polymers; they may be used as plasticizers, antioxidants, light stabilizers and flame retardants. Each of these additives has some important effect on the potential end uses of the polymer. Because these additives can markedly affect the properties of polymer, they must also affect its structure in some way.<sup>10</sup> The degradation of polymers may be produced when polymers encounter the strong acid-base solvents, heating and high pressure. The major products of degradation are monomers and additives. In the present study, packaging made from polyethylene terephthalate (PET) was used as a sample, this packaging was heated at 65°C for 15 minutes. Subsequently, the home-made IR card was attached to the packaging surface and then was collected a spectrum. We expected to observe absorption bands of some organic components released from packaging.



**Figure 4.29** IR spectrum of released organic component in PETE packaging obtained on a PTFE film (—) and spectrum of PTFE film (.....).

The IR spectrum of released organic component in PETE packaging in Figure 4.29 shows absorption bands at 3000-2800  $\text{cm}^{-1}$  assigned for C-H stretching, 1733  $\text{cm}^{-1}$  for C=O stretching, 1539 and 1453  $\text{cm}^{-1}$  for CH aromatic ring and 1019  $\text{cm}^{-1}$  for O-C-C stretching. In addition, the absorption intensity of band at 1158  $\text{cm}^{-1}$  increased after sampling process, it could be identified as a band of sample and to be assigned for C-C-O stretching. From the investigation, it is possible to apply the home-made IR card for determination of the released organic components in plastic packaging, even though their amounts are very small. The thin PTFE film can remove these components from plastic packaging surface.

#### 4.2.5 Gases

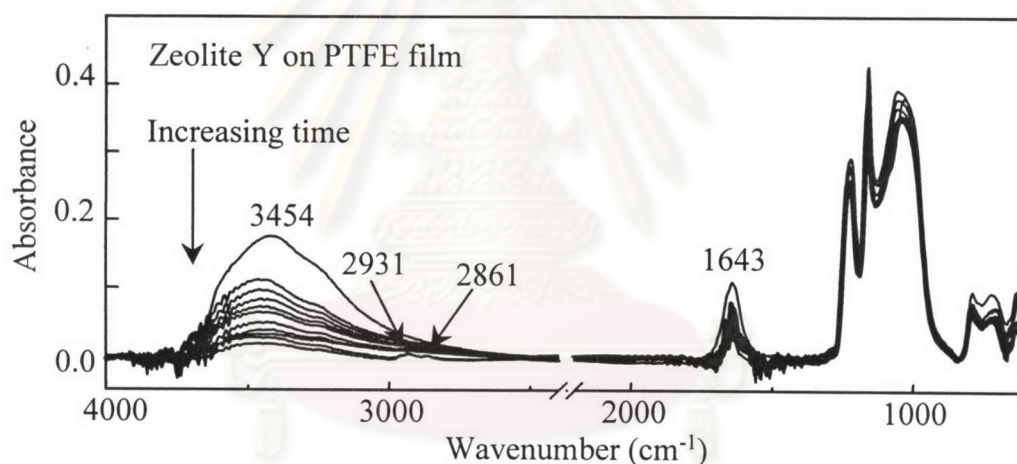
In this section, clay-BNH was smeared onto the surface of PTFE film. This PTFE film was employed to adsorb vapor of volatile organic compound (*i.e.*, benzene). It was found that clay-BNH on the PTFE surface cannot adsorb vapor of volatile organic due to the nature of clay-BNH.

### 4.3 Applications of the home-made IR cards for various research fields

#### 4.3.1 Determination of water in zeolite Y using the home-made IR card

The water of zeolite is an important parameter in determining zeolite properties and for zeolite manufacturing quality control. For instance, zeolite A has important use as a detergent builder. The target moisture content of zeolite A is

typically 18-22 wt % water. A drier material tends to have an altered zeolite structure and reduced cation exchange properties. Water zeolite A tends to lump and show poor flow characteristics, making solids handling difficult in manufacturing. Recently, Simeral and Krygsmann<sup>31</sup> reported the determination of water in zeolite A using low-resolution NMR. In this work, the infrared spectrum of zeolite Y using the home-made IR card is an alternative method for water determination, it illustrates a broad band around  $3500\text{-}3300\text{ cm}^{-1}$  and a narrow band at  $1650\text{ cm}^{-1}$ , these bands are the unique characteristic of water. Because of the PTFE is a non-hygroscopic and hydrophobic material, it does not adsorb water. Therefore, the presence of water peaks in the spectrum is attributed the water in zeolite Y, as previously above mentioned. To confirm this assumption, a zeolite Y on the home-made IR card was heated and vacuumed in the hot cell, the spectra were analyzed at various times.



