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CONTAMINATION ANALYSIS OF POLYMER SURFACE BY ATR FT-IR MICROSPECTROSCOPY

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นฤมล พัทยากร: การตรวจสอบการปนเปื้อนเชิงผิวของพอลิเมอร์ด้วยเอทีอาร์เอฟทีไออาร์ไมโครสเปกโทรสโกปี (CONTAMINATION ANALYSIS OF POLYMER SURFACE BY ATR FT-IR MICROSPECTROSCOPY) อ. ที่ปรึกษา: รศ. ดร. ศุภศร วนิชเวชารุ่งเรือง, อ. ที่ปรึกษาร่วม: ทัสสิมนต์ คงอยู่, 93 หน้า.

การปนเปื้อนเชิงผิว เช่น ฝุ่นหรือฟิล์มบางๆ ถูกศึกษาโดยอุปกรณ์ไมโครไออาร์อีแบบสไลด์ที่มีเพชรที่ผ่านการเจียระไนแล้วและเจอร์มาเนียมซึ่งมีลักษณะทรงกรวยเป็นหัวตรวจวัด เนื่องจากอุปกรณ์ที่ใช้ในการตรวจวัดทั้งสองมีพื้นที่ผิวสัมผัสขนาดเล็ก จึงสามารถวิเคราะห์ตัวอย่างที่มีขนาดเล็กได้ เอทีอาร์สเปกตรัมที่ได้ให้ข้อมูลเชิงผิวของสิ่งปนเปื้อน ซึ่งสิ่งปนเปื้อนสามารถหลุดติดที่ปลายของหัวตรวจวัดได้โดยการสัมผัสโดยตรงหรือใช้ของเหลวที่มีความเหนียวเพื่อช่วยในการดึงสิ่งปนเปื้อนออกจากตัวอย่าง เทคนิคที่พัฒนาขึ้นใหม่นี้เรียกว่าเทคนิคคอนแทคและคลอเล็ค โดยเทคนิกนี้ไม่ทำลายตัวอย่าง ทำได้ง่าย ไม่ต้องมีการเตรียมตัวอย่าง และผลการทดลองถูกต้องและเชื่อถือได้ โดยสามารถแยกสิ่งปนเปื้อนออกจากพื้นผิวรองรับ และทำการศึกษาภายใต้หลักการทำงานของเอทีอาร์ ทำให้ไม่มีอิทธิพลของพื้นผิวรองรับ ปรากฏการณ์ที่ได้รับจากเทคนิคคอนแทคและคลอเล็คร่วมกับอุปกรณ์ไดมอนด์และเจอร์เมเนียมไมโครไออาร์อีแบบสไลด์มีประสิทธิภาพสำหรับการศึกษาการปนเปื้อนเชิงผิวและการศึกษาทางด้านนิติวิทยาศาสตร์

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Surface contamination (i.e., dust and thin film) was characterized by the novel slide-on diamond μIRE, and slide-on Ge μIRE. Due to the small sampling area of the tip, a sample with small size can be analyzed. In this work, characterizations of polymer surface contamination by the slide-on diamond μIRE and the slide-on Ge μIRE were studied. The contaminants on the surface of sample were analyzed. Contamination on a surface can be deposited onto the tip of both μIREs by directly deposition, or by using an organic liquid (i.e., mineral oil or fluorolube) to pick-up the contaminants from the surface. This novel sampling technique was called the *"contact and collect"* technique. This technique is non-destructive, ease to operate, does not require an additional sample preparation, and the result is accurate and reliable. The trace contaminants on a surface can be separated from the substrate, and characterized under the ATR mode without any interference from the substrate. The observed phenomenon suggested that the *"contact-and-collect"* operation with the slide-on diamond and slide-on Ge μIRE have the great potential for surface contamination, and forensic analysis.

Field of study Petrochemistry and polymer science Student's signature Narumon Pattayagorn
Academic year 2006 Advisor's signature
Co-advisor's signature

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CONTENTS

Page

LIST OF FIGURES

Figure Page

Figure Page

LIST OF TABLES

LIST OF ABBREVIATIONS

ATR : attenuated total reflection
d_p : penetration depth
IR : infrared
FT-IR : Fourier transform infrared
ATR FT-IR: attenuated total reflection Fourier transform infrared
Ge : germanium
IRE : internal reflection element
ZnSe : zinc selenide
Si : silicon
cm : centimetre
µm : micrometer
KBr : potassium bromide
TIR : total internal reflection

LIST OF SYMBOLS

ν : frequency

μ : micro

λ : wavelength

c : speed of light

h : Planck’s constant

I : intensity of incident radiation

I_A : intensity of absorbed radiation

I_R : intensity of reflected radiation

I_S : intensity of scattered radiation

I_T : intensity of transmitted radiation

θ : angle of incidence

θ_c : critical angle

CHAPTER I

INTRODUCTION

1.1 Surface Contamination

A material which has been deposited on surface such as floors, tools, benches, glass, etc., is called surface contamination. It may not be tightly deposited, much like dust or it may be fixed by some chemical or physical attraction means such as chemical bonding, adsorption and adhesion. These distinctions of types are important. Surface contamination is classified on the basis of how easily it can be removed and can be divided into a few of categories, such as metallic contamination, particle contamination and organic contamination [1]. The clean of a surface is a major factor in determining how well it performs of objective operation. Surface contamination is a problem in many industries and agricultures. For example, contamination will degrade the strength of subsequent adhesive bonding to the surface. The problem may not be apparent until later in the production process, or not until the product fails after it has been in use for a short period. Early identification and elimination of contamination issues are very important. However, it is often difficult to identify the exact source of a problematic contaminated layer [2].

1.2 Surface Contamination Characterization

Analysis of trace amounts of contaminant material is very important, which especially for applications in food, pharmaceutical industries, forensic science, crime prevention and security measures [3]. The application of surface contamination analytical techniques has been approved to find out the possible causes of the above problem and many laboratories such as time-of-flight secondary ion mass spectroscopy (ToF-SIMS) [4-7], total X-ray fluorescence spectrometry [8-9], thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) [10-13], tandem mass spectrometry [14-17], thermal desorption gas chromatography (TDGC) [18-19], gas chromatography/mass spectrometry (GC/MS) [20-21], pyrolysis–gas chromatography (Py-GC) [22-23], gas chromatography/mass spectrometry/mass spectrometry (GC-MS-MS) [24], liquid chromatography-mass spectrometry/mass spectrometry (LC-MS/MS) [25], high-performance liquid chromatography (HPLC) [26], secondary ion mass spectrometry (SIMS) [27-28], x-ray photoelectron spectroscopy (XPS) [29], scanning electron microscopy (SEM) [30-31]. However, these analytical techniques give us only the information about the distribution of elements but difficulty for samples preparation (separate contaminants from substrate), long time of analysis, low sensitivity for low mass elements, no chemical information, destructive techniques, and sometimes have interference from the substrate.

Among these techniques, Fourier transform infrared (FT-IR) spectroscopy is the well-known technique for its molecular related spectral information. An FT-IR spectrum provides uniquely chemical information of the materials (i.e., chemical structure and composition). The spectral fingerprints of the FT-IR spectrum are directly correlated with the structures of materials. Infrared spectroscopy is a particularly useful surface analytical technique because of its enormous versatility. To study surface contamination, various sampling technique can be employed such as transmission [32-34], external reflection [34], single reflection attenuated total reflection [33, 35-36], multiple reflection attenuated total reflection [37-41] and single reflection attenuated total reflection by diamond IRE [42-44]. The choice of sampling technique depends strongly on the character of the sample and the required information. The chosen method may be non-destructive and does not require additional sample preparation, has short analysis time. The disadvantages of these techniques are the combined information of contaminants and sample.

1.3 Infrared spectroscopy

Infrared spectroscopy is one of the most common spectroscopic techniques. For using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids and solids. Thus, IR spectroscopy is a significant and powerful tool for structural explanation and compound identification. This technique is based on the vibrations of the atoms of a molecule. An FT-IR spectrum provides chemical information unique to the material (i.e., chemical structure and composition) because its molecular information of sample is related with chemical information. An infrared spectrum is obtained by passing infrared radiation through a sample and determining which portion of the incident radiation is absorbed at a particular energy. The energy at which portion of any peak in an absorption spectrum appears corresponding to the frequency of vibration of a part of the sample molecule [45].

1.4 ATR FT-IR Spectroscopy

Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectroscopy is one of the most powerful surface analysis techniques. The ATR technique requires an internal reflection element (IRE) of high refractive index. When incident radiation traveling in an optically dense medium strikes the boundary of a second medium with a relatively lower refractive index with an angle greater than the critical angle. The electromagnetic field known as the ***evanescent field*** decays exponentially within a few micrometers away from the interface into the lower refractive index medium. This electromagnetic field interacts with the material and gives absorption spectrum of surface characteristics of the material. This technique can be applied to any sample that can be contacted with the IRE.

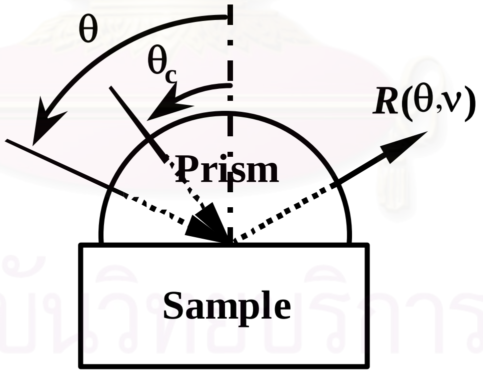


Figure 1.1 The simple optical and geometric arrangements of conventional ATR measurements.

For the limitations of conventional ATR experiment, optical contact between IRE and sample is necessary for obtaining a good spectrum. Due to the largely contact area of the hemispherical Ge IRE (5000 x 5000 μm^2), the information of very small sample size cannot be observed. The characterization of solid samples, especially hard samples always encounter the contact problem. Moreover, a sample can also damage the surface of Ge IRE when pressing with a high pressure. There is always an air gap between the solid sample and the Ge IRE because the system does not have a suitable optical contact. The absorbance degeneration is obtained when the surface of the sample is not smooth and cannot be pressed against the Ge IRE. If the air gap is thick enough, the spectrum of sample may not be able to be observed.

1.5 ATR FT-IR Microspectroscopy

ATR FT-IR microspectroscopy uses infrared radiation to elucidate and quantify the molecular information of microspectroscopic samples, its combined FT-IR spectrometer with infrared microscope. The infrared radiations were traveled within the infrared objective of microscope to coupling of the focused beam into the sample. Thus, FT-IR microscope can be acquired the chemical information of small specimens or of a small area samples to 10-15 μm. The molecular information can be obtained with great resolution at the microscopic level without destroying the sample. Generally speaking, the specialized objective with internal reflection element is set up by a prism mounted on the infrared objective. This used to view the area of selective on sample surface. The infrared objective has solved some of the problems in analysis at a macroscopic level of the conventional ATR technique. The condition of the contact is greatly affect the quality of the obtaining chemical information. For the disadvantages of commercial accessories, they are dangerous when the application is associated with over force. In addition, the hard and rigid which too much applied pressure, the sample can be risk to IRE cracking. Above all, the commercial accessories are very expensive.

Analysis of surface contamination is very important for quality control. Among the applications of the infrared microscope, the ATR microspectroscopy is the very sensitive technique for small sample size. This operation does not require any sample preparation, and short analysis time. Examples of industrial applications of FT-IR microscopy were shown in Table 1 [46].

Table 1 Industrial applications of ATR FT-IR microspectroscopy

Objects	Example applications
Small inclusion	Plastics, Fibers, Films, Ceramics
Impurity	Carbon and Oxygen in Si, Carbon in GaAs
Contaminant (deposit)	Magnetic tapes, Hard disk
Microstructure	Orientation and Crystallinity, Crystal form
Composite material	Laminated films, Polymer alloy, Interface of composites
Biological material	Gallstone, Calculus, Tissue section

1.6 Slide-on Diamonds and Germanium (Ge) as an Internal Reflection Element

From the limitations of the commercial ATR accessories, the homemade slide-on diamond μIRE and slide-on Ge μIRE accessories were developed. The homemade slide-on diamond μIRE and slide-on Ge μIRE are very low cost, having the precision mechanism, removable and easy to handle. It is very easily to clean the diamond μIRE and Ge μIRE. For slide-on diamond μIRE, a gem quality round brilliant cut natural diamond was employed as the μIRE. The diamond μIRE has a very small culet. Since the diamond accounts for its hardness and physical strength, it is available for sampling with optical contact problem in hard and rigid materials, rough surface, irregular shape samples, and sample with small sampling area. For the slide-on Ge μIRE, a miniature cone-shaped Ge μIRE was employed as the μIRE. Due to the small sampling area of Ge μIRE and effectiveness condensation of the coupled radiation interaction under the ATR condition at the tip, a spectral acquisition enable for analyzing a small specimen or a small area with superb spectral ability. The small contact area of the μIRE and the easy to move the stage of microscope, any sampling area of the surface can be selectively analyzed.

1.7 The Objective of This Research

The objective of this research is to develop technique for analysis of polymer surface contamination and to apply the novel ATR FT-IR technique for forensic analysis.

1.8 The Scopes of This Research

1. To develop a novel technique for analysis of polymer surface contamination.
2. To investigate various surface contamination varieties including coating material, polyethylene bag, polypropylene bag, chopstick, banknote, telephone mask.
3. To apply the novel ATR FT-IR technique for forensic analysis.

CHAPTER II

THEORETICAL BACKGROUND

2.1 The Electromagnetic Spectrum

Electromagnetic spectrum refers to the apparently several collection of radiant energy, from cosmic rays to X-rays, visible light to microwaves. Each of which can be considered as a wave or particle traveling at the speed of light. These waves differ from each other in length and frequency, as illustrated in Figure 2.1. Infrared refers to part of the electromagnetic spectrum between the visible and microwave regions.

Infrared (IR) spectroscopy is a popular method for characterizing substance. In the context of infrared spectroscopy, frequency is measured in "wavenumbers", which has the unit of cm^{-1}.

$$\text{wavenumber} = 1 / \text{wavelength in centimeters} \tag{2.1}$$

Frequency, ν (nu), is the number of wave cycles that pass through a point in one second. It is measured in Hz, where 1 Hz = 1 cycle/sec. Wavelength, λ (lambda), is the length of one complete wave cycle. It is often measured in cm (centimeters). Wavelength and frequency are inversely related as follows:

$$\nu = \frac{c}{\lambda} \quad \text{and} \quad \lambda = \frac{c}{\nu} \tag{2.2}$$

where c is the speed of light, 3.0×10^{10} cm.s^{-1}
Energy is related to wavelength and frequency by the following formula:

$$E = h\nu = \frac{hc}{\lambda} \tag{2.3}$$

where h = Planck's constant, 6.626 x 10^{-34} joules.s^{-1}. Note that energy is directly proportion to frequency and inversely proportion to wavelength.

The infrared spectrum can be divided into three regions (Figure 2.2), namely the far-infrared (<400 cm^{-1}), the mid-infrared (400-4000 cm^{-1}), and the near-infrared (4000-13000 cm^{-1}). Most infrared utilizations use the mid-infrared region. The near-infrared and far-infrared regions can provide specific information about materials information.

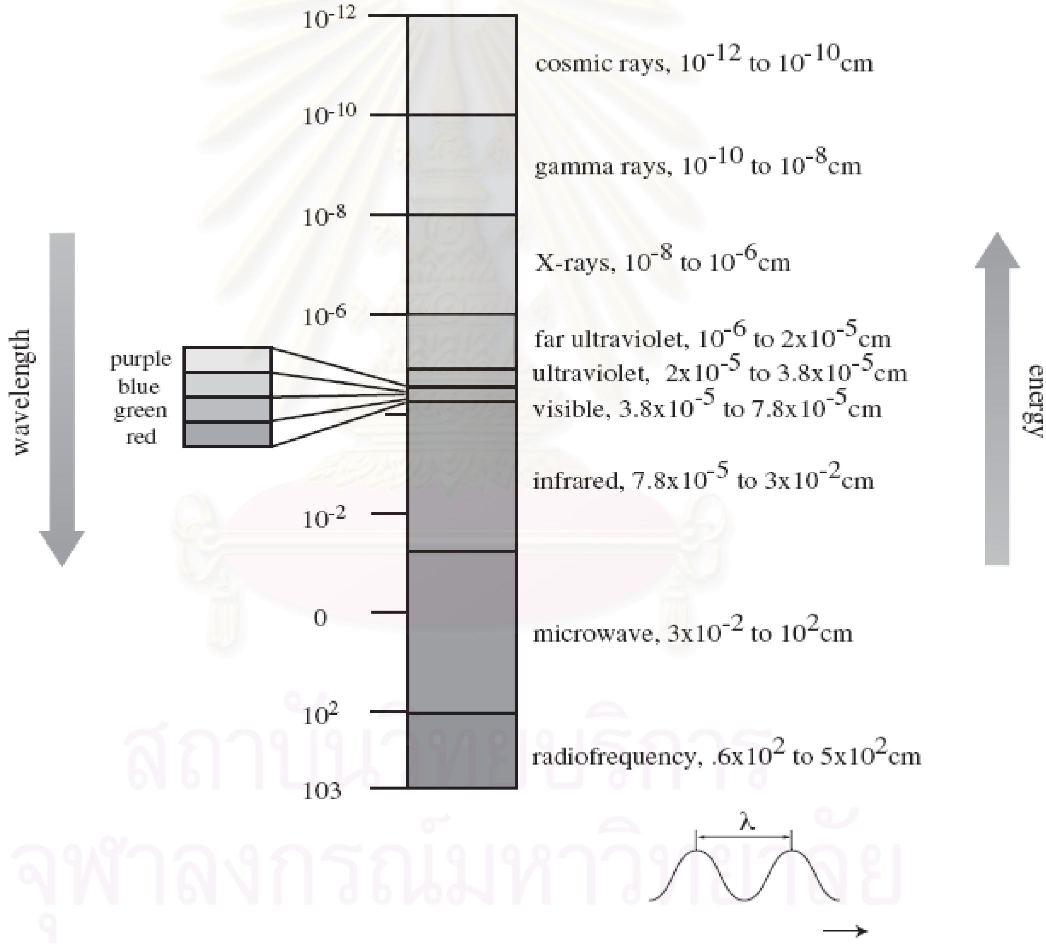
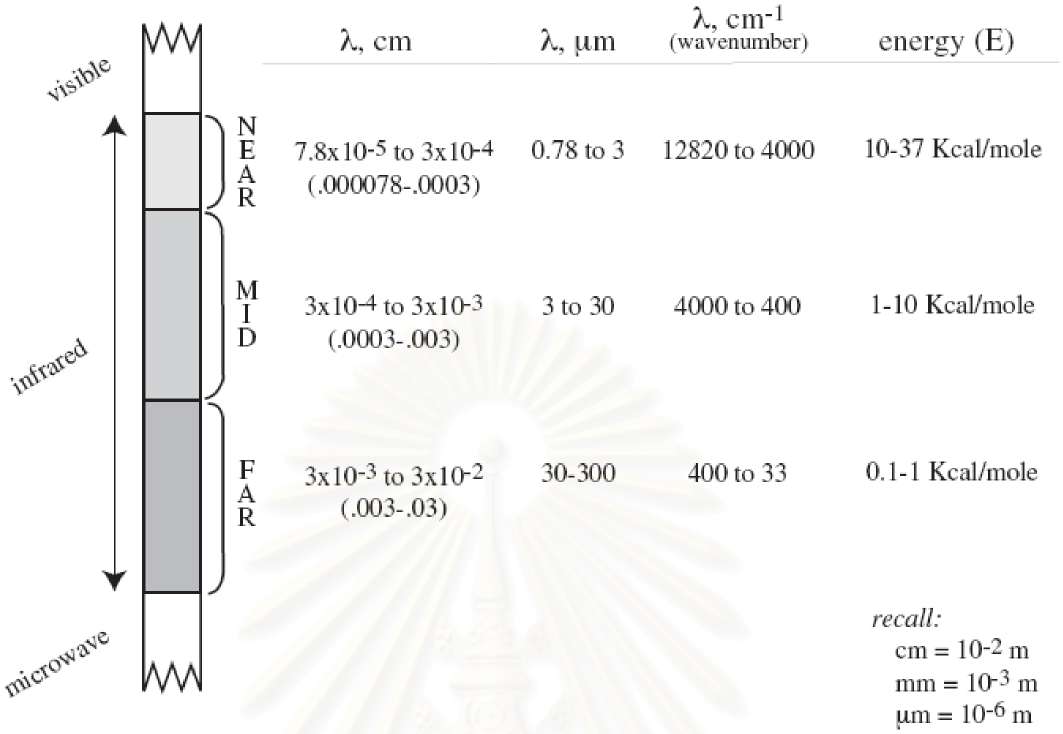


Figure 2.1 The electromagnetic spectrum.



	λ, cm	λ, μm	λ, cm^{-1} (wavenumber)	energy (E)
NEAR	7.8×10^{-5} to 3×10^{-4} (.000078-.0003)	0.78 to 3	12820 to 4000	10-37 Kcal/mole
MID	3×10^{-4} to 3×10^{-3} (.0003-.003)	3 to 30	4000 to 400	1-10 Kcal/mole
FAR	3×10^{-3} to 3×10^{-2} (.003-.03)	30-300	400 to 33	0.1-1 Kcal/mole

recall:
cm = 10^{-2} m
mm = 10^{-3} m
μm = 10^{-6} m

Figure 2.2 The IR regions of the electromagnetic spectrum.

2.2 Basic Concepts of Spectroscopy

A basic concept of infrared spectroscopy is a technique based on the vibrations of the atoms in a molecule. An infrared spectrum is obtained by passing infrared radiation through a sample, and determining what portion of the incident radiation is absorbed at individual energy. The energy was absorbed in any peak appears corresponding to the frequency of a vibration of a sample molecule.

Light is an electromagnetic wave. In its basic monochromatic form, light can be explained as oscillating electric and magnetic fields that multiply in space [47] (Figure 2.3). The electric and magnetic components are orthogonal to each other, and to the direction of propagation.

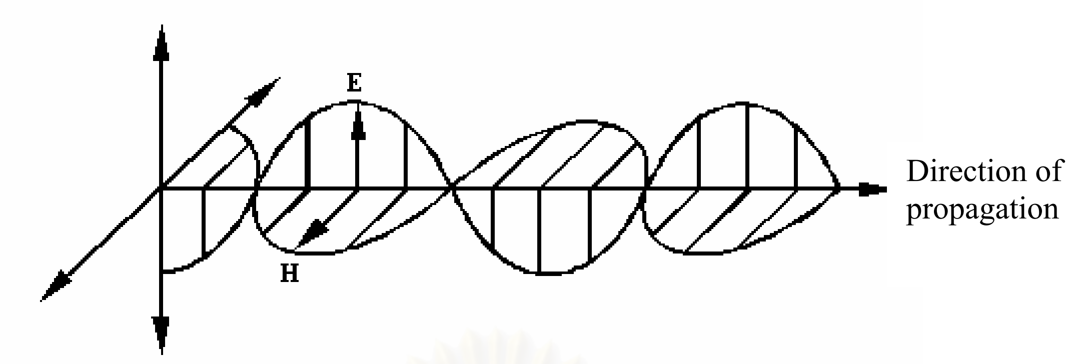


Figure 2.3 A linearly polarized electromagnetic wave in the direction of propagation. The electric (**E**) and magnetic (**H**), components are orthogonal to each other and to the direction of propagation. In non-polarized light, the electric component is randomly oriented in an infinite number of trends, but remains always perpendicular to the direction of propagation.

When an electromagnetic radiation strikes on a material, infrared rays of the incident radiation may be reflected, scattered, transmitted, or absorbed. This is depending on the experimental plan, which different rays may be detected. A schematic illustration for an interaction between light and matter is showed in Figure 2.4. The total amount of incident energy is the total of reflected, scattered, transmitted, and absorbed light. This process can be revealed as follows [47]:

$$I_0 = I_R + I_S + I_T + I_A \qquad 2.4$$

where I_0 is the intensity of the incident radiation and I_R, I_S, I_T, and I_A are the intensities of reflected, scattered, transmitted, and absorbed light, respectively. The intensity of each beam strongly depends on the intensity and wavelength of the incident radiation. Moreover, also the optical properties of the samples, the concentrations of species, and the geometry of the experimental setup were considered.

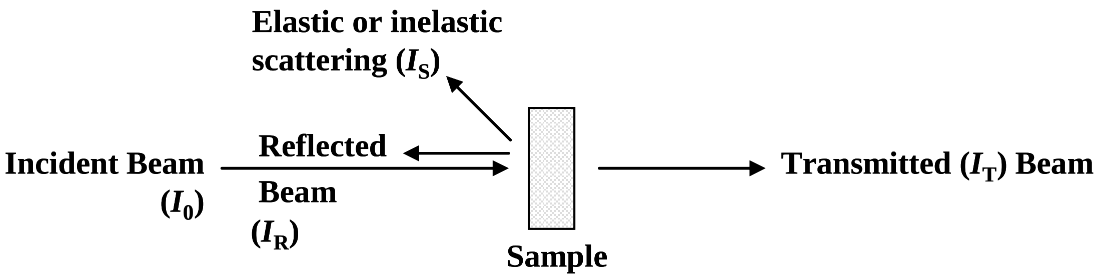


Figure 2.4 Interactions of light with matter.

In view of the electromagnetic radiation when a specimen is included between a light source and a detector (Figure 2.4). The sample absorbs a portion of the incident radiation. If we need to measure the ratio of the sample attenuated (I) and nonattenuated (I_0) intensities of the radiation, the measurement of the amount of light transmitted by the sample is very important when reflection and scattering of light is ignored. The relationship of proportional light can be quantitatively related to the chemical information of the sample by the Beer-Lambert law as follows [47]:

$$I / I_0 = e^{-A(\nu)} = e^{-c_2 \varepsilon(\nu) l} \tag{2.5}$$

where $A(\nu)$ is the sample absorbance at wavenumber ν, c_2 is the concentration of the absorbing functional group, $\varepsilon(\nu)$ is the wavenumber-dependent absorption coefficient, and l is the film thickness for the infrared radiation at a normal incidence to the surface of sample.

2.3 Principles of Light Reflection and Refraction

The light reflection and refraction occur when an electromagnetic radiation strikes a boundary between two medium with distinction of refractive indices. The regulation reflection method requires that the angle of incidence is equal to the angle of reflection radiation. If electromagnetic radiation passes from one medium to another that has a distinct refractive index, the change of beam direction occurring causes the differences propagation velocity through two medium. If light propagates through an incident medium with refractive index n_0 and come in a medium with refractive index n_1 (Figure 2.5), the light pathway will be converted and the range of refraction is given by the Snell's law as follows [71]:

$$n_0 \sin\alpha = n_1 \sin\beta \qquad 2.6$$

where α and β are the angles of incidence and refraction radiation.

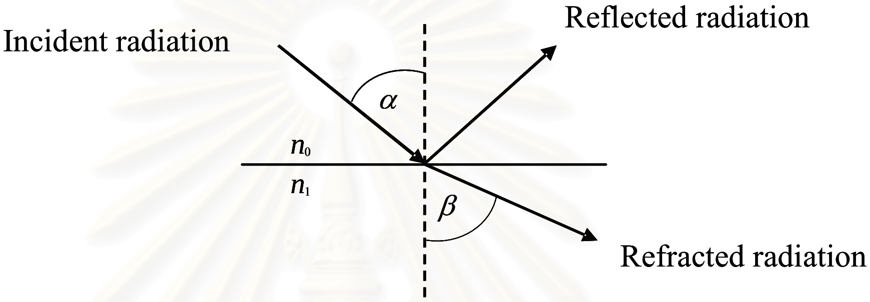


Figure 2.5 Reflection and refraction of a wave at a dielectric interface based on Snell's Law.

And the total internal reflection appears when light traveling in higher refractive index medium impinges on surface of a lower refractive index medium (*i.e.*, $n_0 > n_1$ shown in Figure 2.5). The incident angle must greater than the critical angle as shown in Figure 2.6. When the angle of the incidence equals the critical angle (θ_c), there is no light from the higher refractive medium travels across the interface into the lower refractive medium. The critical angle can be derived from Snell's law and given by Equation 2.7.

$$\theta_c = \sin^{-1}(n_1 / n_0) \qquad 2.7$$

where n_0 and n_1 are the refractive indices of the higher refractive medium and that of lower refractive medium.

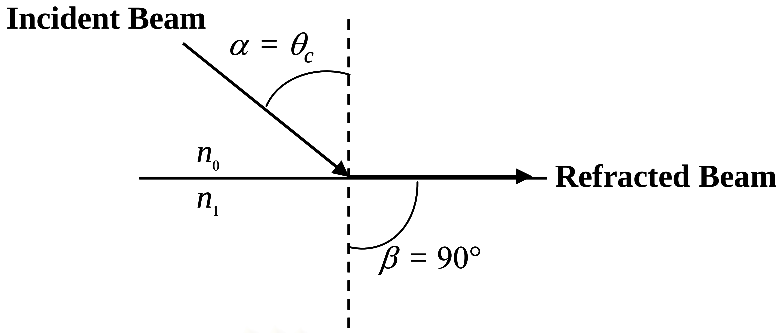


Figure 2.6 The total internal reflection occurs when light travels from higher refractive medium with a reflective index of n_0 and impinges at the surface of the lower refractive medium with a reflective index of n_1 ($n_0 > n_1$) at an angle equals the critical angle.

2.4 Normal Modes of Vibration

The interactions of infrared radiation with material can be understood in terms of changes in dipoles moment of molecule associated with vibrations and rotations of molecule. To learn with a basic model of a molecule, let us say that the masses bond together like the spring. For example of the easy case of diatomic molecules, the molecules have three translational degree of freedom and two rotation degrees of freedom. The atoms of the molecules can be relatively moved such as bond lengths. This is the report of stretching and bending moves that are the same as *vibrations*. A molecule can absorb the infrared radiation when the entrance infrared radiation is of the same frequency as the fundamental modes of vibration of the molecule [48]. The example of the stretching and bending vibrations of organic group, $-CH_2$, are illustrated in Figure 2.7. For a molecule which absorbing infrared radiation it must endure a net change in dipole moment. Vibrations can be subdivided into two types, depending on the bond length or bond angle is changing:

- stretching (symmetric and asymmetric) modes

Asymmetrical stretching

Symmetrical stretching

- bending (scissoring, rocking, wagging and twisting) modes

Scissoring, or bending in-plane

Rocking, or bending in-plane

Wagging, or bending out-of-plane

Twisting, or bending out-of-plane

Figure 2.7 Stretching and bending vibrational modes for a CH_2 group.

2.5 Practical Sampling Techniques of Infrared Spectroscopy for Surface Contamination Analysis

Infrared spectroscopy is the most widely used tool in the world today for the identification of organic compound. Among the reasons for the excellence of the technique is its simplicity, versatility, and accuracy. The functional group of chemical information can be easily collected from an infrared spectrum. Thus, unknown materials can usually be identified. Currently, there are several techniques for obtaining infrared spectra of the samples. Each has its own unique advantages and disadvantages for suitable quality of observed chemical information. The popular sampling techniques for characterization of surface contamination included transmission, and reflection.

2.5.1 Transmission Technique

The transmission technique concerns about passing the infrared light through the material, and detecting that portion of the beam that is transmitted (Figure 2.8). The transmission technique is a widely used technique for the characterization of solid samples in the transmission mode by pressing the sample with a KBr pellet. The compound is placed under high pressure until a pellet were tidily formed (which can be transparent to infrared light). For analysis of surface contamination, this mode is not applicable for surface contaminants because of its destructive nature, required additional sample preparation, long time analysis. Moreover, the required spectra have the interference of substrate.

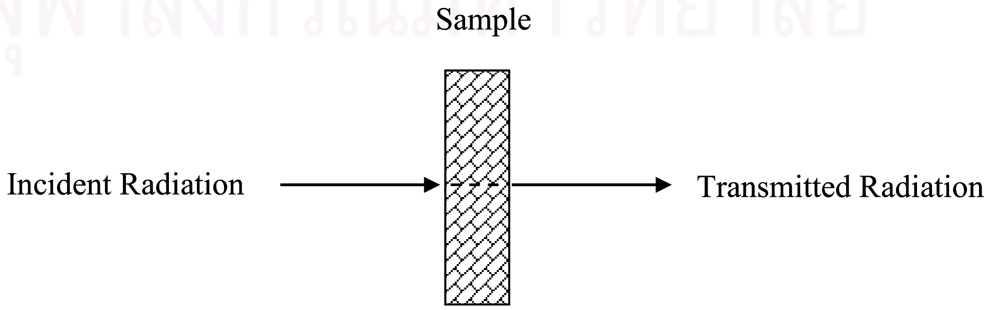


Figure 2.8 Simplified schematic diagram of the transmission measurement.

2.5.2 External Reflection Technique

External reflection infrared spectroscopy is a very rapid and non-destructive determination of the material. External reflection techniques differ from transmission techniques. The infrared beam is bounced off the sample by the angles of incidence are equal to the angles of reflections. The reflection happens at smooth surface such as mirror. For the analysis of surface contamination, if the contaminants are on the surface, a reflection method could be the first technique to identify the unique chemical information of the contaminants. The disadvantages of this technique are that the infrared beam penetrating into the depth of a sample is not accurately known, and difficult to remove the contaminant from the sample so the acquired spectra having interference of substrate.

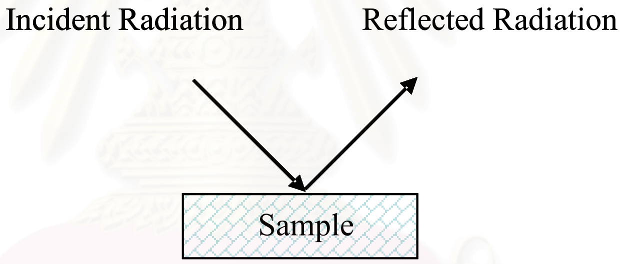


Figure 2.9 Schematic diagram showing external reflection measurement of surface contamination.

2.6 ATR FT-IR Spectroscopy

Surface contamination analysis with vibrational spectroscopic techniques is suitable and more important, because of the acquiring more detailed chemical information. Major advantage of the surface analysis by ATR FT-IR is its ability to give molecular information under ambient atmosphere. This technique is non-destructive and easy to measure.

For ATR FT-IR technique, incident light travels from the IRE, and impinges the IRE/sample interface by incident angle is greater than the critical angle. The phenomenon is defined as total reflection phenomenon when the incident light is totally reflected at the interface of material and IRE, no light travels across the interface and no reflection losses due to absorption. When the sample is absorbing, there is a reflection loss due to absorption by the sample. The phenomenon is defined as attenuated total reflection (ATR) phenomenon when reflectance of the beam leaving interface is less than unity as shown in Figure 2.10.

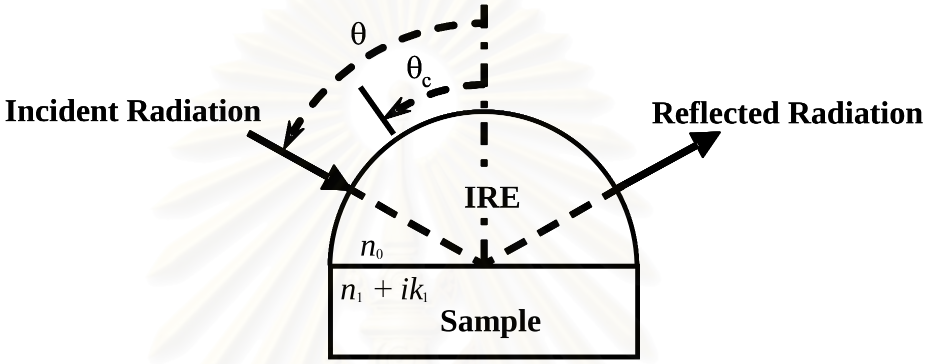


Figure 2.10 Ray tracing under total internal reflection.

Though the lights do not travel across the boundary, there is a strong electric field at the interface region of the IRE and sample. The electric field decays exponentially within a few micrometers from surface of the IRE, this electric field known as the *evanescent field*. Interaction between the evanescent field and the matter is the cause of reflection loss in ATR experiments. This field is very powerful at the interface and exponentially decays as a function of distance from the interface of IRE and sample. The decay of the evanescent field is the unique characteristic that produces the ATR technique as a powerful surface characterization. The decay pattern of the evanescent field can be expressed in terms of the distance from IRE and sample interface by the following expression:

$$\left\langle E_z^2(\theta,\nu)\right\rangle = \left\langle E_0^2(\theta,\nu)\right\rangle e^{-2z/d_p(\theta,\nu)} \tag{2.8}$$

where $d_p(\theta,\nu)$ is the penetration depth. $\left\langle E_0^2(\theta,\nu)\right\rangle$ and $\left\langle E_z^2(\theta,\nu)\right\rangle$ are the mean square evanescent filed at the interface and the depth *z*, respectively. The evanescent field characteristic at the boundary between the IRE, and the sample is shown in Figure 2.11 [49].

The penetration depth is described as the depth where the electric field strength decays to 1/e of its value at the interface of IRE and matter and given in term of material characteristics and experimental parameter by:

$$d_p = \frac{1}{2\pi \nu n_0 \left(\sin^2\theta - (n_1/n_0)^2\right)^{1/2}} \qquad 2.9$$

where ν is the frequency of the infrared radiation and θ is the angle of incidence. The angel of incidence is much greater than the critical angel. From equation 2.9, the penetration depth is inversely varied as ν and simultaneously inversely varied as the square root of sine square of the angel of incidence.

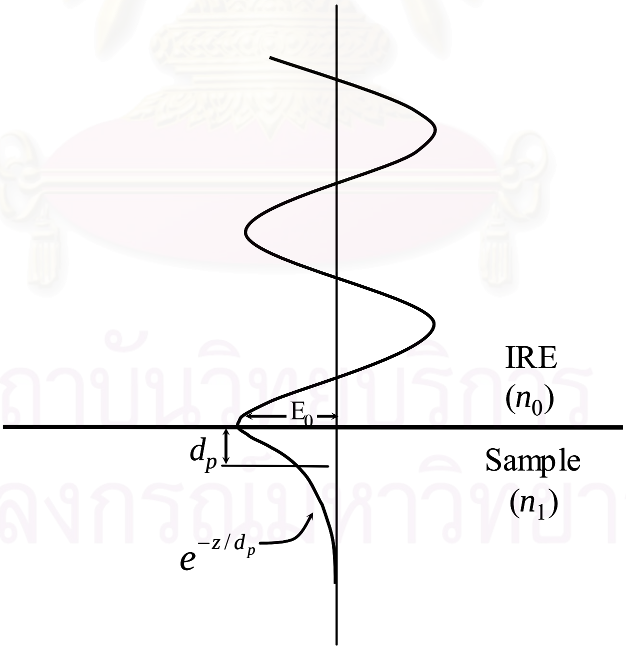


Figure 2.11 The evanescent field at the boundary between the IRE and the sample.

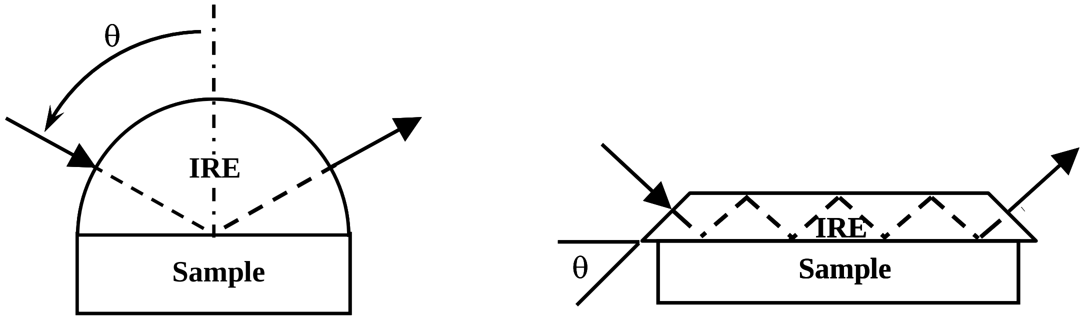
2.7 Internal Reflection Elements (IRE)

The internal reflection element (IRE) is an infrared transparent material used in internal reflection spectroscopy to obtain internal reflection spectra of matters. The internal reflection element (IRE) must have a high reflective index than that of the sample. The IRE must transparent throughout the mid-infrared radiation and also resist physical or chemical contact from samples. Table 2.1 shows the information of optical and mechanical properties of the different IRE [50].

Table 2.1 Properties of materials used for internal reflection elements.

Material	Reflective index At 1000 cm^{-1}	Useful range (cm^{-1})	Maximum use (temperature (°c))	Hardness (kg mm^{-2})
Gemanium	4.02	5,500-600	100	780
Silicon	3.42	8,300-660	300	1150
Zinc selenide	2.43	20,000-460	315	120
Diamond	2.417	45,000-~2,500, ~1650-200	550	8820

Speaking generally, the IRE shape included variable-angle with single reflection and multiple reflection planar crystal (Figure 2.12). When the sample is placed against the IRE, ATR FT-IR spectra are obtained when infrared radiation is coupled into the IRE. The chemical information obtained from the absorption spectrum depends on many factors such as reflective index of IRE, angles of incidence, number of reflections, aperture, number of scans, etc.



A. Single Reflection

B. Multiple Reflection

Figure 2.12 Selected IRE configurations commonly used in ATR experimental setups: (A) single reflection variable-angle hemispherical crystal, and (B) multiple reflection single-pass crystal.

2.8 ATR FT-IR Microspectroscopy

The introduction of microscope which includes high-quality infrared and visible optics has given the applicability of the technique. The present reflectance objectives are available to permit a wide range of analyses on selected area without sample preparation, which are employed wide range within the electronics industry to study materials of interest such as semiconductors, packaging materials, glasses, polymers, adhesives, etc. The advantage of infrared microscope is the selected area for characterization. But some samples are presented the special problems such as composite materials, and rough surface materials. So, the using of general infrared microspectroscopy has the limitation [51].

2.9 Novel ATR FT-IR Microspectroscopy

From the limitations of the conventional ATR FT-IR microspectroscopy, the homemade slide-on diamond μIRE and slide-on Ge μIRE accessories were developed by Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University. The homemade slide-on diamond μIRE, and slide-on Ge μIRE are low cost, having the precision mechanism, removable, and easy to handle. Due to the hole of the homemade slide-on diamond μIRE and slide-on Ge μIRE, the image of the sample can be visualized through an optical microscope. Therefore, a small sample, or a small area on the surface of the sample can be selectively observed.

2.9.1 Faceted Diamond μIRE

A novel technique for ATR FT-IR spectral acquisition by infrared microscope with gem quality faceted round brilliant cut diamond as an IRE. Due to the sharp tip, chemical resistance to any material, strength and hardness of diamond, and it offers optical transparency in mid-infrared region, which are suitable for using as an IRE. Thus, the ATR FT-IR spectra of small sample size, hard sample or roughness sample can analyze by using diamond μIRE. Under the ATR condition, the material was placed against the tip of diamond μIRE. Since the high refractive index of diamond (n_{diamond} = 2.417), the total internal reflection is observed when radiation traveling within the diamond impinges the interface with the angle of incidence greater than the critical angle. The evanescent field exponentially decaying as a function of depth from the surface of the material with lower refractive index and the total internal reflection phenomenon in the diamond IRE were occurred at the pavilion facet instead of the culet (i.e., the sharp tip of the faceted diamond). ATR FT-IR absorption of a material having an optical contact with the pavilion facet can be observed. Thus, it can be versatile employed for characterization of the various materials [52].

For the transparency in mid-infrared region of the diamond, it has three major absorption bands in the mid infrared region, namely **one-phonon** (1400-900 cm^{-1}), **two-phonon** (2650-1500 cm^{-1}), and **three-phonon** (3900-2650 cm^{-1}) absorptions as shown in Figure 2.13. The absorption in the one-phonon region depends on the concentration of nitrogen impurity within the diamond structure. The two-phonon region is the absorption of diamond crystal structure, although is always over absorbing but it has little effect on analytical application because the organic materials do not absorb light in this region. The three-phonon region is very weak therefore the absorption of the diamond has insignificantly impact on the measurement of the sample. The ray tracing of infrared radiation in diamond are shown in Figure 2.14 [53].