**Figure 4.30** IR spectra of zeolite Y on a home-made IR card: OH stretching band at  $3454\text{ cm}^{-1}$  and  $\text{H}_2\text{O}$  bending at  $1643\text{ cm}^{-1}$ . From the top to bottom: spectra of unheated sample and the sample heated for 30, 60, 90, 120, 150, 180, 210, 480, 540 and 720 seconds, respectively.

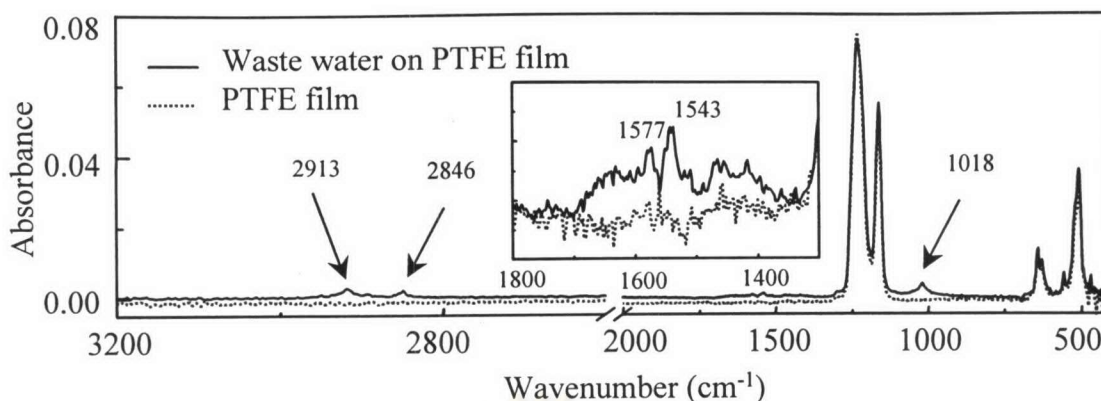
Figure 4.30 shows the infrared spectra of zeolite Y on the home-made IR card. The spectrum of the unheated zeolite Y shows a very strong broad band of water at  $3454\text{ cm}^{-1}$  and a sharp band at  $1643\text{ cm}^{-1}$ . A 30 seconds heating, the absorption intensities of water bands decrease rapidly. After 30 seconds, the absorption intensities of water bands slightly decrease with increasing heating time. The small bands at  $2931$  and  $2861\text{ cm}^{-1}$  were observed for heating time for 720



seconds, indicates that the absorption of C-H stretching of hydrocarbons was partly hidden under the structural OH stretching band. From this resulting shows that the quality determination of water content of zeolite Y can be achieved by using the home-made IR card technique. The ease of sample preparation made determination of water useful for products and process analysis of water in zeolite Y in further research.

#### **4.3.2 Determination of organic compounds suspended in waste water**

Soils and ground water contain the residue of human agricultural practices (fertilizers, pesticides, *etc*) and improperly disposed of industrial wastes. These contaminants can be classified into organic, inorganic, radioactive and acid/base. They have been increasing hazardous to the environment and many of them are known to be toxic. Even though contaminant presenting in the ground water/soil is low quantity but its concentrations are non-negligible. As a consequence, to qualify these pollutants in contaminant areas is of importance. Current methods for analysis of contaminants in water and soil involve sample enrichment by liquid-liquid extraction, solid-phase extraction for water or liquid-solid extraction for soils. In addition, organic compounds can be analyzed by gas chromatography (GC), gas chromatography-mass spectrometer (GC-MS) as well as liquid chromatography. Another technique has been interested from researchers in present day, it is attenuated total reflection Fourier transform infrared (ATR FT-IR). In general, these techniques have been involved with complex experimental procedures and time consuming separation steps with expensive operation costs. As a result, we used the home-made IR card to analyze the suspended contaminants in waste water, and expected that the home-made IR card should coarsely analyzed if quantity of contaminants was high enough to determine.



**Figure 4.31** IR spectra of organic compound in waste water obtained on PTFE film (—) and PTFE film (·····).

In this study, waste water sample was obtained from Klong Saen Saeb, the sampling point was in front of Thep Lee La temple. A stirring rod was attached to waste water surface in order to the contaminated molecules deposited on its surface. Subsequently, a home-made IR card was closely attached to stirring rod surface and then was analyzed. Figure 4.31 shows spectrum of organic compound suspended in waste water. The absorption bands of aliphatic hydrocarbons were rather clearly observed at 2913 and 2846  $\text{cm}^{-1}$ . The evidently small band at 1018  $\text{cm}^{-1}$  should assigned to be O-C-C stretching of ester compounds, and very small bands at 1650-1400  $\text{cm}^{-1}$  might be ring mode of aromatic. From observation illustrates that the obtained spectrum was not evidence enough to specify accurately type of organic compounds in waste water. But it can show that the coarse quality information of waste water contain organic pollutants. This resulting illustrates that the utilization of the home-made IR card as the primarily sensor in the water pollution research.