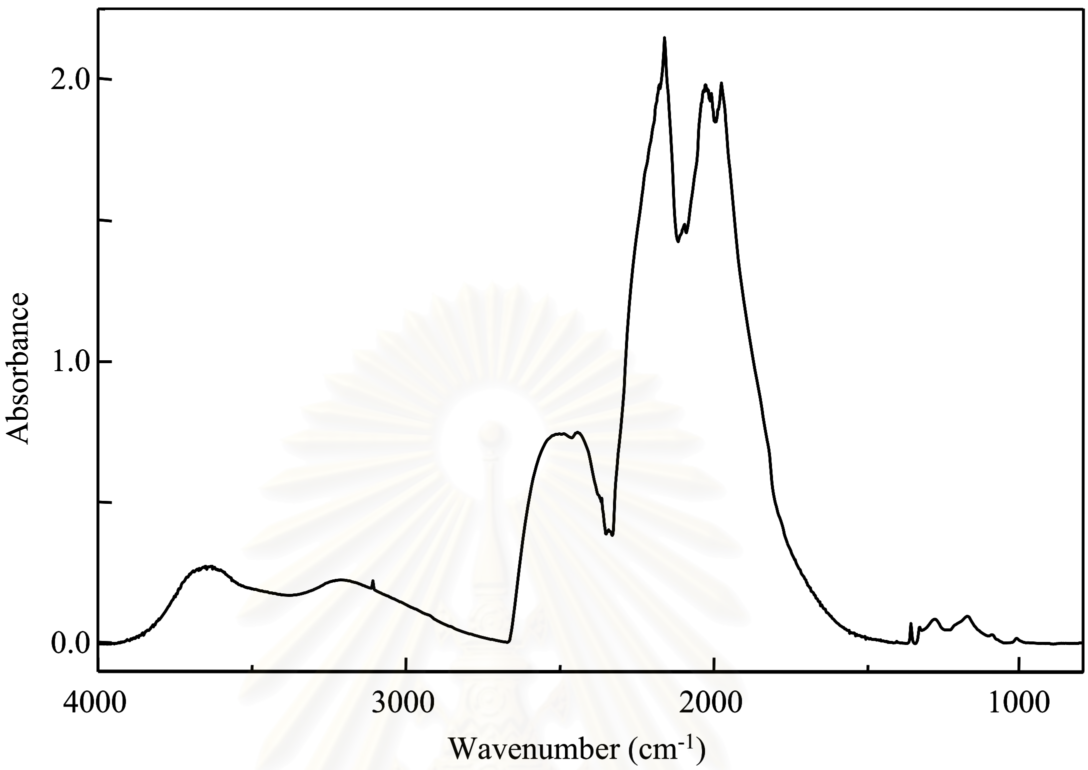
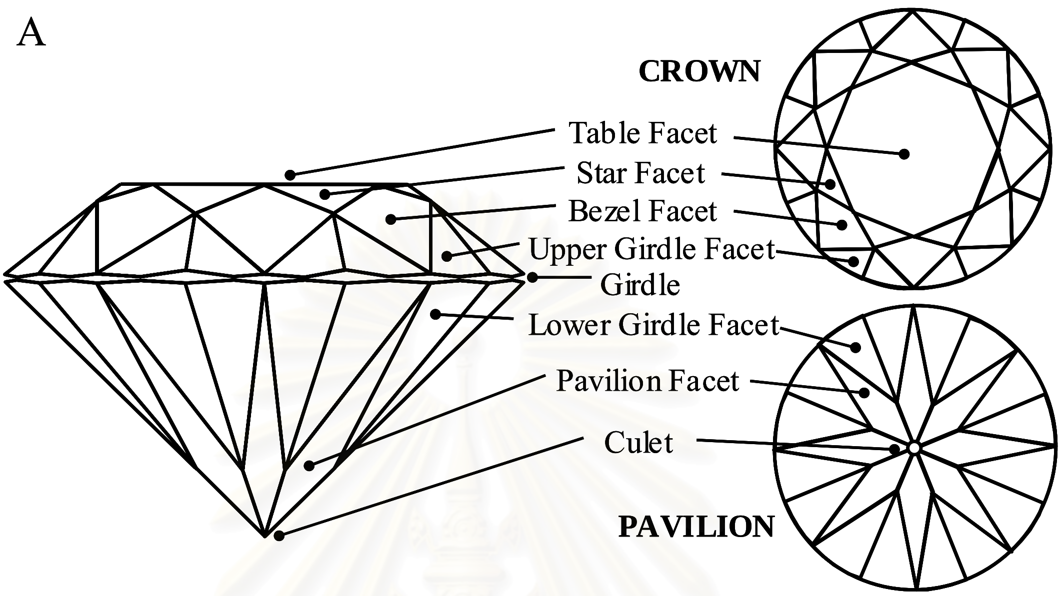
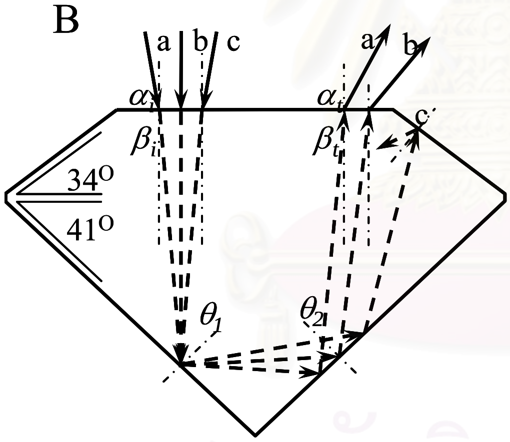


Figure 2.13 Transflectance spectra of diamond μIRE.





Ray	Angle (degree)					
	α_i	β_i	θ_1	θ_2	β_t	α_t
a	4.84	2	43	55	14	35.78
b	0	0	41	57	16	41.77
c	4.84	2	39	59	38	N/A

Figure 2.14 A schematic drawing of a round brilliant cut diamond with: (A) Tolkowsky's recommended cut proportion, (B) Ray tracing of the incident radiations travel within a round brilliant cut diamond and a summary of angles at diamond/air interface.

A schematic illustration of ray tracing within the 15X Schwarzschild Cassegrain infrared objectives, and the coupling of the focused beam to the focus plane with angles of incidence beam ranging from 15.6^{o} to 35.5^{o} are shown in Figure. 2.15 A. When the slide-on diamond μIRE was placed across the infrared beam from the infrared microscope, the ray tracing with in the diamond μIRE are occurred as shown in Figure 2.15 B. The image of the sharp tip of diamond was shown in Figure 2.15 C. Due to the sharp of the diamond tip (~30x30 μm), a very small sample can be analyzed by the slide-on diamond μIRE.

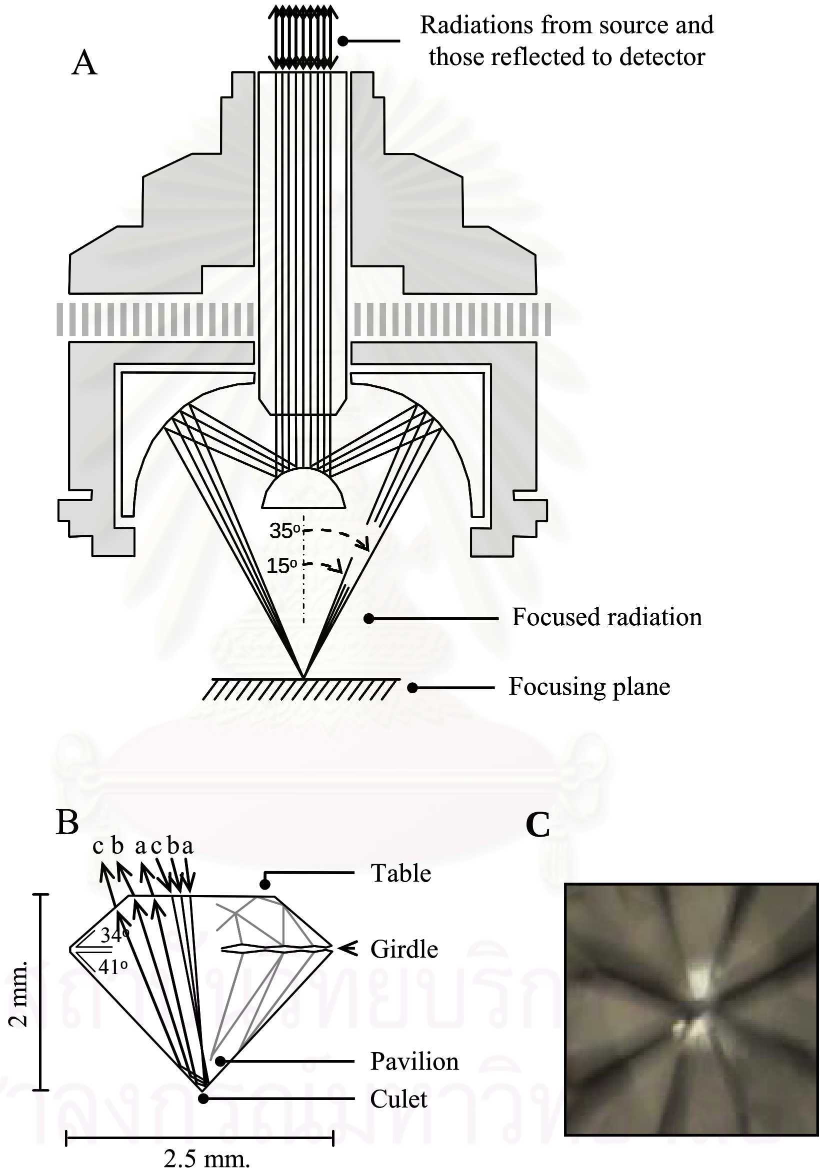


Figure 2.15 A schematic illustration of ray tracing within the slide-on diamond μIRE.

2.9.2 A Dome-Shaped Ge μIRE

The dome-shaped Ge μIRE was developed for ATR FT-IR spectral acquisition by using the focus beam from infrared microscope. A schematic illustration of ray tracing within the 15X Schwarzschild Cassegrain infrared objectives, and the coupling of the focused radiation to the focus plane are shown in Fig. 2.16 A. The objectives microscope focuses the infrared beam to the reflecting plane with angles of incidence beam ranging from 15.6^{o} to 35.5^{o}. A spectral acquisition of sample under the ATR FT-IR condition can be observed when the infrared microscope coupling the focused radiation by the angle of incidence at the sampling surface greater than the critical angle into a specially designed Ge μIRE making of high refractive index materials as shown in Figure 2.16 B. Since the contact area is small (less than 100 μm in diameter, Fig. 2.16 C), a good contact was achieved with a minimal force exerting on the tip. To eliminate the interferences from the internal reflection from the radiation at an angle of incidence smaller than the critical angle, an opaque circular adhesive tape was covered on the center of the hemispherical dome of Ge μIRE. Due to an effective of the coupled radiation and a competency from infrared microscope, ATR FT-IR spectra of a small specimen or a small sample area can be acquired with high spectral quality.

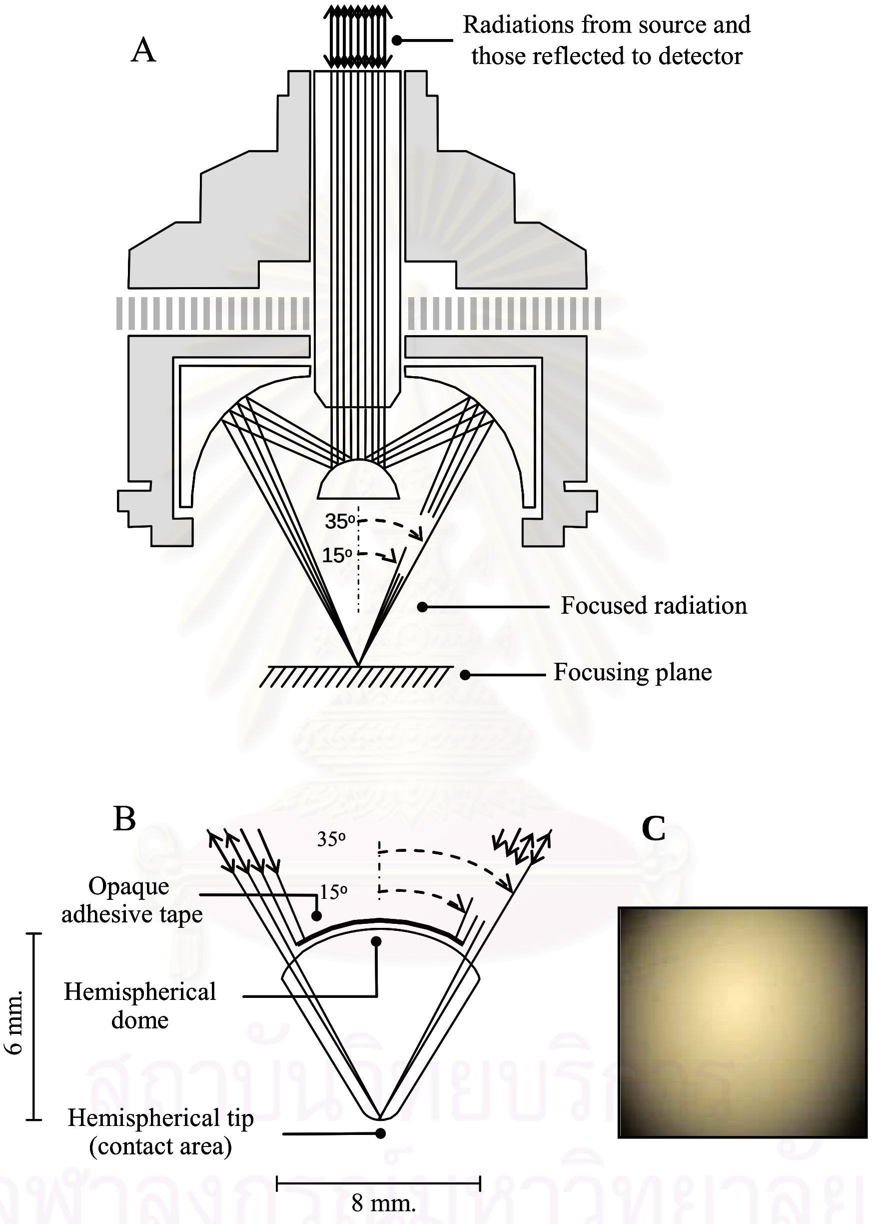


Figure 2.16 A schematic illustration of ray tracing within the slide-on Ge μIRE.

CHAPTER III

EXPERIMENTAL SECTION

Normally, the contaminants are found in many low levels. It is very difficult to clarify their chemical information. Moreover, the cause of contamination is also difficult to study. For studying the surface contamination, various sampling techniques can be employed such as transmission, reflection, and attenuated total reflection techniques. The choice for sampling technique depends on the nature of the sample and the required information. A non-destructive, small sampling technique, short analysis time or internal reflection method is attractive for many uses.

3.1 Materials and Equipments

3.1.1. Samples

1. Food packaging samples
    - 1.1 Coating material (Poly(bisphenol A-co-epichlorohydrin) coated on tin plate)
        - 1.1.1 Uncontaminated coating
        - 1.1.2 Contaminated coating
    - 1.2 Polyethylene bag
        - 1.2.1 Outside surface
        - 1.2.2 Inside surface
    - 1.3 Polypropylene bag
        - 1.3.1 Untreated polypropylene bag
            - 1.3.1.1 Outside surface
            - 1.3.1.2 Inside surface
        - 1.3.2 Thermal treated by microwave radiation at 50, 60, 70, 80, 90 and 100 °C
            - 1.3.2.1 Outside surface
            - 1.3.2.2 Inside surface

        - 1.4 Chopstick (sample with different brand names)
            - 1.4.1 Surface
            - 1.4.2 Peeled by knife
2. Forensic samples
    - 2.1 Zip lock® bag
        - 2.1.1 Uncontaminated Zip lock® bag
        - 2.1.2 Drug-contaminated Zip lock® bag
    - 2.2 Banknote
        - 2.2.1 Uncontaminated banknote
        - 2.2.2 Drug-contaminated banknote
3. Case study sample
    - 3.1 Uncontaminated mobile phone mask
    - 3.2 Contaminated mobile phone mask

3.1.2 Instruments

1. Nicolet 6700 FT-IR spectrometer (Thermo Electron Corporation, Madison, WI, USA) equipped with a mercury-cadmium-telluride (MCT) detector
2. Continuμm™ infrared microscope with 15X Cassegrain infrared objectives and 10X glass objective
3. Variable-angle single-reflection attenuated total reflection accessory (The Seagull™, Harrick Scientific, USA) with a hemispherical Ge IRE.
4. Homemade slide-on diamond μIRE accessory equipped with a gem-quality round brilliant cut diamond μIRE (0.1005 ct type IaB natural diamond)
5. Homemade slide-on Germanium (Ge) μIRE accessory equipped with a miniature cone-shaped Ge μIRE

3.2 Default Spectral Acquisition

Nicolet 6700 FT-IR Spectrometer

Instrumental Setup	
Source	Standard Globar^{TM} Infrared Light Source
Detector	MCT/A
Beam splitter	KBr

Acquisition Parameters	
Spectral resolution	4 cm^{-1}
Number of scans	256 scans
Spectral format	Absorbance
Correction	None

Advanced Parameters	
Zero filing	None
Apodization	Happ-Genzel
Phase correction	Mertz

Continuμm^{TM} infrared microscope

Instrumental Setup	
Objective	15X Schwarzchild-Cassegrain
Aperture size	150 x 150 μm

3.3 Homemade Slide-on Diamond μIRE

The homemade slide-on diamond μIRE consists of two parts as shown in Figure 3.1. The first part is the slide-on housing, which contained quick-released spring loaded that designed for fixing the slide-on diamond μIRE, which is employed for adjusting the still location of the slide-on diamond μIRE in order to obtain a high energy throughput. The second part is the slide-on diamond μIRE that equipped with a gem-quality round brilliant cut diamond IRE (0.1005 ct type IaB natural diamond) which mounted in a stainless steel supporting. The homemade slide-on housing was fixed on the 15X Schwarzschild-Cassegrain infrared objectives and the slide-on diamond μIRE was slid into slide-on housing as shown in figure 3.2. The incident infrared radiation from the infrared microscope is coupled onto the table facet of the diamond μIRE. The amount of light was controlled by the aperture of the microscope. The infrared radiation was focused at the culet of the diamond μIRE. The contact area of the slide-on diamond μIRE was ~30 μm in diameter. Due to the small contact area of the diamond μIRE and the easily operation of the microscope stage (i.e., moving stage up and down), ATR FT-IR spectra of small sample size can be observed. This technique is non-destructive and has short analysis time.

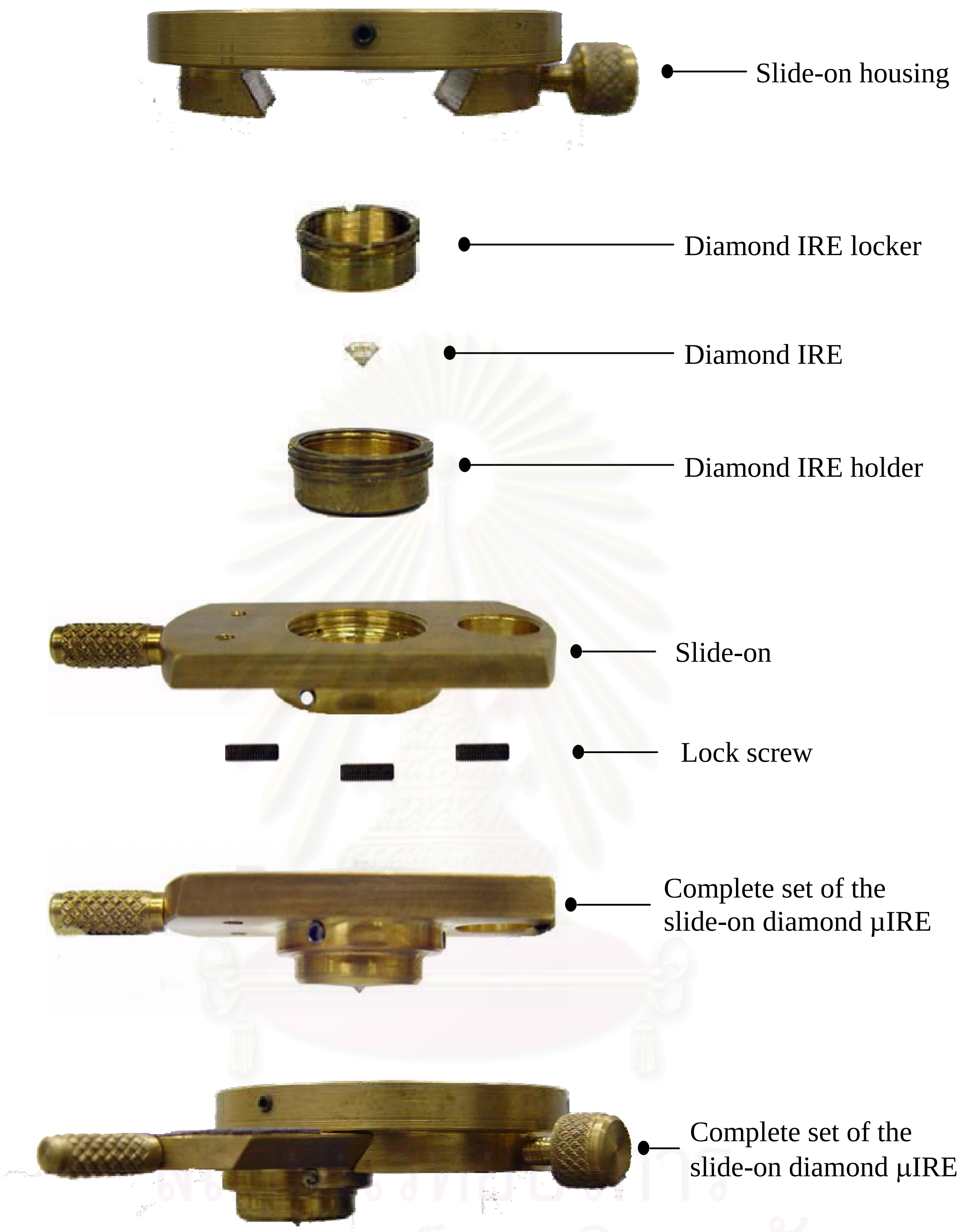


Figure 3.1 The homemade slide-on diamond µIRE accessory.

Figure 3.2 The homemade slide-on diamond μIRE was fixed on the 15X Schwarzschild-Cassegrain infrared objectives: (A) picture of Nicolet 6700 FT-IR spectrometer equipped with infrared microscope, (B) slide-on diamond μIRE was fixed on Continuμm^{TM} infrared microscope, (C) slide-on diamond μIRE was fixed on infrared microscope and aligned to high energy throughput, and (D) infrared microscope.

3.4 Homemade Slide-on Germanium (Ge) μIRE

A homemade slide-on Ge μIRE has the same configuration as that of the homemade slide-on diamond μIRE but the miniature cone-shaped Ge μIRE is employed as the IRE. The homemade slide-on Ge μIRE was fixed on the 15X Schwarzschild-Cassegrain infrared objectives as shown in figure 3.4. The homemade slide-on Ge μIRE is capable for analyzing sample in reflectance mode. The incident infrared radiation from the infrared microscope is coupled onto the tip of the Ge μIRE. The contact area of slide-on Ge μIRE was circular with a contact area of ~100 μm in diameter. Due to the effectiveness coupled radiation under the ATR condition at the tip, a spectral acquisition of a small specimen or a small sample area with excellent spectral quality can be observed. The small contact area of the Ge μIRE and the easy procedure of the microscope making the analysis is non-sample preparation, non-destructive, and has short analysis time.