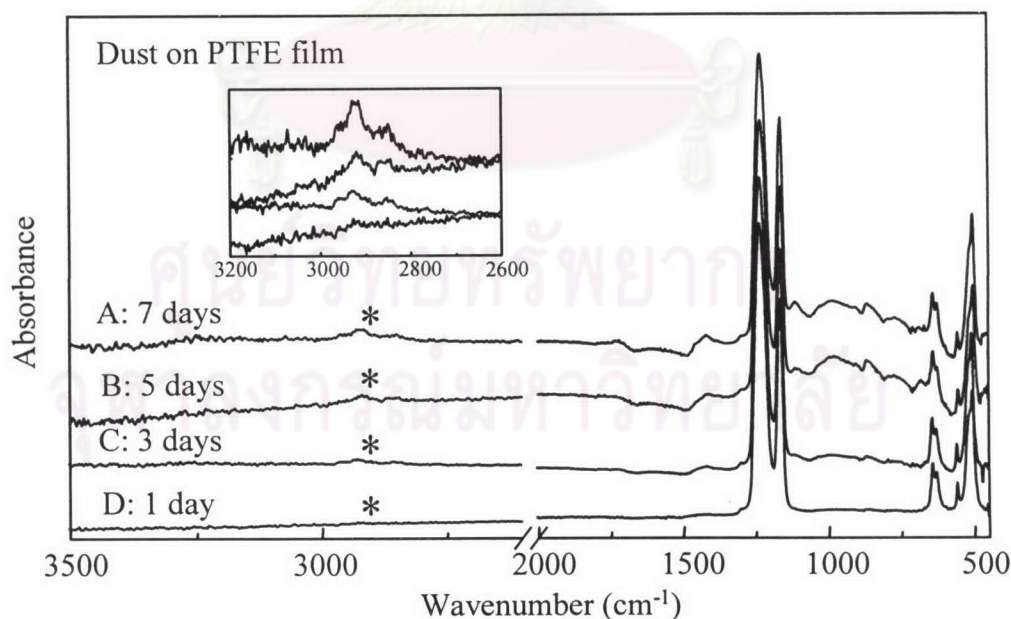
### 4.3.3 Determination of atmospheric dust particles from the heavy road traffic

Air pollution is the most serious problem in large cities. There are many sources of particulate air pollution: large industrial plants, medium- and small-scale industries, refuse burning, households burning biomass for cooking and heating, vehicles exhaust, re-suspended road dust, construction, particles migrating from other regions and naturally occurring dust. These sources emit particles of varying sizes—small particles affect to health much more than large particles. Therefore, it is

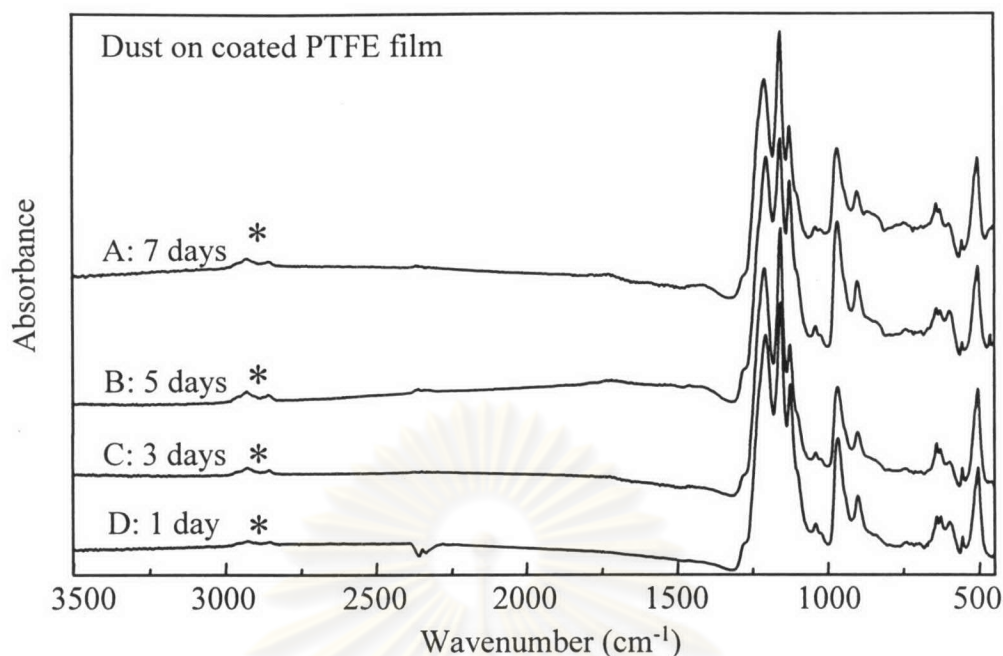
important to have a good understanding of the level of exposure of the general public to particulate air pollution, of the relative contributions of these different sources (referred to as source apportionment) and of the characterization of different types of particulate air dust.