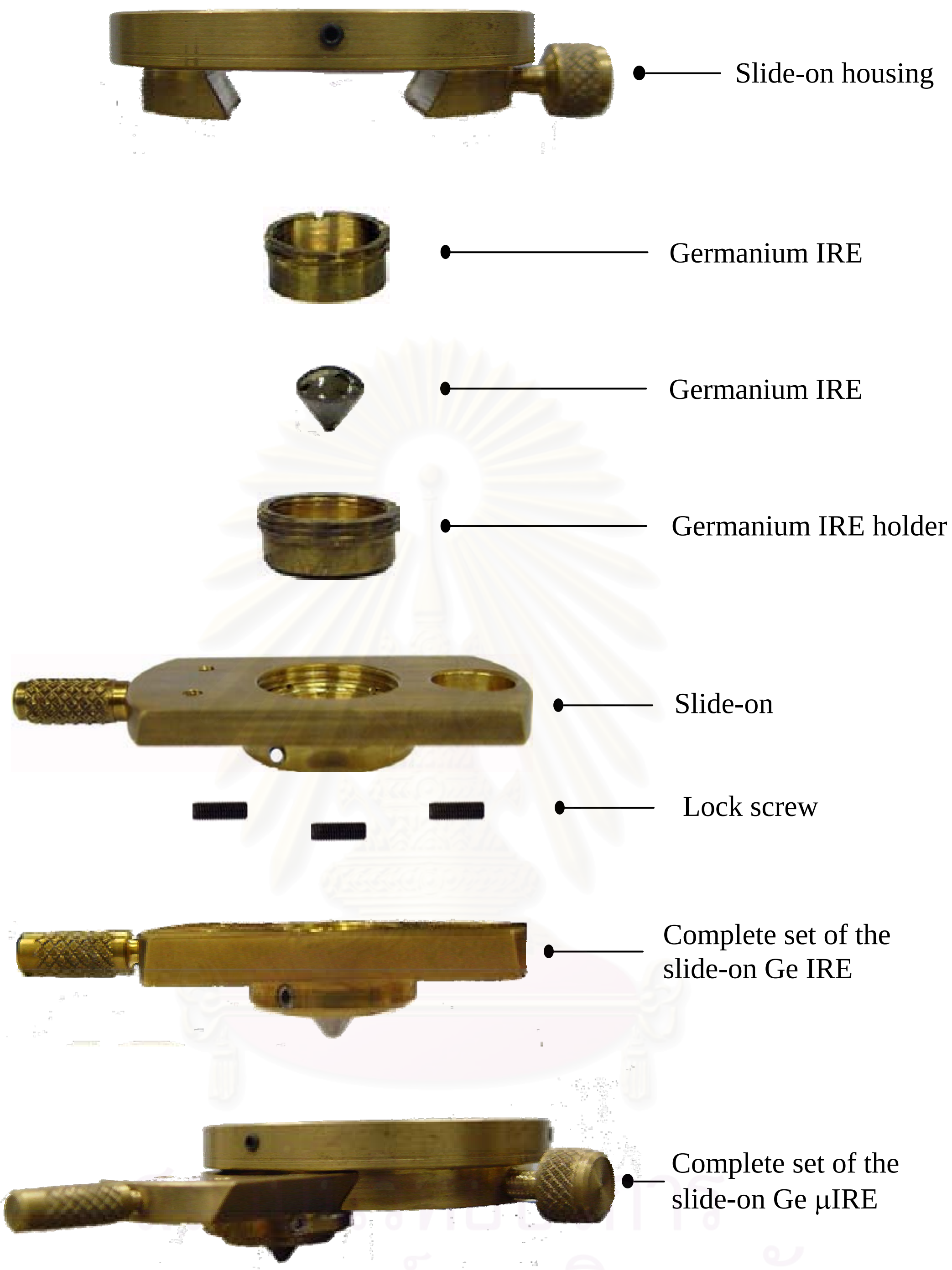


Figure 3.3 The homemade slide-on Ge μIRE accessory.

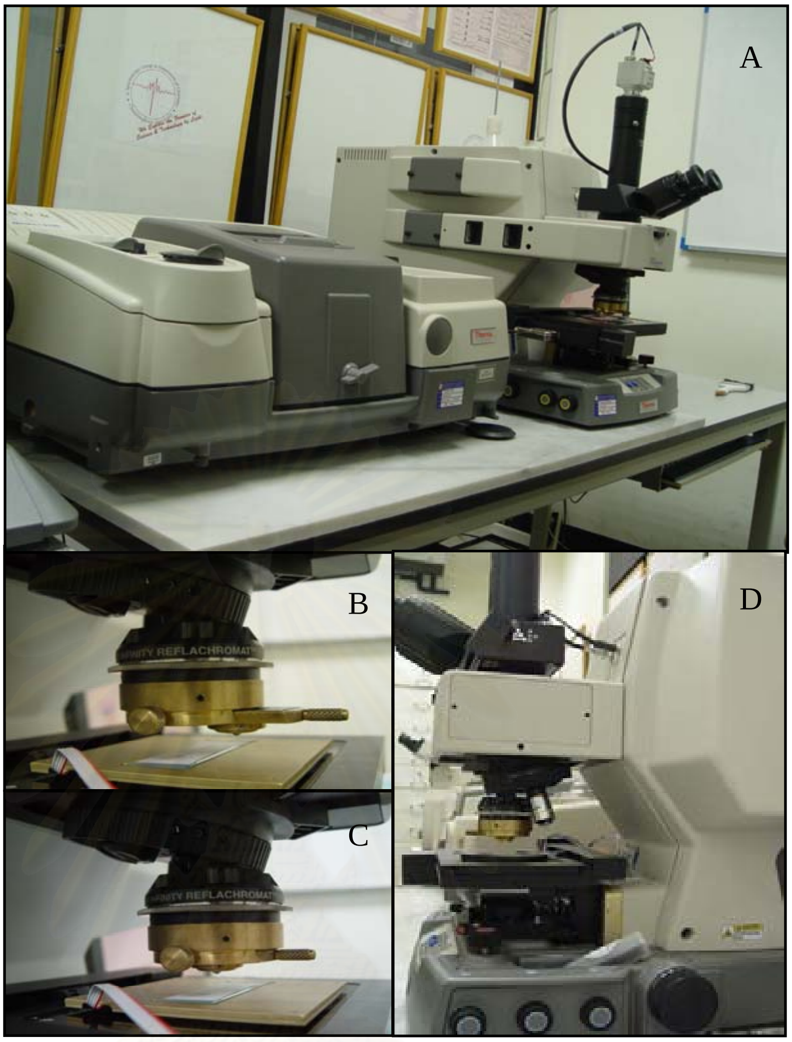


Figure 3.4 The homemade slide-on Ge µIRE was fixed on the 15X Schwarzschild-Cassegrain infrared objectives: (A) picture of Nicolet 6700 FT-IR spectrometer equipped with Continuµm^{TM} infrared microscope, (B) slide-on Ge µIRE was fixed on Continuµm^{TM} infrared microscope, (C) slide-on Ge µIRE was fixed on Continuµm^{TM} infrared microscope and aligned to high energy throughput, and (D) infrared microscope.

3.5 Surface Characterization by FT-IR Spectroscopy

3.5.1 Experimental Procedure for Transmission Technique

For the transmission experiment, the spectrum of a sample was performed by the Nicolet 6700 FT-IR spectrometer. Due to the thin film of polypropylene is transparent, this sample was not required additional sample preparation (grinded and pressed with a KBr pellet). For getting the spectral acquisition of sample, the sample was mounted on a sample holder and spectrum was acquired with resolution of 4 cm^{-1} at 32 scans.

Figure 3.5 Nicolet 6700 FT-IR spectrometer for transmission technique**.**

3.5.2 Experimental Procedure for External Reflection Technique

The external reflection spectrum was acquired by a Continuμm^{TM} infrared microscope that attached to the Nicolet 6700 FT-IR spectrometer. The microscope was operated in the reflection mode. Reflection with normal incidence from a gold mirror was exploited as a background spectrum (Figure 3.6 B). Appropriating background was obtained for each series of sample measurements with the same apertures conditions. For getting the spectral acquisition of sample, the sample was placed on the stage of microscope (Figure 3.6 C). The sample was perpendicularly aligned to the incidence radiation by using the adjusting knobs in order to obtain a high energy throughput. The infrared radiation was coupled in to the sample by a built-in 15X Cassegrain infrared objective.

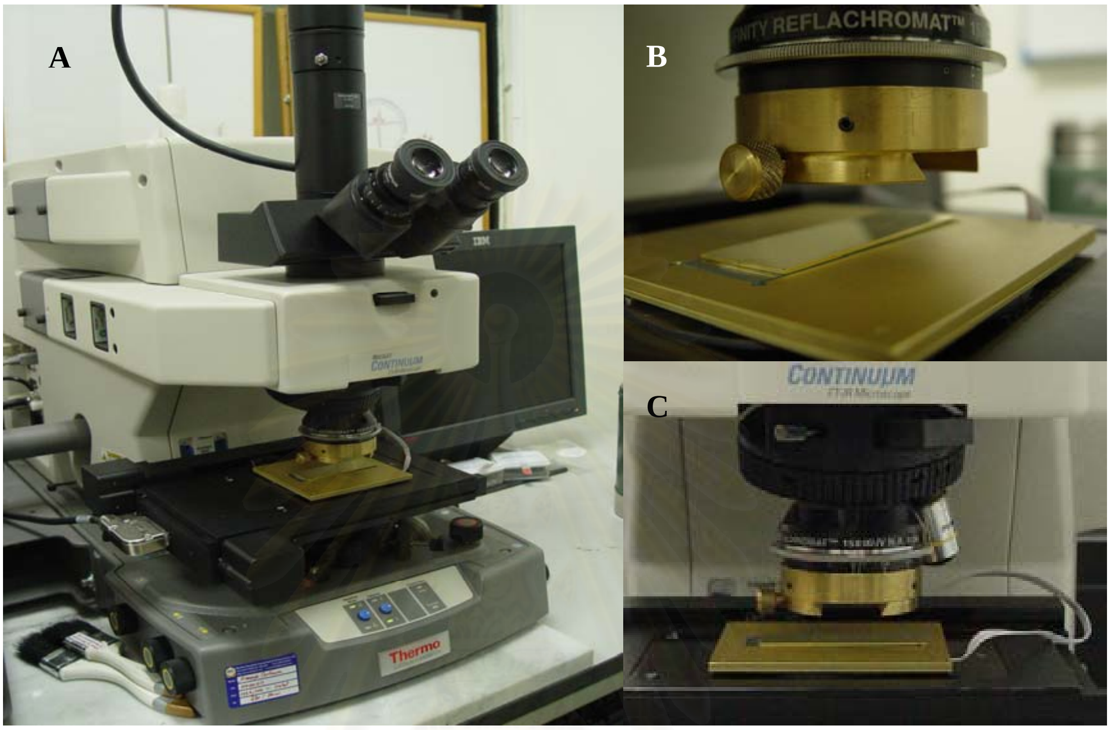


Figure 3.6 Experimental procedure for external reflection technique: (A) picture of Continuμm^{TM} infrared microscope, (B) gold mirror used for background, and (C) collect spectrum of tin plate.

3.5.3 Experimental Procedure for the Conventional ATR Technique

For the conventional ATR experiment, a commercial ATR accessory (the Seagull^{TM}, Harrick Scientific, USA) with a hemispherical Ge IRE was employed for all conventional ATR spectral acquisition. The Seagull^{TM} accessory (Figure 3.8 B) was placed in the compartment of the spectrometer as shown in Figure 3.8 C. Since the angle of incidence in the ATR experiment must be greater than the critical angle, the infrared radiation was coupled through the hemispherical Ge IRE at the angle of 30^{o}. The single beam spectrum from the Ge IRE without sample was employed as a background for all acquired ATR FT-IR spectra. For getting spectral acquisition of contaminants, an aluminium plate was placed against the bottom surface of the hemispherical Ge IRE. The pressure is applied onto the sample in order to ensure an optical contact between the sample (uncontaminated coating or contaminated coating) and the IRE, and ATR spectra of the sample were collected. After that the sample was removed from hemispherical Ge IRE, and made sure that the removable substance contacted with hemispherical Ge IRE, and then collected spectrum.

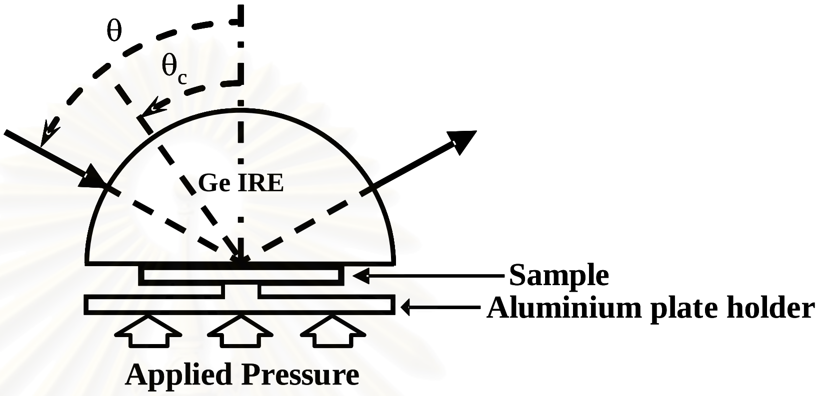


Figure 3.7 Experimental procedure for ensuring the optical contact between a sample and the hemispherical Ge IRE.

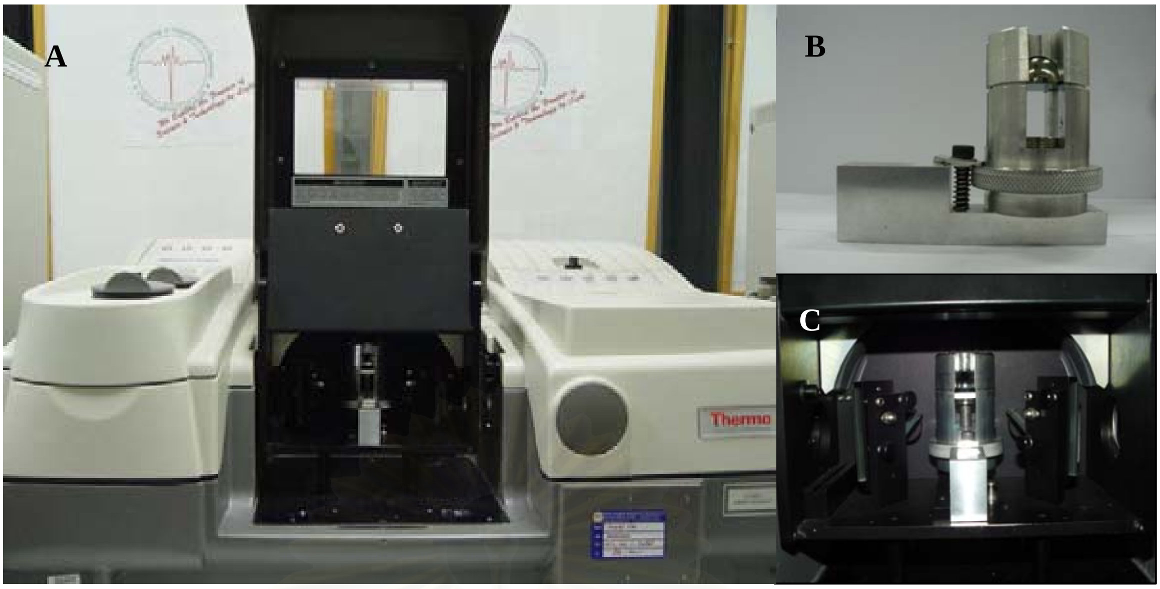


Figure 3.8 A commercial ATR accessory (the Seagull^{TM}, Harrick Scientific, USA) with a hemispherical Ge IRE for conventional ATR technique: (A) picture of spectrometer, (B) hemispherical Ge IRE was fixed on holder, and (C) The Seagull^{TM} accessory.

3.5.4 Experimental Procedure for a Homemade Slide-on Diamond µIRE

The spectrum of a sample was performed by a Continuµm^{TM} infrared microscope that attached to the FT-IR spectrometer. When performing the infrared microscopy with the slide-on diamond µIRE, the slide-on diamond µIRE was slid into the position, and fixed on the built-in 15X Schwarzschild Cassegrain infrared objective. A background spectrum was collected through the slide-on diamond µIRE without sample. The analyzing procedures were performed by the following three modes: firstly, a survey mode - the sample is put on the stage of the microscope for viewing and selecting the sampling area to analyze; secondly the contact mode - the stage is raised, the sample is brought into close contact with the diamond µIRE. The elevation was stopped when the sensor plate indicated an onset of a critical pressure on the sensor plate. Thirdly, an ATR mode - for infrared analysis, the ATR FT-IR spectrum of the specimen at the position of good contact was collected. To achieve the same degree of contact for all measurements, a contact alert sensor plate was employed.

Due to the small contact area of the diamond µIRE and operation of the microscope is easily performed (i.e., moving stage up and down), a novel procedure called “***contact-and-collect***” technique was developed in order to non-destructively measure spectra of surface contaminations. When the tip of the diamond µIRE was brought into an optical contact with a surface of sample, some of the contaminants on the surface (i.e., dusts, small particles, and/or a thin removable film) were stuck with the µIRE. These contaminants can be cumulatively collected on the tip by repeating contacts at various positions on the surface. To enhance the collecting efficiency of contaminant on a surface, a thin film of viscous liquid such as mineral oil or fluorolube (both of them have simple spectral envelops, easy molecular information and ready available in any laboratory) was employed as a collecting agent. By planting a thin film of the liquid at the tip of the IRE, contaminants on the surface can be transferred onto the diamond tip upon a soft contact. To effectively control the size of a collecting agent, a thin film of the collecting agents was smeared on a glass slide and brought into an optical contact with the µIRE. When removing the glass slide, a thin liquid film was left on the tip of the µIRE and repeating the contacts at various positions on the surface at several times.

3.5.5 Experimental Procedure for Homemade Slide-on Germanium (Ge) µIRE

A homemade slide-on Ge µIRE was employed for all spectral acquisitions. The spectrum of a sample was performed as the use of slide-on diamond µIRE experimental procedure. The smooth surface of the tip of Ge µIRE can be easily scratched and damaged, thus an excellent care must be taken when making a contact with sample. It is noted that the contact alert sensor plate also prevents a possible damage of the brittle surface of the slide-on Ge µIRE.

CHAPTER IV

RESULTS AND DISCUSSION

Analytical detection of trace amount or surface contamination of material is important for application in food and pharmaceutical industries, forensic science, crime prevention, and security measurements. Vibrational spectroscopic method such as Fourier transform infrared (FT-IR) spectroscopy is one of the most powerful techniques usable for chemical information identification due to the real chemical specificity of these methods [54].

4.1 Characterization of Contaminants on Coating Tin Plate

4.1.1 External Reflection Technique

Infrared microspectroscopy has been widely used in the semiconductor industry and food industry for many years. In addition, the reflectance objectives are now available for permitting a wide range of analyses on a selected surface area without sample preparation. For polymer-coated metal of food packaging, FT-IR reflection spectrum of uncontaminated polymer-coated metal for food packaging was shown in Fig. 4.1 A. FT-IR spectrum of the contaminated polymer-coated metal, which having fine powder contaminants on the surface was shown in Fig 4.1 B. When viewing with an oblique or grazing angle, the reflecting surface of the contaminated coating appeared white. When viewing with right angle, both metals appeared the same. Since the metal substrate was reflective, the specular reflection spectra of both coating acquired with the microscope showed absorption-like spectral features. The observed spectra did not reveal any significant difference. Due to the thickness of the coating, their absorptions were very high and out of linear range. As the results, the subtracted spectrum in Fig. 4.1 C did not show any signals of the contaminated powder. The subtracted spectrum in Figure 4.1 C showed the same spectral features as that of the coating. This is due to the difference of the coating thickness and nonlinearity effect of the high absorbance. The reflection technique does not appropriate for surface contamination of this type.

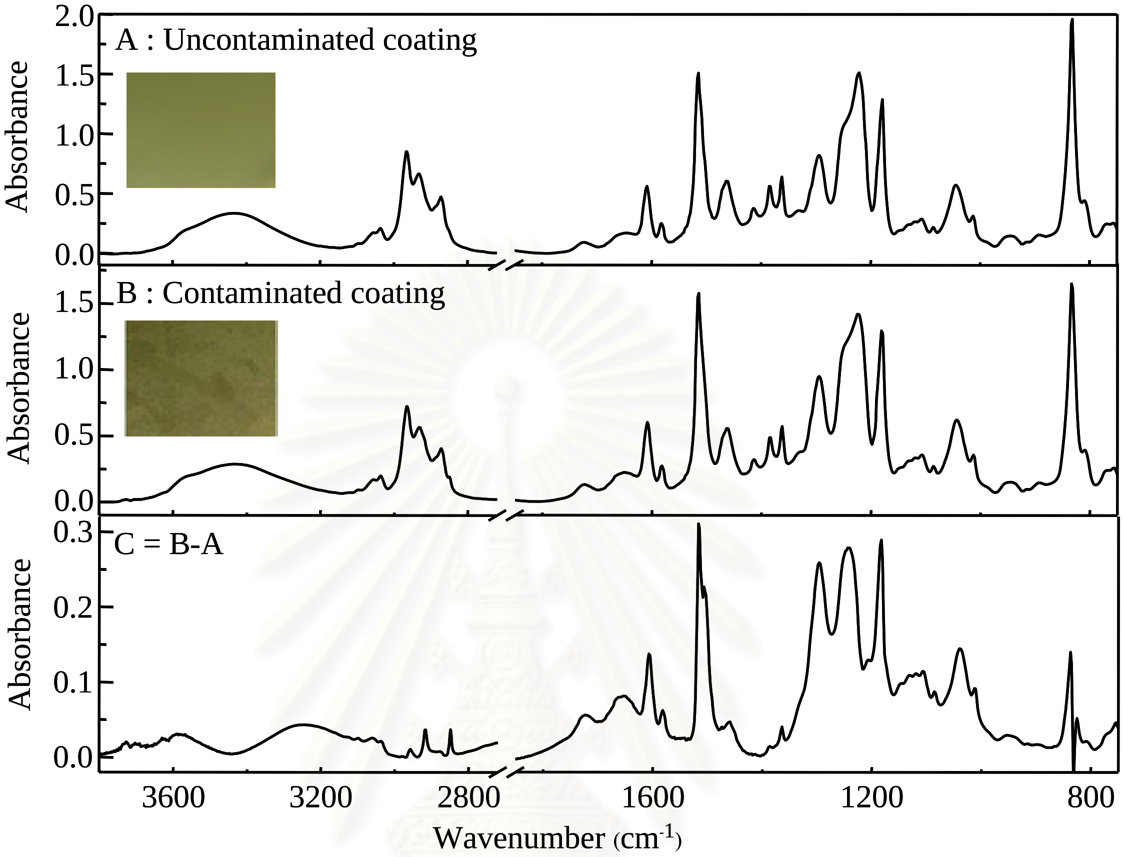


Figure 4.1 FT-IR spectra of coating material on tin plate acquired by reflection technique: (A) spectrum of uncontaminated coating, (B) spectrum of contaminated coating, and (C) the subtracted spectrum.