The elevated concentrations of fine particles near busy roads indicate that road traffic is an important source of atmospheric particles. The total emissions of road traffic are caused by different contributions. From tail pipes are emitted as well as gaseous precursors. In addition, the road traffic contributes to the fine particle load of the atmosphere by abrasion and re-suspension of particles (street dust, tyre wear, brake wear).

For the main purpose of this study is to determine types of atmospheric dust from road traffic. The sampling area was Pathumwan Road in front of Chulalongkorn University, about 1 m above the ground situated in a center island of road 4 m from the gate of Faculty of Science. PTFE film and coated PTFE film with Fluorolube were employed as substrates for characterization of the deposited dust particles. The sampling period varies from 1 to 7 days.



**Figure 4.32** IR spectra of atmospheric dust from heavy road traffic obtained on PTFE film for different sampling times.



**Figure 4.33** IR spectra of atmospheric dust from heavy road traffic obtained on coated PTFE film with Fluorolube for different sampling times.

Figure 4.32 and Figure 4.33 show IR spectra of atmospheric dust on PTFE film and coated PTFE film, respectively. In case of the use of PTFE film with coating Fluorolube, the absorption bands of hydrocarbon at  $3000\text{--}2800\text{ cm}^{-1}$  were clearly observed within 1 day, absorption intensities of hydrocarbon peaks significantly increase with increasing sampling times. On the other hand, no absorption bands of hydrocarbon on the PTFE film within 1 day but their absorption intensities slightly increase with increasing sampling times. As a result, the coating of the home-made IR card with Fluorolube results in the enhancing detection of small amount particles. A high viscosity of Fluorolube caused the accumulation of much dust particles on the PTFE surface and Fluorolube works as a matrix material to reduce light scattering. Therefore, the evidence of absorption bands of hydrocarbon compound on the coated PTFE film is more evident than that of on PTFE film. But the absorption bands at below  $1300\text{ cm}^{-1}$  are difficult to identify because of Fluorolube also absorbed this region. However, the absorption bands of dust at below  $1300\text{ cm}^{-1}$  can be observed of the PTFE film. Regarding to Figure 4.32, the presence of absorption bands at  $1500\text{--}600\text{ cm}^{-1}$  were coarsely observed in 3 days and these bands were evidently observed after 3 sampling days. The absorption bands at  $1500\text{--}600\text{ cm}^{-1}$  may attribute to the mineral materials (*i.e.*, quartz and clay).

The results above illustrate that the home-made IR card is a technique that will be useful for developing with other techniques to determine atmospheric dust. The obtained spectrum of dust was sufficiently identified and qualified in this observation.

#### **4.4 Surfaced-enhanced home-made IR card**

The home-made IR card cannot make as surface-enhanced IR card because PTFE film ripped during in a vacuum chamber held at a pressure  $2.0 \times 10^{-1}$  Torr. Therefore, gold cannot deposit on the PTFE surface.

#### **4.5 Drawback of the home-made IR card**

The information obtained from study of efficiency of thin PTFE film IR card for sample analysis will be employed to confirm potential and useful of the home-made IR card technique. The problems encountered by the home-made IR card include:

1. According to the uniform of PTFE film, the commercial IR card was produced by pre-stretched film across the aperture creating a highly uniform with process. On the other hand, the home-made IR card was produced by stretching PTFE film with normal process (stretched PTFE film with a little force from hand of human) causing non-uniform thickness. In addition, the film thickness is difficult to control as equal through in each sheet. However, the non-uniform thickness of the home-made IR card has no effect on the spectrum of sample. Because the spectrum of PTFE will be subtracted when the PTFE is used for sample analysis.
2. For quantitative analysis of volatile liquids, a non-uniform of thin PTFE film has not an efficiency to give quantitative information due to the capillary-thin-film of volatile liquid hold on the thin PTFE film cells in a short period time. However, the home-made IR card from thin PTFE film has a potential to achieve qualitative analysis.
3. Due to the thickness of PTFE film is rather thin, when it is employed, applying the sample onto the PTFE surface is done carefully.