4.1.2 Conventional ATR Technique

Fig. 4.2 A shows ATR FT-IR spectra of the same polymer-coated metals shown in Fig 4.1. Although the same spectral features were observed, the contaminated coating did reveal the distinct absorptions in the CH-stretching region at 2918 and 2850 cm^{-1}. After removing the sample from the commercial hemispherical Ge IRE, any separable or removable contaminants are collected on hemispherical Ge IRE while its unique spectral feature can be acquired without any influence from the substrate. The observed spectrum of removable contaminants on the contaminated coating revealed the distinct absorptions in the CH-stretching region at 2918 and 2850 cm^{-1}. The intensity of residual peaks in CH-stretching region are less than the intensity of CH-stretching region of uncontaminated coating peak because the total residue was not accompanied with surface of hemispherical Ge IRE. Since there was no contamination on the uncontaminated coating, there was no significant absorption features in the CH-stretching region of the observed spectrum after the contact between the IRE and the specimen. The conventional ATR technique is appropriate for characterization of surface contamination. However, this technique requires a sample preparation because a hard and the rigid of tin plate can scratch the surface of hemispherical Ge IRE.

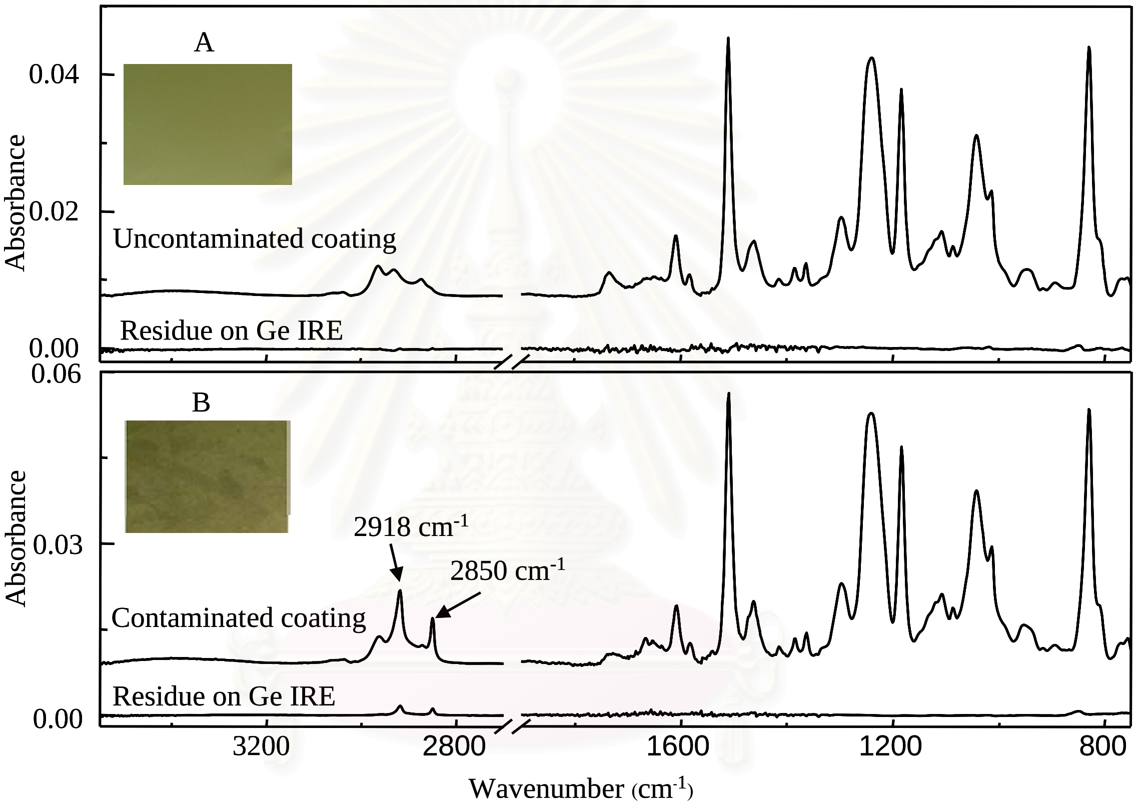


Figure 4.2 ATR FT-IR spectra of coating material on tin plate acquired by convention ATR technique: (A) spectrum of uncontaminated coating and residue, and (B) spectrum of contaminated coating and residue.

4.1.3 Homemade Slide-on Diamond μATR Technique

A gem quality round brilliant cut natural diamond was employed as an IRE for ATR measurement. The transflectance spectrum of the diamond IRE is shown in Figure 4.3 A.

In the current spectral acquisition with the homemade slide-on diamond μIRE, the specimen was simply brought into contact with the diamond μIRE and the ATR spectrum was acquired. The single beam spectrum from the slide-on diamond μIRE without sample was employed as a background for all acquired ATR FT-IR spectrum. The ATR spectrum of coating material on tin plate attached to the culet of homemade slide-on diamond μIRE is shown in Figure 4.3 B. However, the ATR spectrum acquired by the homemade slide-on diamond μIRE was noticed the high noise level in the two-phonon region. This is due to the saturated absorption of the diamond. The results indicated that an infrared spectrum of a sample can be acquired by the slide-on diamond μATR technique.

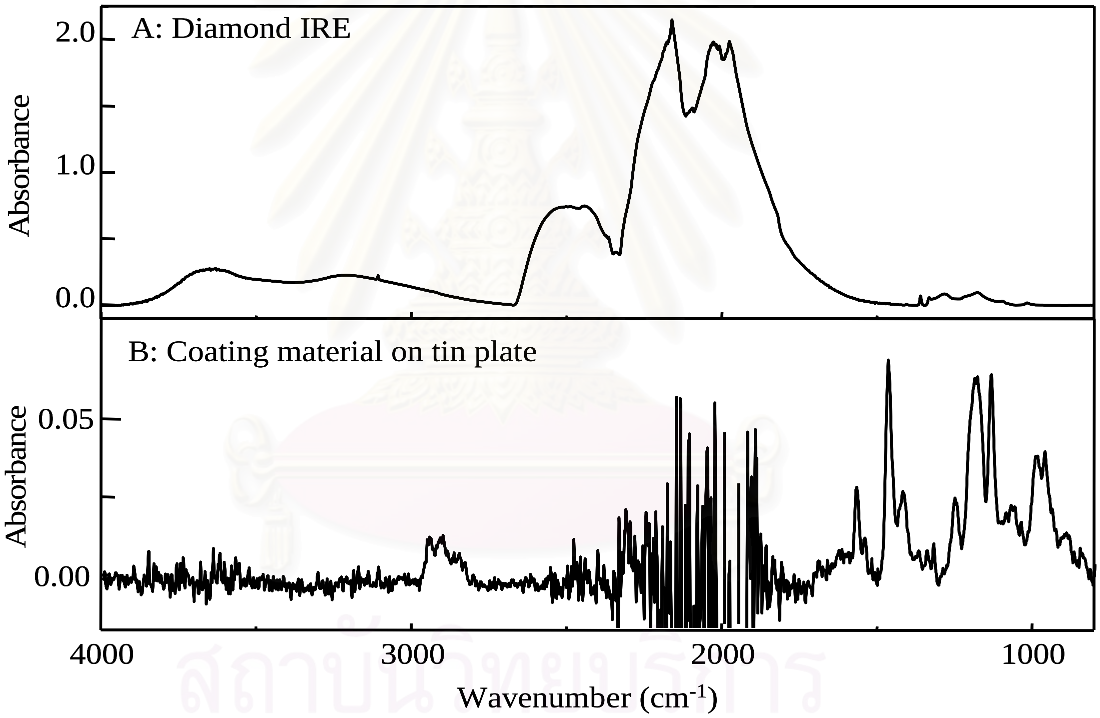


Figure 4.3 ATR FT-IR spectra of coating material on tin plate acquired by homemade slide-on diamond μIRE: (A) spectrum of diamond μIRE, and (B) spectrum of coating material on tin plate.

After collecting spectrum, the observed spectra of coating material did not show any significant difference. The spectrum of contaminated coating did not show any peak of contaminants, due to the small sampling area of diamond μIRE and the contaminants on specimen are dispersed. Thus, the peak of contaminants cannot be observed (Figure 4.4). The analysis of surface contamination by homemade slide-on diamond μIRE is not appropriated of this sample because the distribution of contaminants on contaminated coating which is difficult to analyze the selected area and cannot observe the contaminants spectra without interference of substrate.

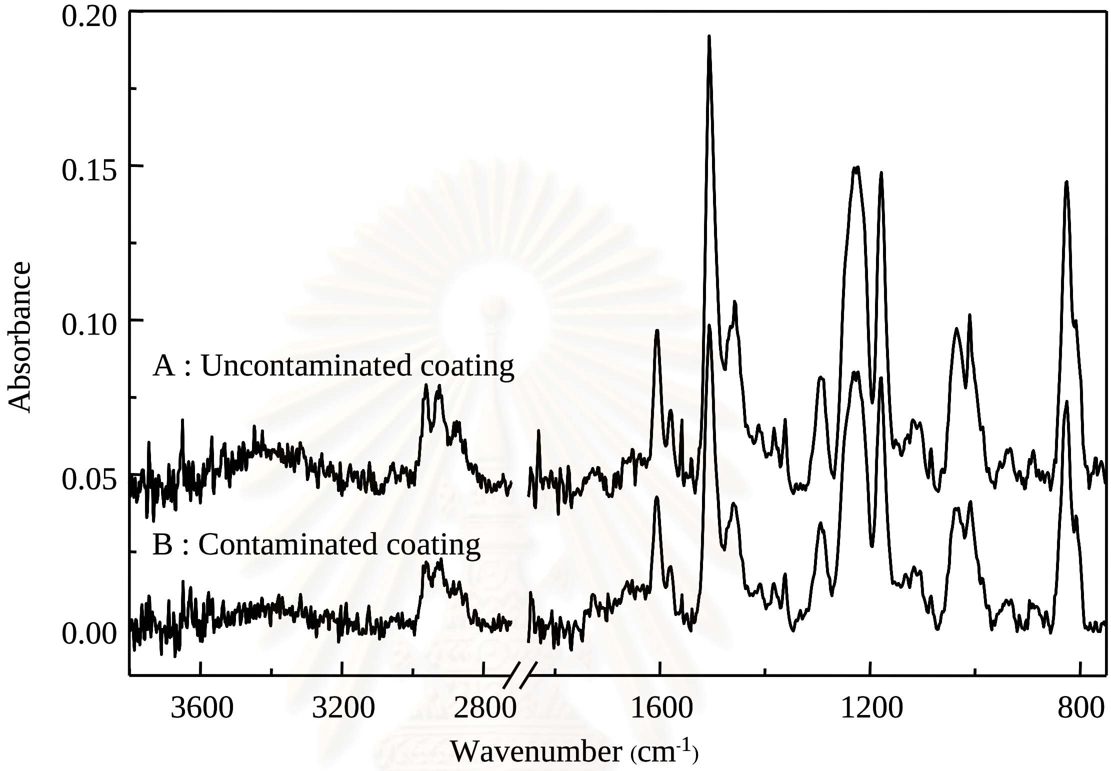


Figure 4.4 ATR FT-IR spectra of coating material on tin plate acquired by slide-on diamond μIRE: (A) spectrum of uncontaminated coating, and (B) spectrum of contaminated coating.

Due to the limitation of the prior operation, the novel operation was developed. The novel operation technique which separating of the contaminants by a physical or chemical means might induce the additional contaminations from the polymeric substrate and without interference of substrate; a nondestructive technique called the "*contact-and-collect*" technique was developed, and employed. A thin film of an organic liquid with a simple spectral envelop (i.e., mineral oil and fluorolube) was utilized as a collecting agent for accumulately pickup the removable contaminants (i.e., powders and thin film). By simply bringing the investigated surface into contact with the coated diamond μIRE, any separable or removable contaminant will be stuck at the tip of the μIRE. Once, a large amount of the contaminant was collected (i.e., by making a large number of contacts), its unique spectral feature can be acquired without any influence of the substrate.

Fig 4.5 shows ATR FT-IR spectra of the collecting of residue on the surface of the slide-on diamond μIRE. For the uncontaminated coating, there was no collecting residue on the clean μIRE (Fig. 4.5 A1), the mineral-oil-coated IRE (Fig 4.5 A2) and the fluorolube-coated IRE (Fig. 4.5 A3). For the thin-film-coated IRE, the amount of the collecting agent was decreased after a subsequently contact. The unchanged spectral envelops suggested that the surface of the polymeric coating was free of the contaminant.

For the contaminated surface (Fig. 4.5 B), the fingerprint absorption of the contaminant can be observed by the "*contact-and-collect*" operation. Though the contaminant powder cannot be picked up by the clean μIRE (Fig. 4.5 B1), it can be collectively picked up at the tip of the mineral oil or fluorolube coated diamond μIRE (Figs. 4.5 B2 and 4.5 B3). While the absorptions associated with the collecting agents decreased after applying a subsequently contact, those associated with the contaminant was increased. When the mineral oil was employed as a collecting agent (Fig. 4.5 B2), the CH-stretching of mineral oil was overlapped with that of the contaminant. However, the symmetric stretching and the asymmetric stretching of the methylene group shift to that of the contaminant (i.e., absorptions at 2918 and 2850 cm^{-1}) as the mount of the contaminant was increased via the subsequently contacts. The speculation that the absorptions at 2918 and 2850 cm^{-1} being associated with the contaminant was confirmed by Fig. 4.5 B3. When confirming by fluorolube, the band due to the C-F stretching vibration does not have an absorption in the CH stretching region, was employed as a collecting agent. The increased absorptions at 2918 and 2850 cm^{-1} were directly associated with the contaminants. The coupled between spectrometer and microscope are suitable and successful to determine the trace of surface contamination. This operation without required sample preparation, very rapid analysis and can be characterize the trace material without interference of substrate.

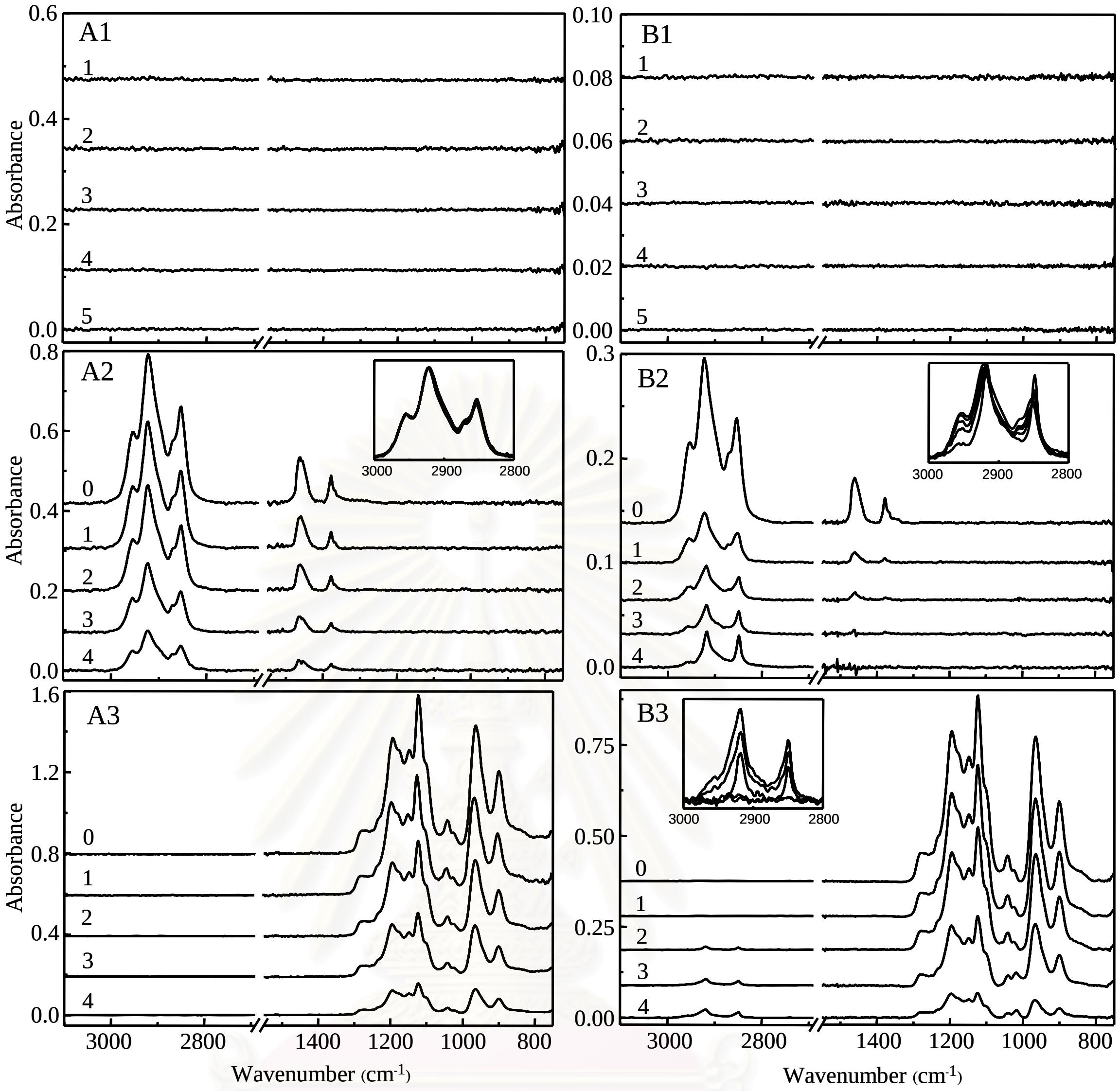


Figure 4.5 ATR FT-IR spectra of collecting residue on the surface of the slide-on diamond μIRE: (A1, A2, A3) spectra of uncontaminated coating contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively; and (B1, B2, B3) spectra of contaminated coating contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

4.1.4 Homemade Slide-on Ge μATR Technique

The novel internal reflection elements (IRE) made of a cone-shaped Ge was employed for ATR FT-IR spectral acquisition using an infrared microscope. Fig. 4.6 shows ATR FT-IR spectra of the polymer-coated metals. Although the same spectral features were observed, the contaminated coating revealed the distinct absorptions in the CH-stretching region at 2918 and 2850 cm^{-1}. Fig. 4.6 C, the subtracted spectrum did show the signature of the contaminated powder. However, the subtracted spectra in Figure 4.6 C did not show any uniquely feature of the contaminant due to the interference of the substrate in the fingerprint region. This technique does not appropriate for surface contamination of this operation.

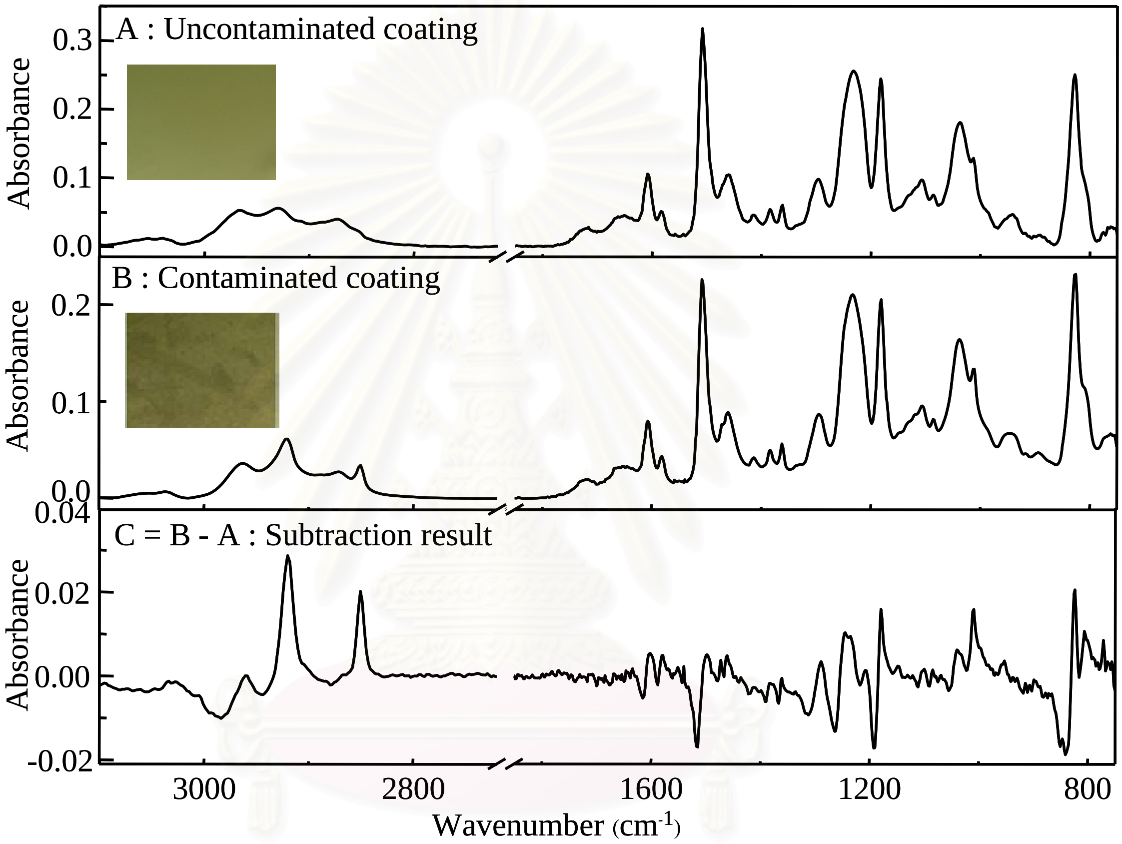


Figure 4.6 FT-IR spectra of coating material on tin plate acquired by slide-on Ge μATR technique: (A) spectrum of uncontaminated coating, (B) spectrum of contaminated coating, and (C) subtracted spectrum between uncontaminated and contaminated coating.

Due to the small sampling area of the slide-on Ge μIRE, a sample with small size can be analyzed. Contamination (powder or thin film) on a surface can be deposited on the tip of the Ge μIRE by direct deposition or by using an organic liquid (i.e., mineral oil or fluorolube) to pick-up the contaminants from the sample surface. Fig 4.7 shows ATR FT-IR spectra of collecting residue on the surface of the slide-on

Ge μIRE. It shows any uniquely feature of the contaminant. The spectral acquisitions have the same trend of the slide-on diamond μATR technique.

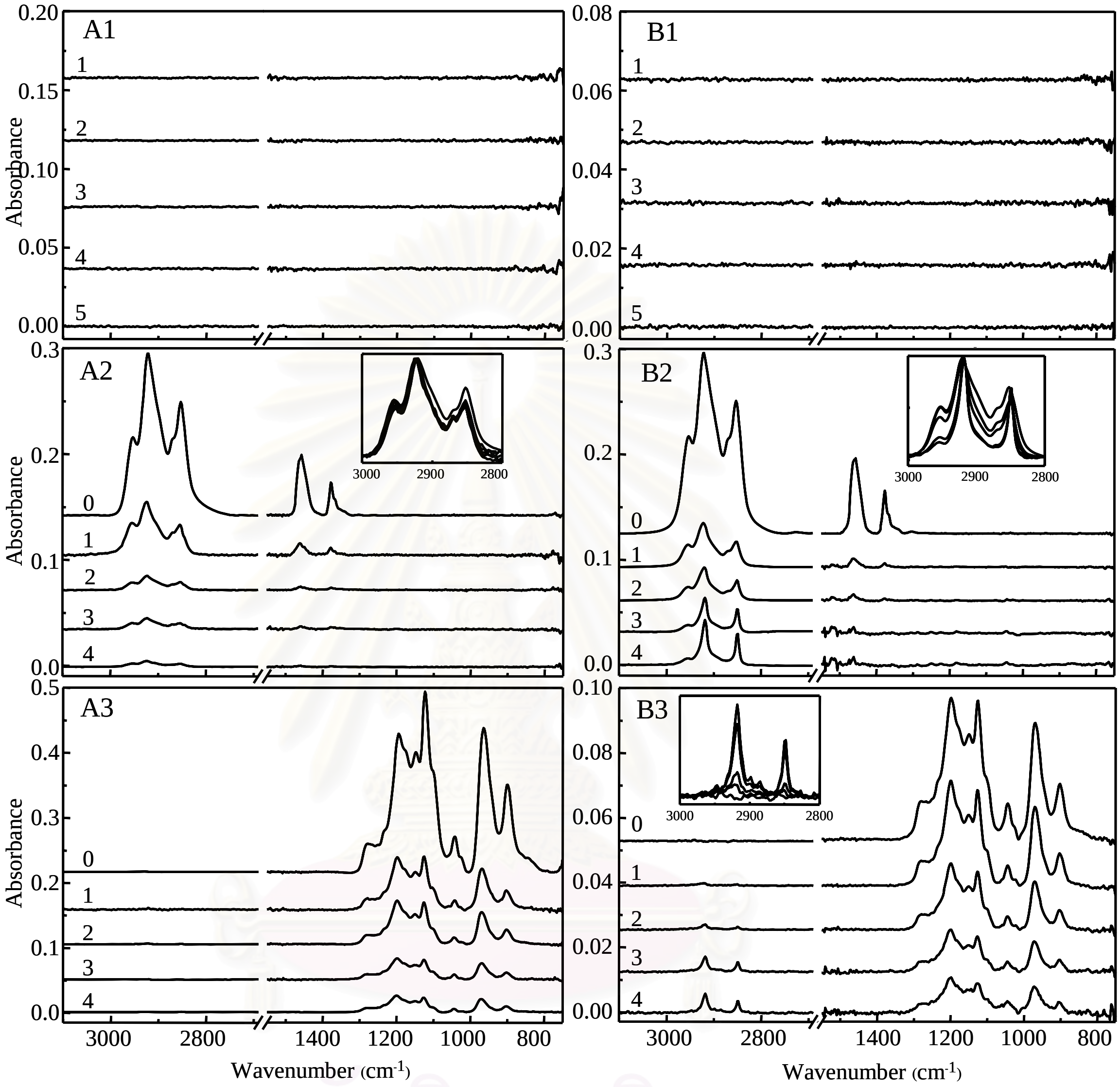


Figure 4.7 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge μIRE: (A1, A2, A3) spectra of uncontaminated coating contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively and (B1, B2, B3) spectra of contaminated coating contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

The *“contact-and-collect”* technique using the slide-on diamond μIRE and the Ge μIRE was successfully employed for surface contamination of coating material. Due to the sticky of collecting agent, this operation can separate contaminants without any interference of their substrate. The *“contact-and-collect”* technique was operated under physical attraction due to the small contact area of the μIRE and the easy operation of the microscope stage (i.e., moving stage up and down). Moreover, sampling area of the surface can be selectively analyzed.

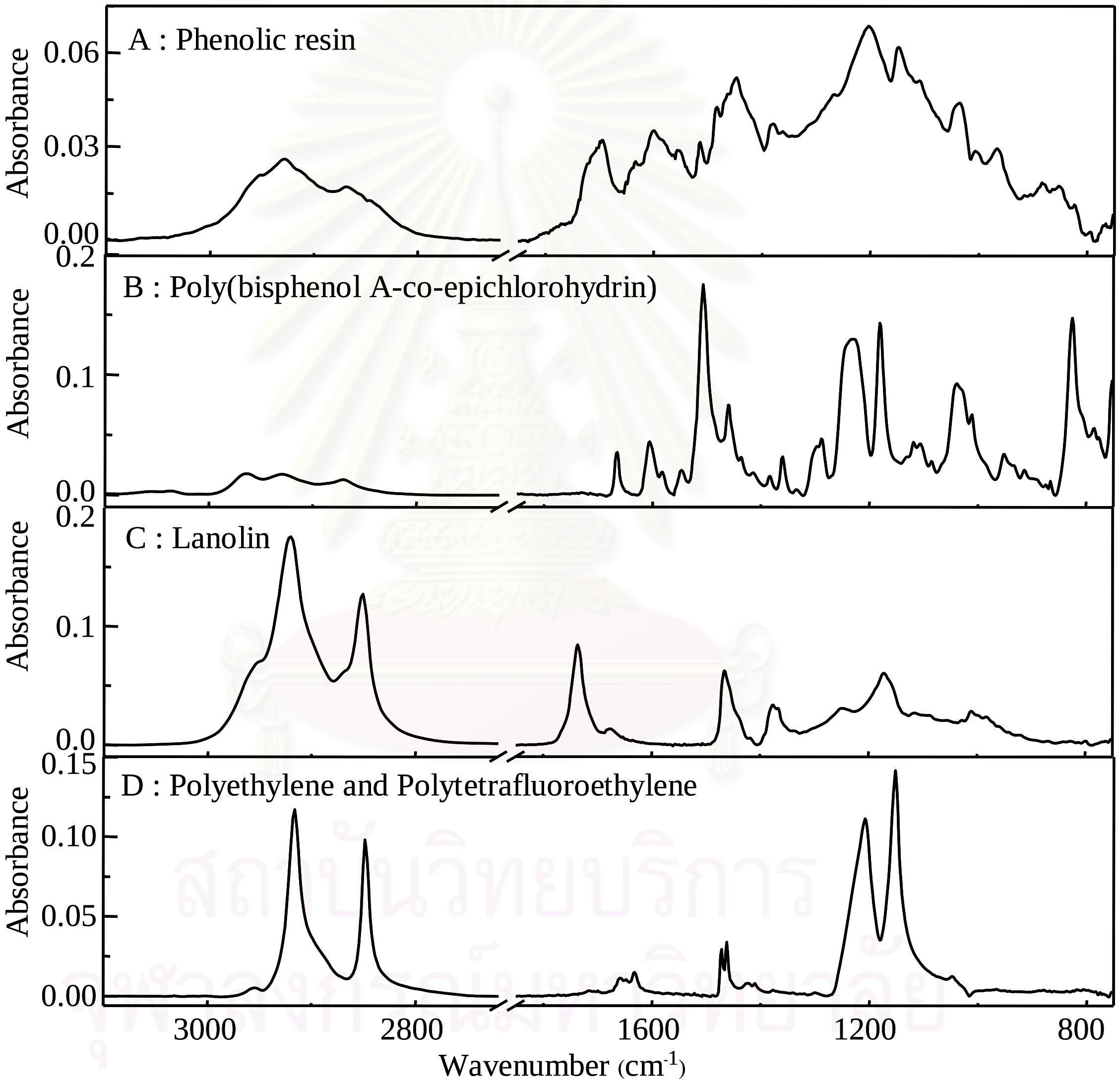


Figure 4.8 ATR FT-IR spectra of raw material of coating on tin plate: (A) spectrum of phenolic resin, (B) spectrum of poly(bisphenol A-co-epichlorohydrin, (C) spectrum of lanolin, and (D) spectrum of polyethylene and polytetrafluoroethylene.

Since the contaminants were optically contacted with the slide-on Ge μIRE when the spectrum was acquired, the CH-stretching absorptions of contaminants were directly associated with the raw material of coating material as shown in Fig. 4.8. According to the ATR FT-IR spectra of all materials employed in the coating, the fine powder contaminant might associate with one component employed as a lubricant for the coating process (i.e., a mixture of polyethylene and polytetrafluoroethylene). The contaminants and the mixture of polyethylene and polytetrafluoroethylene were compared as shown in Fig. 4.9. ATR FT-IR spectra of the CH_2 stretching asymmetric and symmetric at 2918 and 2850 cm^{-1} of polypropylene was the same feature but the spectra in range 1000-1300 cm^{-1} of polytetrafluoroethylene of contaminants were not observed because polytetrafluoroethylene likely bound with metal. Thus, the reveal of contaminants on the surface of contaminated tin plate are polyethylene. The cause of contamination on tin plate may be the condition of coating process being not appropriated such as the temperature is not stable, the composition of raw material is not compatible, *etc*.

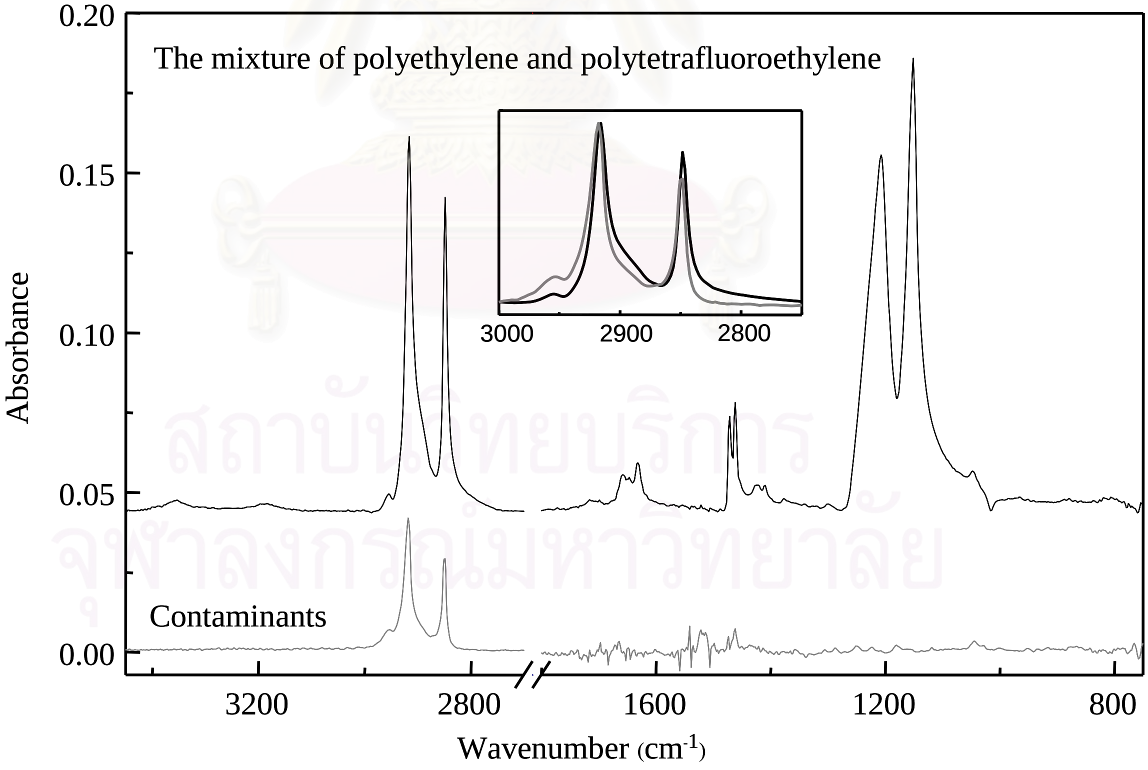


Figure 4.9 Spectral comparisons of contaminants and raw material.

4.2 Characterization of Contaminants on Polypropylene Bag

The general analysis of additives in polymers is important due to widely application of polypropylene films in packaging of food products. Additives must be incorporated into polymers and the co-polymers in order to maintain and give the physical properties to ensure the efficient processing. All additives used in food contacting plastics must be approved for safety for using and it is also necessary to ensure that the additives are a good quality and do not contaminate or off-odor to packaged foodstuffs.

For surface identification of the polypropylene bag, appropriate technique for analysis of surface contamination on polypropylene bag should be used by transmission technique because of the transparency of material. After collecting spectrum by using transmission technique, the observed spectra of polypropylene bag did not show any significance. The obtained spectrum shows over absorption band which out of linear range as shown in Fig. 4.10. The spectrum did not show the significant peak of additives. Thus, the transmission technique does not appropriate for surface contamination of this sample.

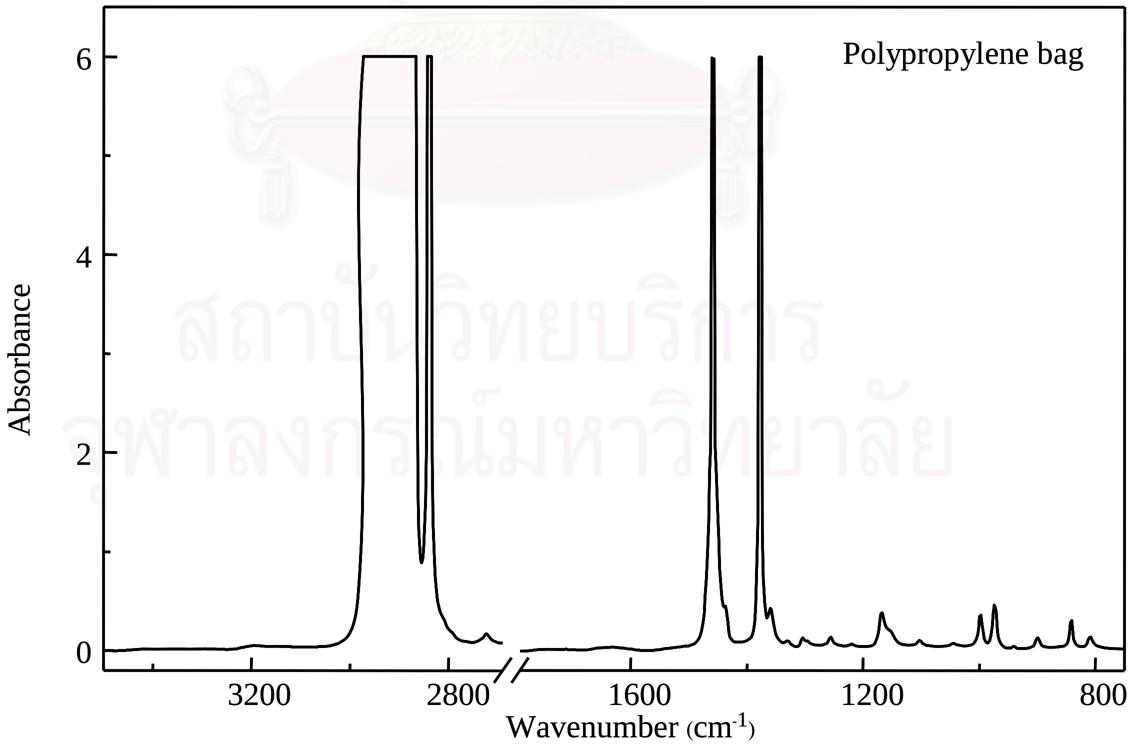


Figure 4.10 Transmission spectrum of untreated polypropylene bag.

According to the limitation of transmission technique, the application of a new μIRE was introduced. After contacting the polypropylene bag with slide-on Ge μIRE, the observed spectrum showed absorption of polypropylene bag which assigned as follows in Table 1: aliphatic CH stretching was clearly seen in the range 3000-2800 cm^{-1}, and the CH bending in the range 1500-1350 cm^{-1}. After spectral acquisition of untreated polypropylene bag and thermal treatment polypropylene bag by microwave radiation at 50, 60, 70, 80, 90 and 100 °C to study the influence of temperature which has an impact on polymer degradation because it may get free form and attend with food. This may be harmful of life. The observed spectra indicate that thermal treatment in range 50-100 °C did show the reformation or degradation of compound in polypropylene bag, due to the decreasing absorptions at region 1630 and 3100-3300 cm^{-1} (Figure 4.11). For the application of polypropylene bag, this chemical substance can be accompanied with food and caused the harmful for users. The observed spectra of contaminants cannot be decided because the spectral feature is very low levels and the polypropylene bag has the high absorption, it will be concealed the chemical information of contaminants.

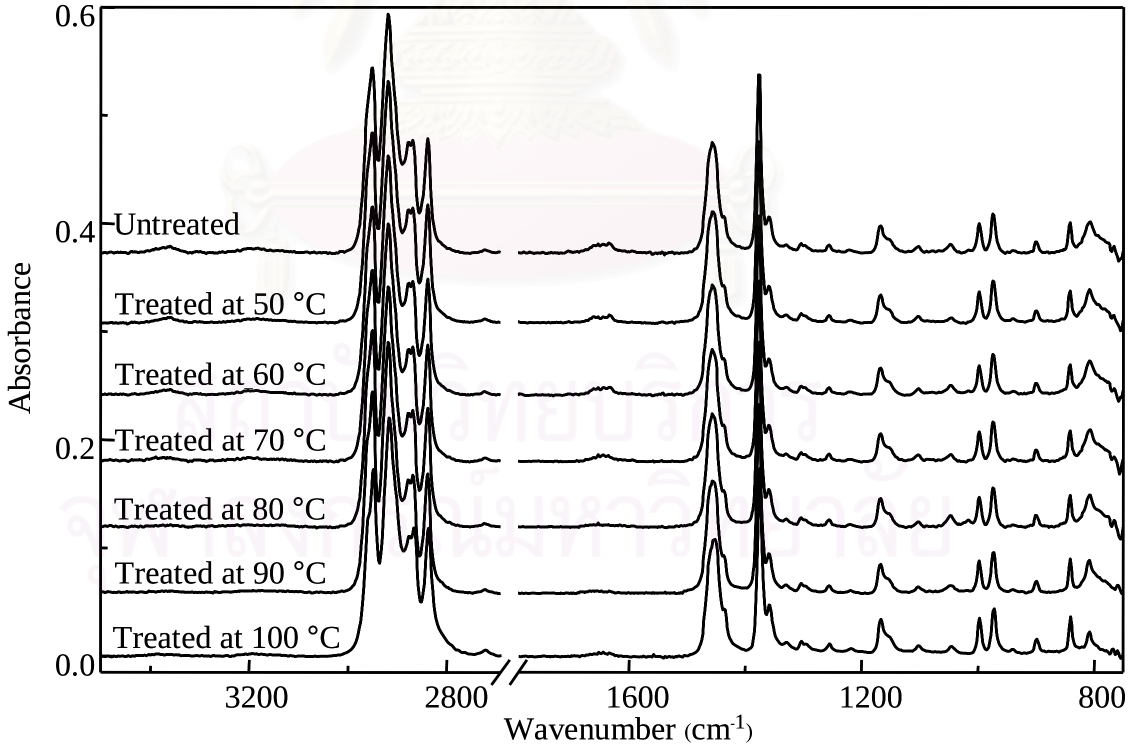


Figure 4.11 Spectra of untreated and thermal treated polypropylene bag by using the slide-on Ge μIRE.

Table 4.1: ATR spectral bands and corresponding assignments for polypropylene

Wavenumber (cm^{-1})	Assignments
2949	Asymmetric CH stretching of CH_3
2917	Asymmetric CH stretching of CH_2
2867	Symmetric CH stretching of CH_3
2837	Symmetric CH stretching of CH_2
1453	Out of plane CH bending of CH_3
1375	In plane CH bending of CH_2
1167	Asymmetric CH rocking of CH_3
997	Asymmetric CH rocking of CH_3
972	Asymmetric CH rocking of CH_3
841	CH rocking of CH_2
808	CH rocking of CH_2

To use the novel ATR FT-IR technique for analysis of surface contamination on polypropylene bag, the application of the slide-on Ge μIRE for a thin film contaminant on a solid surface was demonstrated and the results were shown in Fig. 4.12. A thin film of a contaminant on the surface of polypropylene bag can be detected by ATR FT-IR microspectroscopy. The spectral fingerprint of the contaminant can be observed by the "*contact-and-collect*" operation. After a number of contacts, a sufficient amount of the contaminant was accumulated on the surface of the clean Ge tip while a reasonably good spectral quality of the material was obtained. The spectral acquisitions were obtained both outside and inside of untreated polypropylene bag. When the tip of the slide-on Ge μIRE was brought into an optical contact with a polypropylene bag, some of the contaminants on the polypropylene bag were efficiently pick-up and stuck with the IRE. After removing the polypropylene bag, the trace amount of the contaminant on the IRE can be characterized under the ATR mode without any interference of sample. For the thin-film-coating IRE with mineral oil and fluorolube (Fig 4.12 A2, B2, A3 and B3), the amount of the collecting agent were decreased after a subsequently contact but the amount of contaminants were increased.

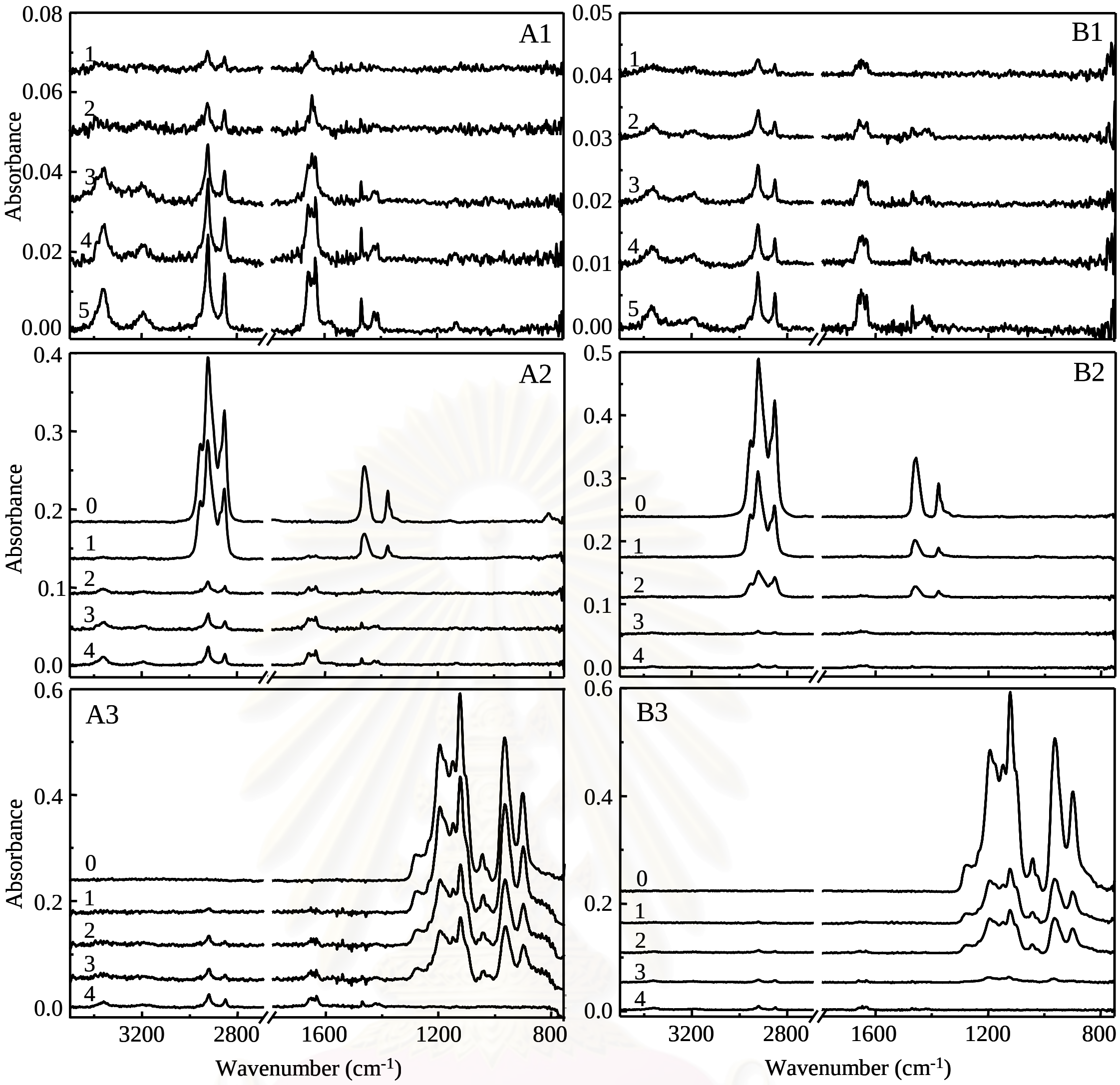


Figure 4.12 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge μIRE: (A1, A2, A3) spectra of outside untreated polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE respectively, and (B1, B2, B3) spectra of inside untreated polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

Since the contaminants were optically contacted with the IRE when the spectrum was acquired, the absorptions of oleamide (from library) and contaminants on polypropylene bag were the same feature as shown in Fig. 4.13. Thus, the observed spectra of contaminants can be assigned to oleamide (*cis*-9-octadecenamide) employed as a lubricant (slip agent). The slip agent may diffuse or migrate to a film surface to improve or increase the rate of processing and to improve surface-released properties during extrusion, injection molding, compression molding, *etc* [55].

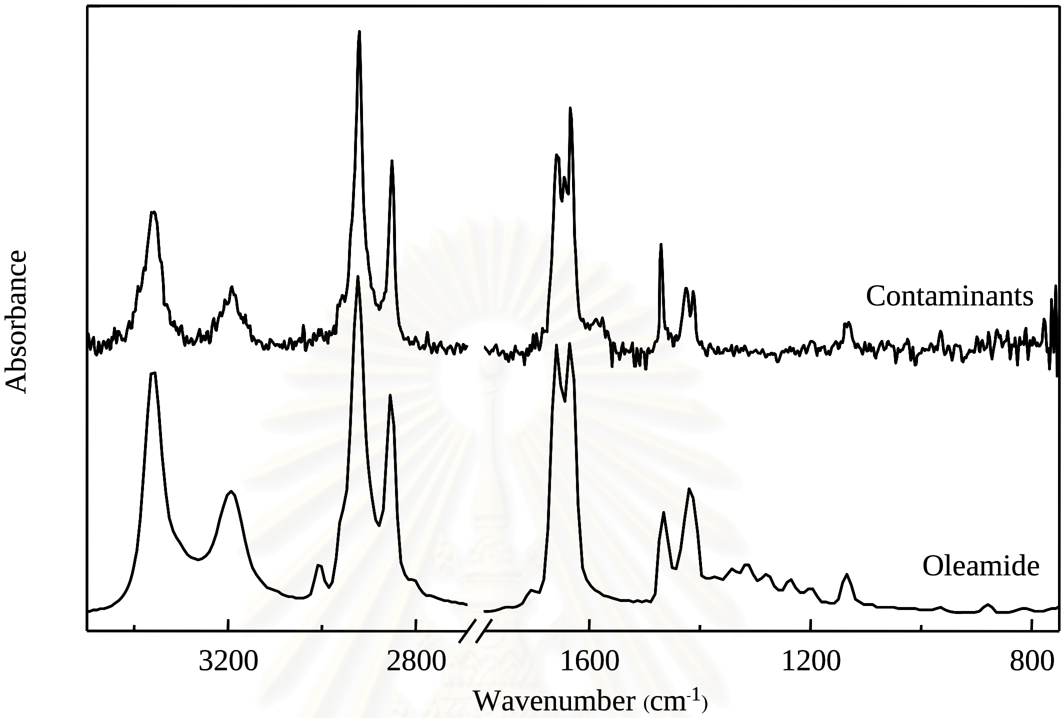


Figure 4.13 Spectral comparisons of contaminants and oleamide.

The fatty acid amide, *cis*-9-octadecenamide (oleamide) is an endogenous fatty acid primary amide that accumulates in the cerebrospinal fluid under sleep deprivation conditions and induces sedation and physiological sleep in animals [56, 57]. It induces several effects, such as reduction of body temperature, slow movement, and a reduction in ache perception. In addition, it increases sleeping, impairs immunological and memory responses [58]. Moreover, after contacting with oleamide, one may cause drowsiness.

Table 4.2: ATR spectral bands and corresponding assignments for oleamide

Wavenumber (cm^{-1})	Assignments
3366	Asymmetric NH stretching of NH_2
3187	Symmetric NH stretching of NH_2
2921	Asymmetric CH stretching of CH_2
2850	Symmetric CH stretching of CH_2
1660	CC stretching of C=C
1634	CO stretching of C=O of amide
1424	CN stretching of C-CO-NH_2

For thermal treatment of the polypropylene film, the slip agent was remained, and the observed spectra of oleamide were expected as shown in Fig 4.14-4.19. Since the melting point of oleamide is approximately 80 °C and the boiling point is above 200 °C [59], the highest temperature for thermal treatment is at 100 °C. Therefore, the oleamide was melted but was not decomposed and oleamide could be detected from the polypropylene bag by using slide-on Ge μIRE. The spectral acquisition showed the resemblance with untreated polypropylene bag, the absorption increased after subsequently contacts and the absorption of the contaminants were increased while that of the liquid film was decreased. The oleamide may diffuse or migrate to a film surface after the film is formed [60]. Nowadays polypropylene is used in many applications such as food packaging or container; therefore the contamination of oleamide can occur and may play an important impact role on life.

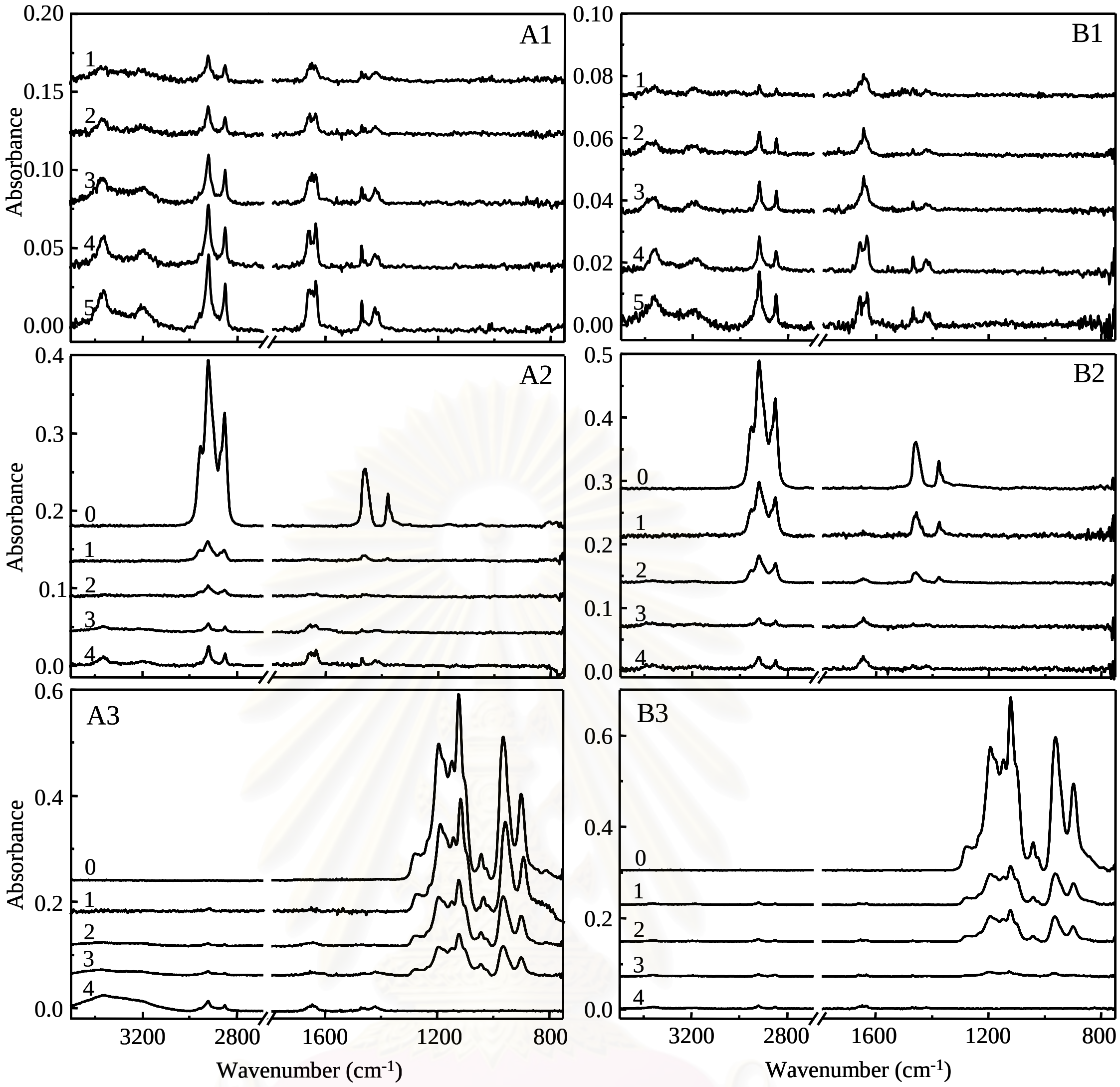


Figure 4.14 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge µIRE: (A1, A2, A3) spectra of thermal treatment at 50°C of outside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE respectively, and (B1, B2, B3) spectra of thermal treatment at 50°C of inside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

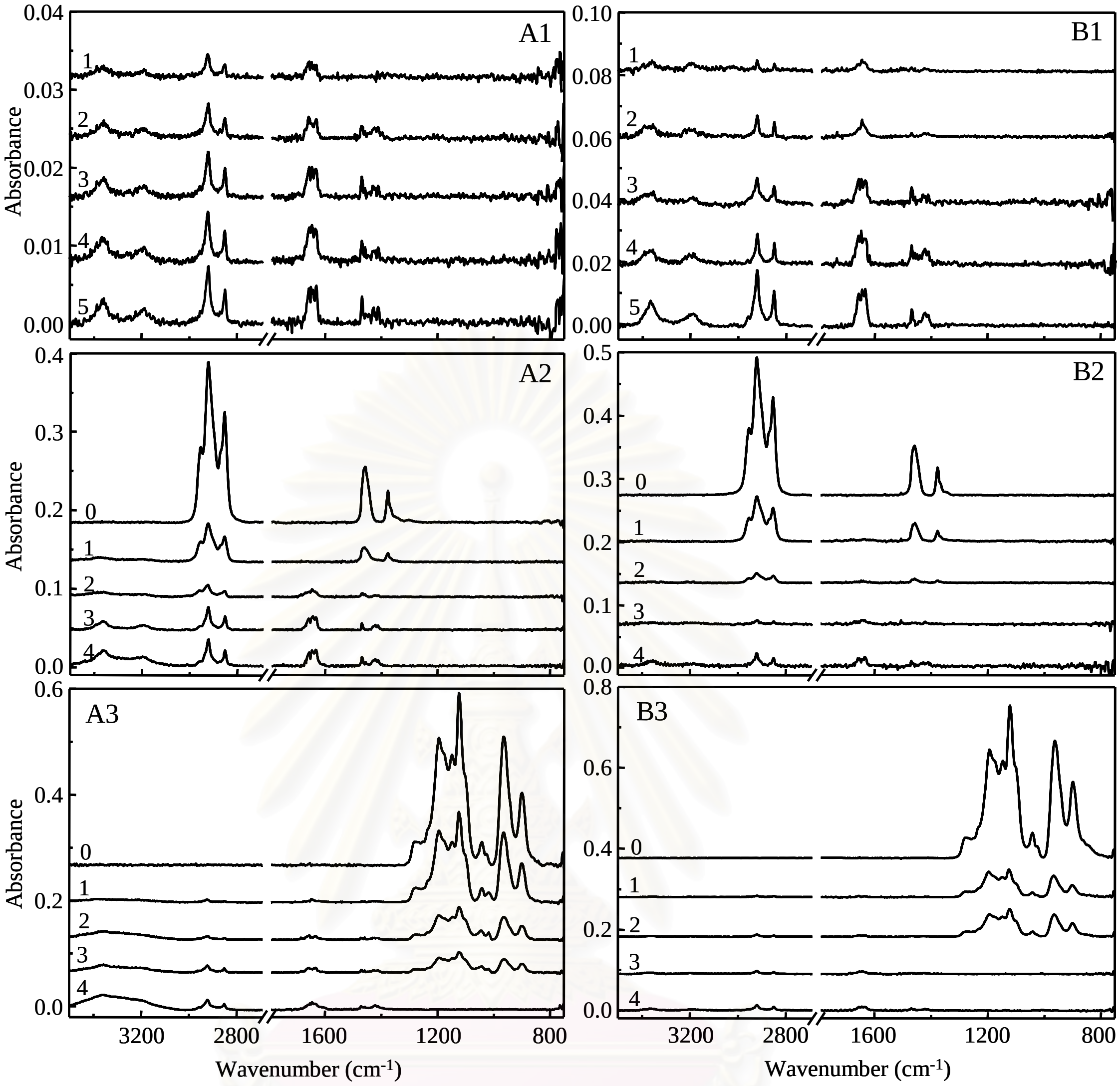


Figure 4.15 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge μIRE: (A1, A2, A3) spectra of thermal treatment at 60°C of outside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE respectively, and (B1, B2, B3) spectra of thermal treatment at 60°C of inside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

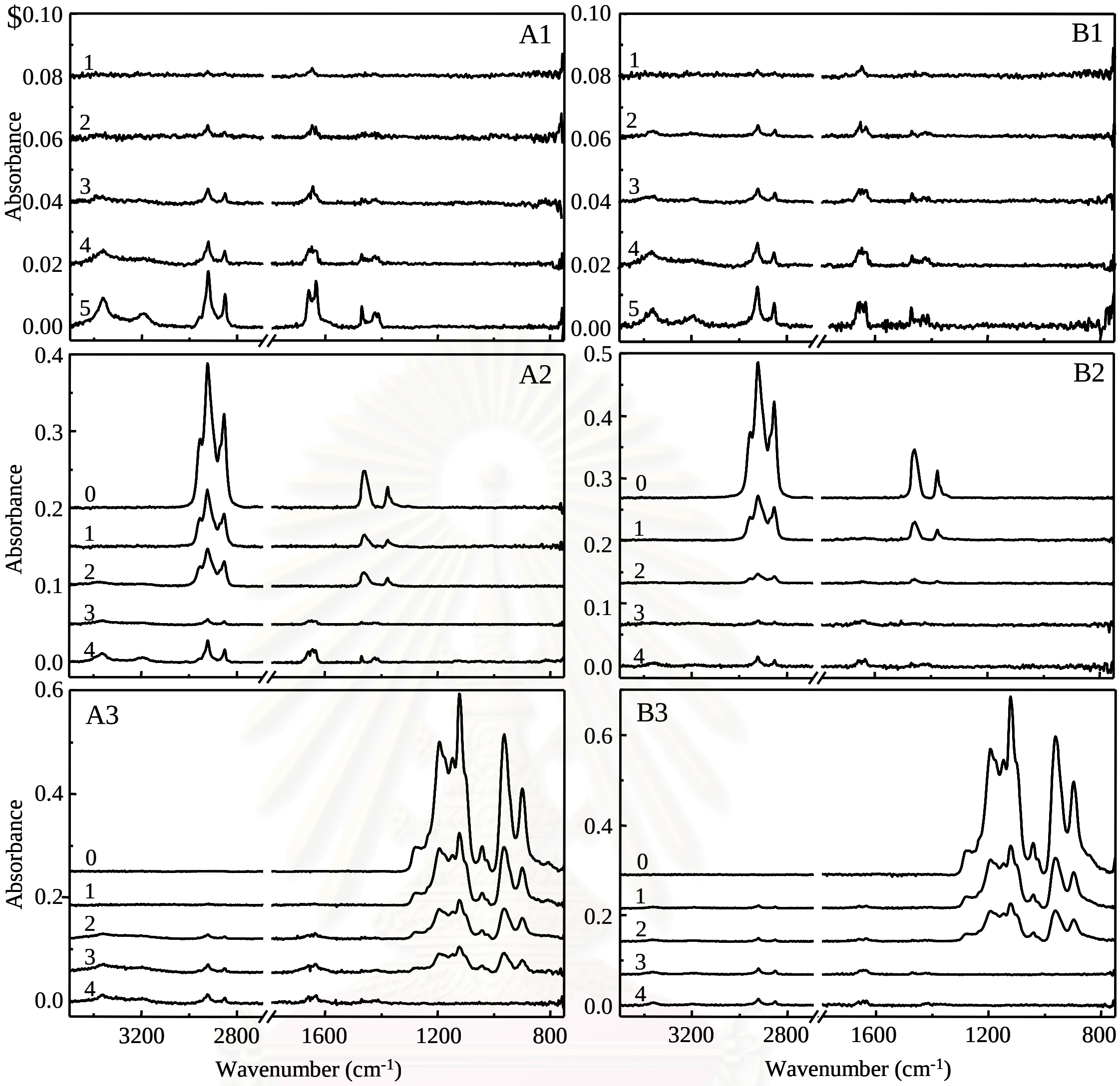


Figure 4.16 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge µIRE: (A1, A2, A3) spectra of thermal treat at 70°C of outside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE respectively, and (B1, B2, B3) spectra of thermal treatment at 70°C of inside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

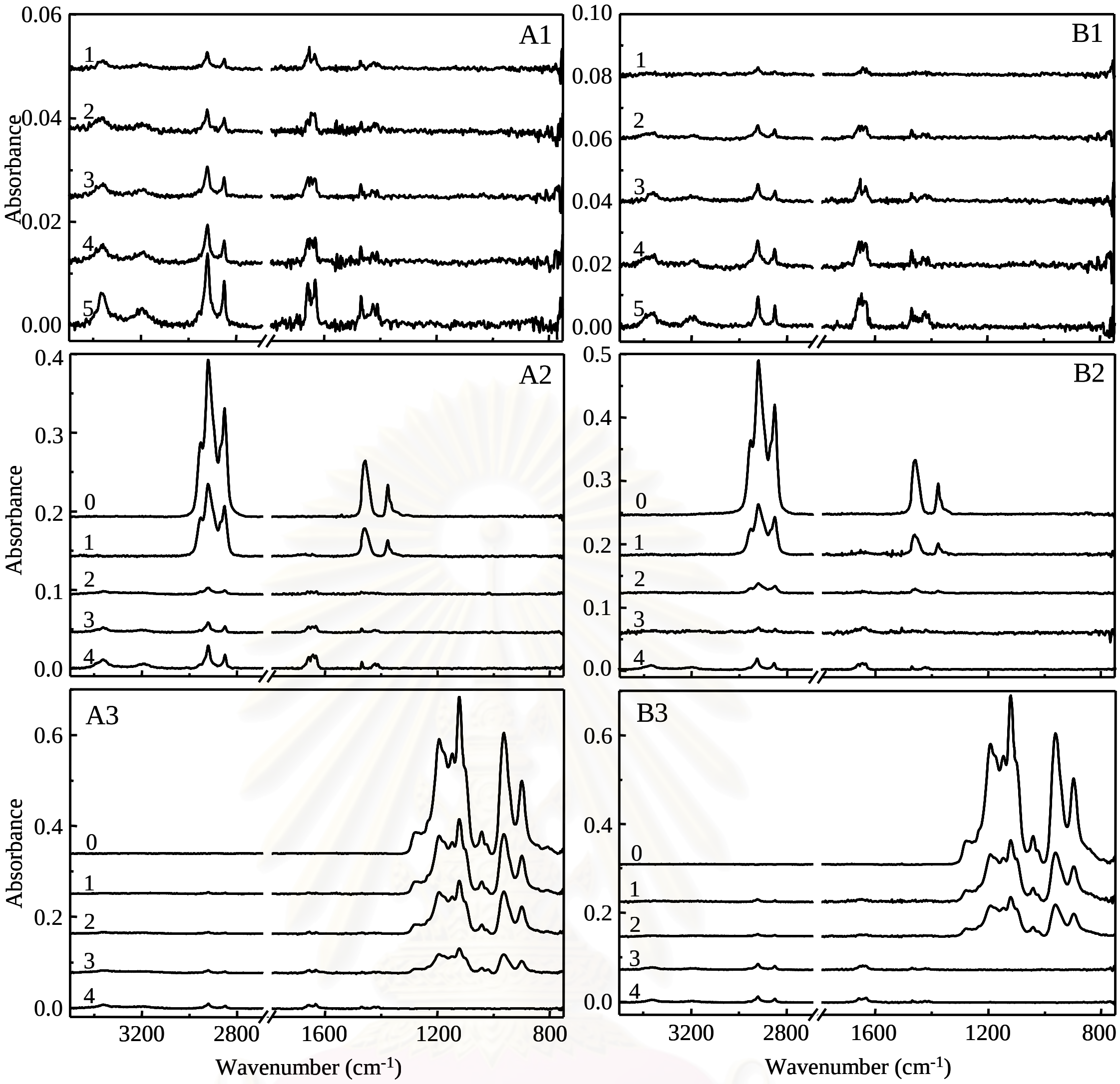


Figure 4.17 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge µIRE: (A1, A2, A3) spectra of thermal treatment at 80°C of outside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE respectively, and (B1, B2, B3) spectra of thermal treatment at 80°C of inside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

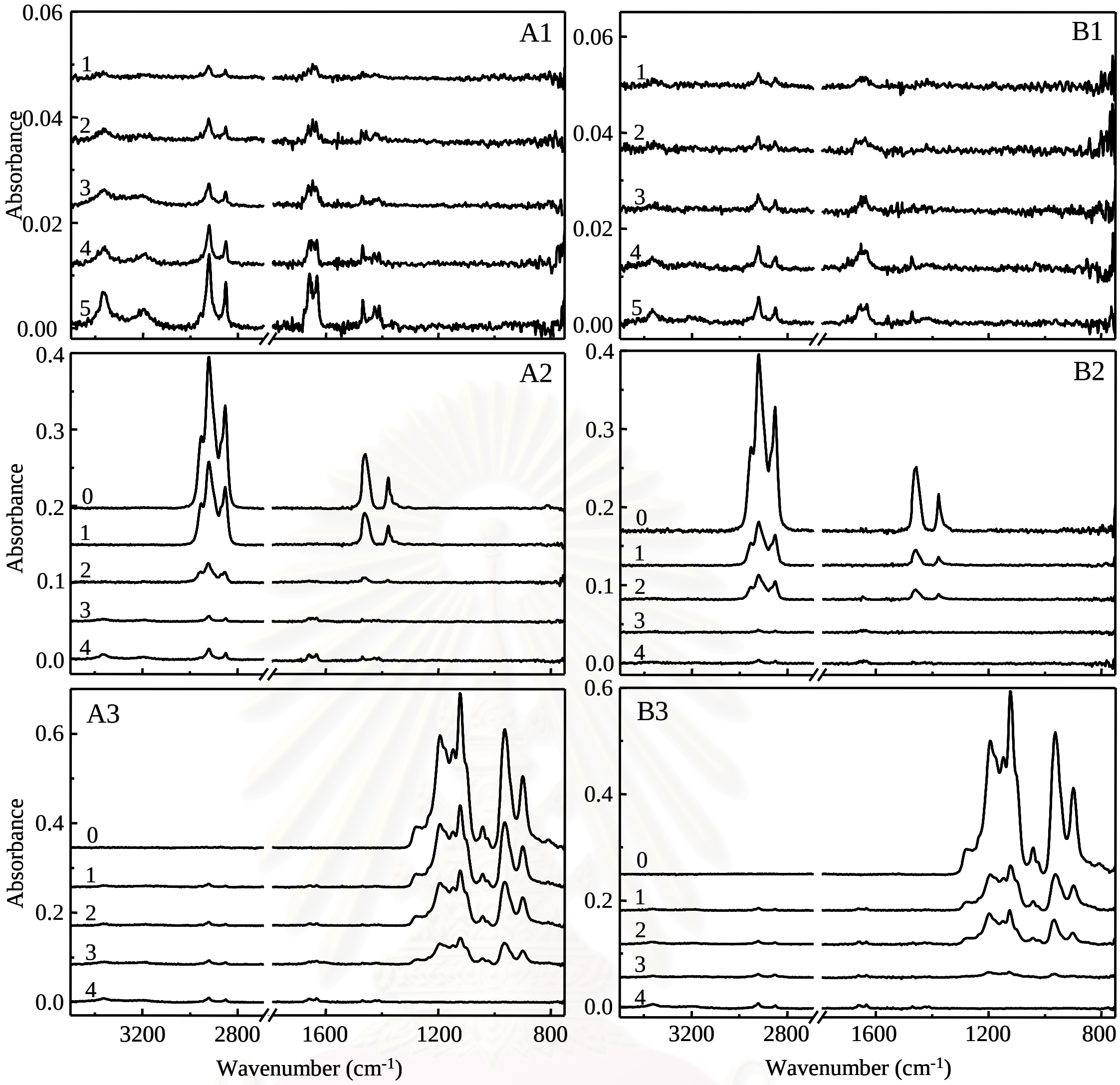


Figure 4.18 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge µIRE: (A1, A2, A3) spectra of thermal treatment at 90°C of outside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE respectively, and (B1, B2, B3) spectra of thermal treatment at 90°C of inside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

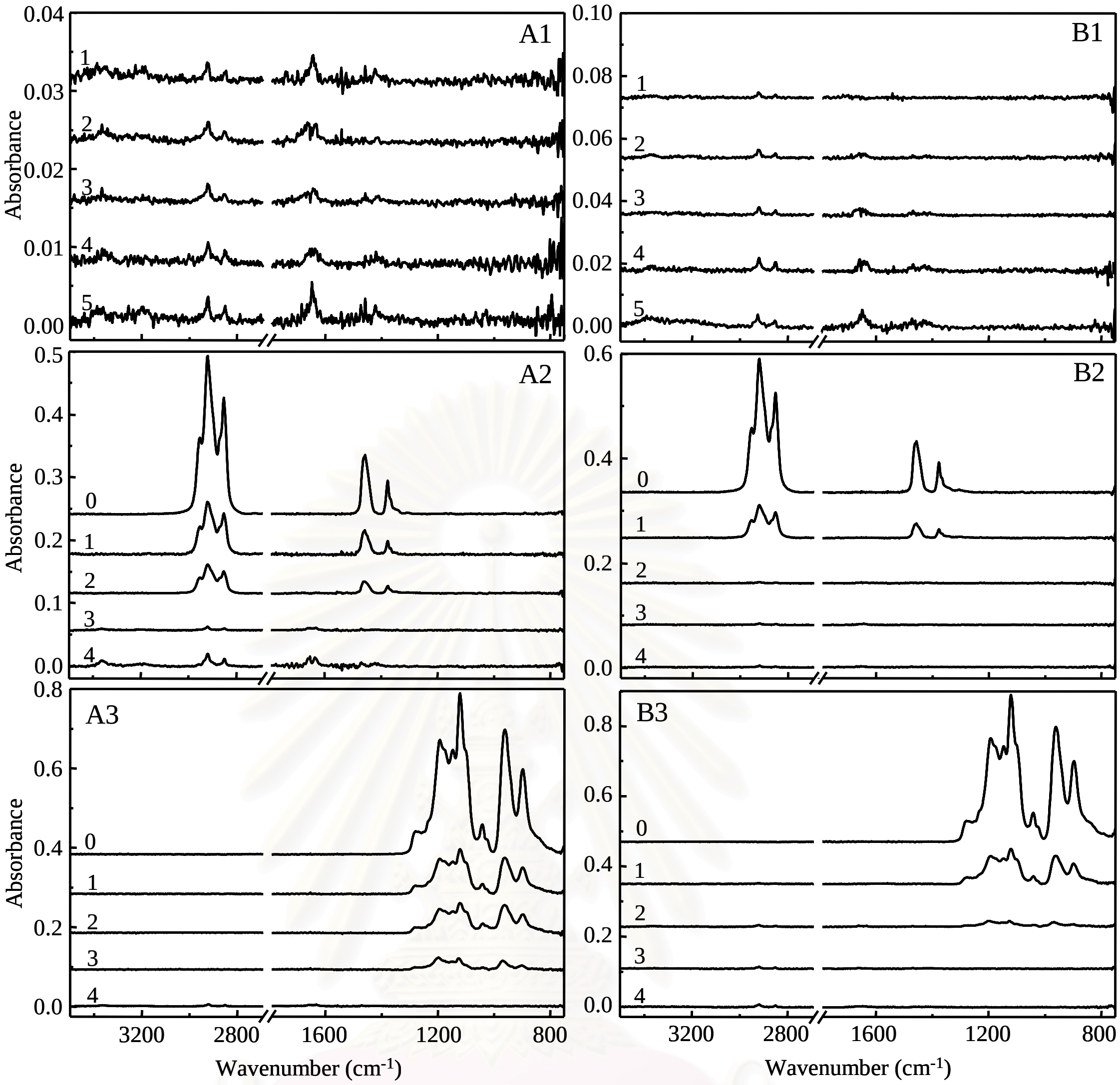


Figure 4.19 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge µIRE: (A1, A2, A3) spectra of thermal treat at 100°C of outside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE respectively, and (B1, B2, B3) spectra of thermal treatment at 100°C of inside polypropylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

4.3 Characterization of Contaminants on Polyethylene Bag

Polyethylene, the first commodity plastic using for food packaging, came into general use. Since it used to the finish goods as a packaging material for a wide range of foods and drinks because of its relatively low cost, its versatile properties, and easy manufactured and converted. The substance may be migrated from polyethylene plastics to foodstuffs including residue, low molecular-weight polymers, and any additives which used in the manufacturing process.

Similar phenomena were observed when a surface analysis of the polyethylene bag was performed. For the outside and inside of polyethylene bag, a trace residue or contaminant was not observed even after a large numbers of subsequently contacts with the clean µIRE (Fig 4.20 A1 and B1). For the thin-film-coated µIRE (Fig 4.20 A2, B2, A3, B3), the amount of the collecting agent was decreased after a subsequently contact. The unchanged spectral envelops suggested that the surface of the polyethylene bag was free of contaminants.

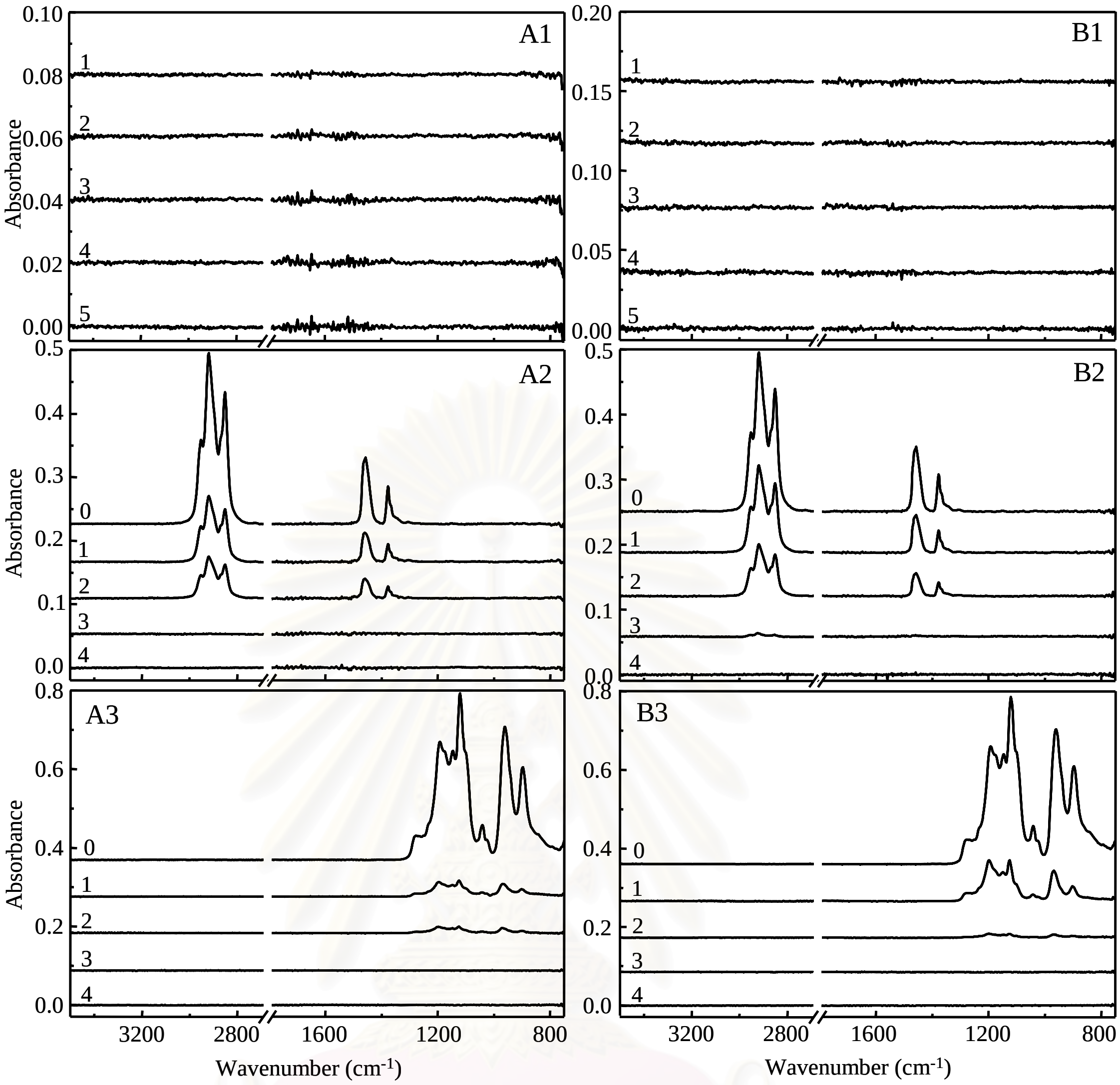


Figure 4.20 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge µIRE: (A1, A2, A3) spectra of outside polyethylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE respectively, and (B1, B2, B3) spectra of inside polyethylene bag contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

4.4 Characterization of Contaminants on Chopsticks

Chopsticks are commonly made of wood. Chopsticks are the tool and are used for pinching some food. In many disposable chopsticks using in restaurants, it looks whiter than regular wood. If the manufacturer of disposable chopsticks use good quality wood, so the special processing and bleaching are not necessary. However, some small manufactures use low quality wood for costs reduction. So, the chopsticks are dark and difficult to sell. In order to make the chopsticks with better quality, some manufactures may be used chemical for bleaching the wood. If the chopsticks have the contamination, the contaminants may be stuck with food, that cause the harmful or health danger.

To demonstrate more application of the slide-on diamond μIRE and the slide-on Ge μIRE, the results were shown in Fig. 4.21. ATR FT-IR spectra of contaminants on the surface and peeling off by knife by using slide-on diamond μIRE (Fig. 4.21 A1, A2) and slide-on Ge μIRE (Fig. 4.21 B1, B2) were acquired. For ATR FT-IR spectra on surface of chopstick in different brand names, the spectral feature of were clearly different due to the several additives were used to improve the quality of chopstick (Fig 4.21 A1 and B1). For ATR FT-IR spectra on peeling off by knife of each chopstick (Fig 4.21 A2 and B2), the spectral features of the chopsticks were the same. The observed spectra shown absorption of chopstick which can be assigned to cellulose.

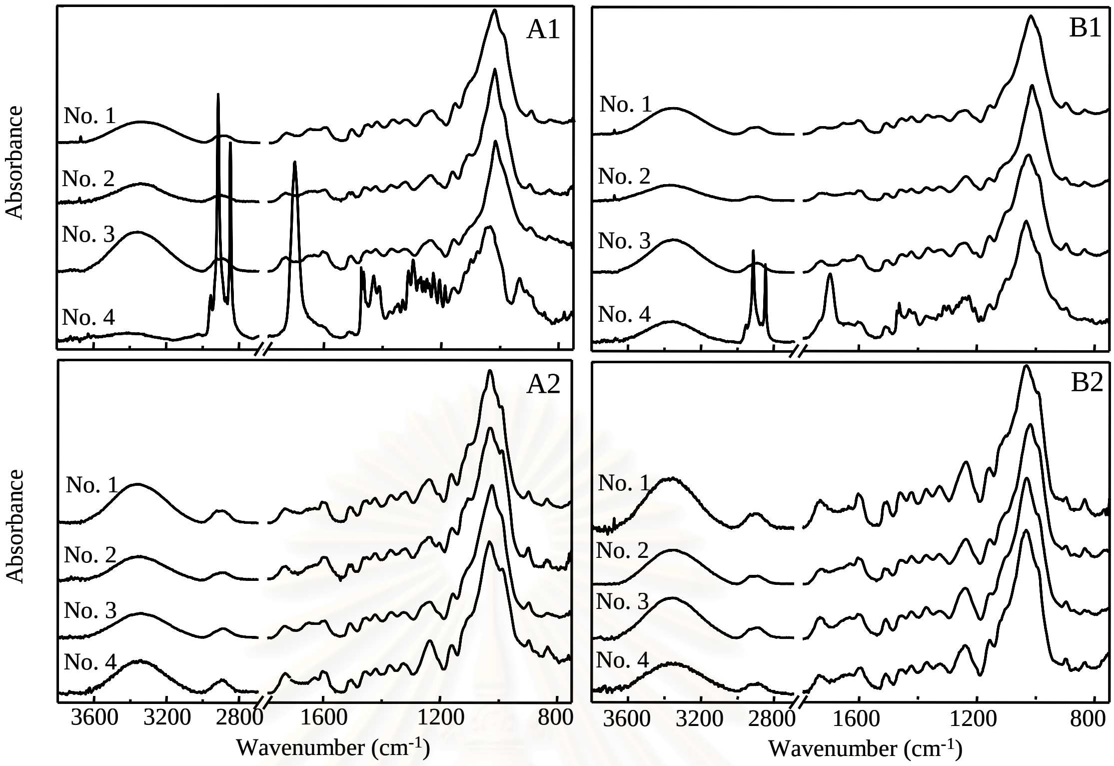


Figure 4.21 ATR FT-IR spectra of chopstick: (A1, A2) spectra of surface and peeled off by knife of chopsticks in different brand names contacted with slide-on diamond µIRE, and (B1, B2) spectra of surface and peeled off by knife of chopsticks in different brand names contacted with slide-on Ge µIRE, respectively.

Table 4.3: ATR spectral bands and corresponding assignments for cellulose

Wavenumber (cm^{-1})	Assignments
3327	OH stretching
2800-2900	CH stretching
1728	C=O stretching
1451	Asymmetric CH bending of CH_3
1368	CH bending of CH_3
1015	Asymmetric CO stretching of C-C-OH
1026	CO stretching of C-O-C

Fig 4.22 shows ATR FT-IR spectra of contaminants on surface from chopstick brand name No.1 by using “*contact-and-collect*” technique with slide-on diamond μIRE and slide-on Ge μIRE. Fig. 4.22 A1 shows ATR FT-IR spectra of collecting residue on the surface of chopstick clearly obtained very high dominant peak of contaminants assigning as talc, ATR FT-IR spectra were shown significant absorption features at 1014 cm^{-1}. The ATR FT-IR spectra of contaminants employed on the surface of chopsticks brand name No. 1, talc may be a coating material which was used to increase smoothness for coating process of chopstick. Due to the small contact area (i.e. as small as 30 μm in diameter) of the slide-on diamond μIRE, it is enabling for spectral acquisition of a surface with high absorption. The small culet of the diamond μIRE was also very useful for the spectral acquisition of small or roughness solid samples.

For the thin-film-coated IRE with mineral oil and fluorolube (Fig. 4.22 A2, A3), ATR FT-IR spectra showed the amount of the collecting agent was decreased after a subsequently contact but those associated with the contaminant increased. Also in Fig 4.22 B1, B2, B3 show ATR FT-IR spectra of contaminants on surface of chopstick brand name No.1 by using “*contact-and-collect*” technique with slide-on Ge μIRE. The spectral features have the same results of the slide-on diamond μATR technique. The feature of the contaminants peaks were obtained, spectra show dominant peak of contaminants assigning as talc.

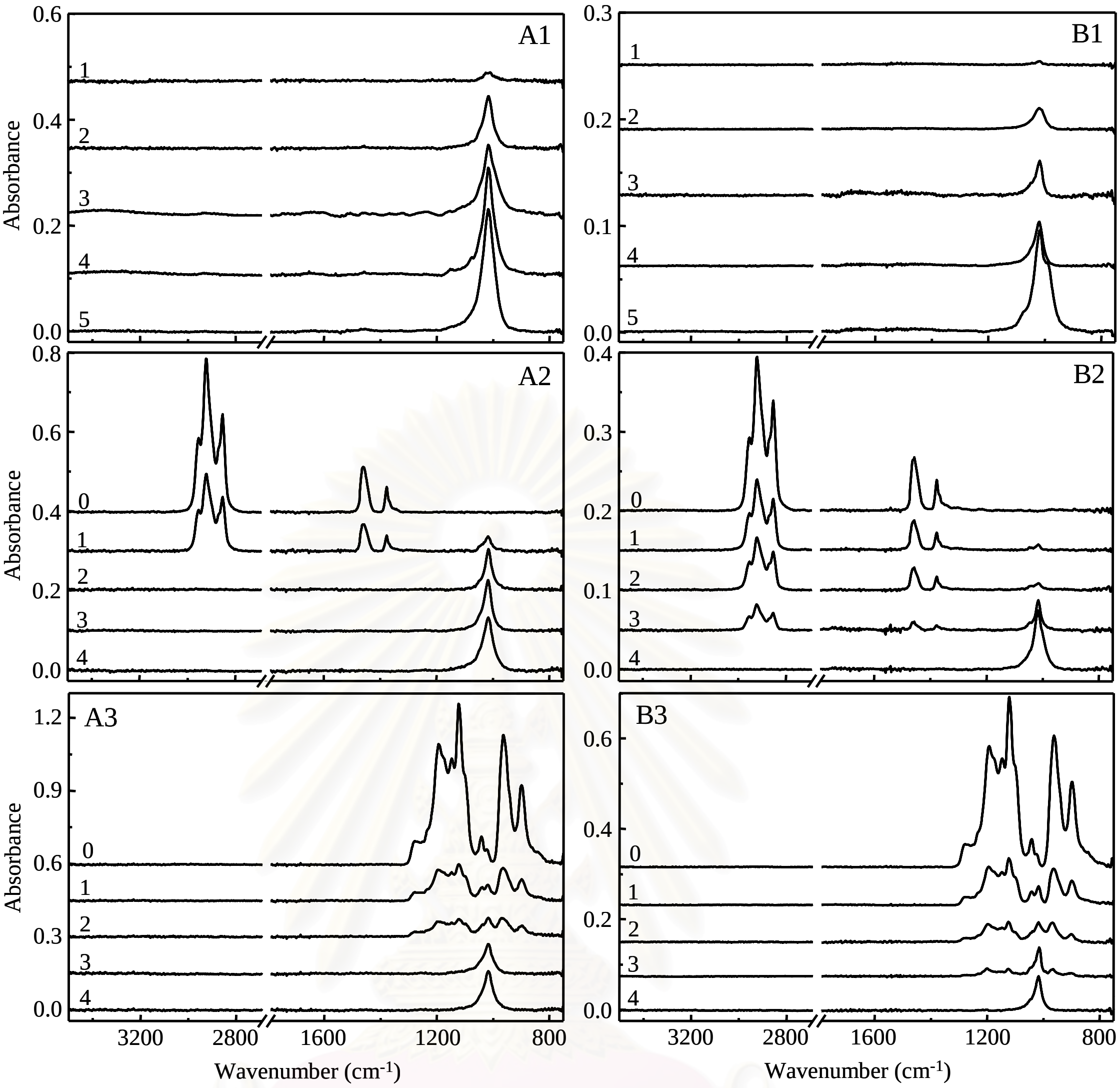


Figure 4.22 ATR FT-IR spectra of collecting residue of surface of chopstick brand name No.1: (A1, A2, A3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on diamond μIRE, and (B1, B2, B3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on Ge μIRE. The numbers indicated times of contacts between the IRE and the contaminated surface.

For ATR FT-IR spectra of collecting residue on the surface of the slide-on diamond μIRE (Fig. 4.23 A1, A2, A3) and slide-on Ge μIRE (Fig. 4.23 B1, B2, B3) of chopstick brand name No. 1, which peeled off by knife, the spectrum of inside chopstick were shown free-contaminant. That is, the amount of the collecting agent was decreased after a subsequent contact but contaminants powder cannot be picked up by the clean μIRE and coated μIRE. ATR FT-IR spectra show the peeled off by knife of chopsticks brand name No. 1 by using both IREs were the same results.

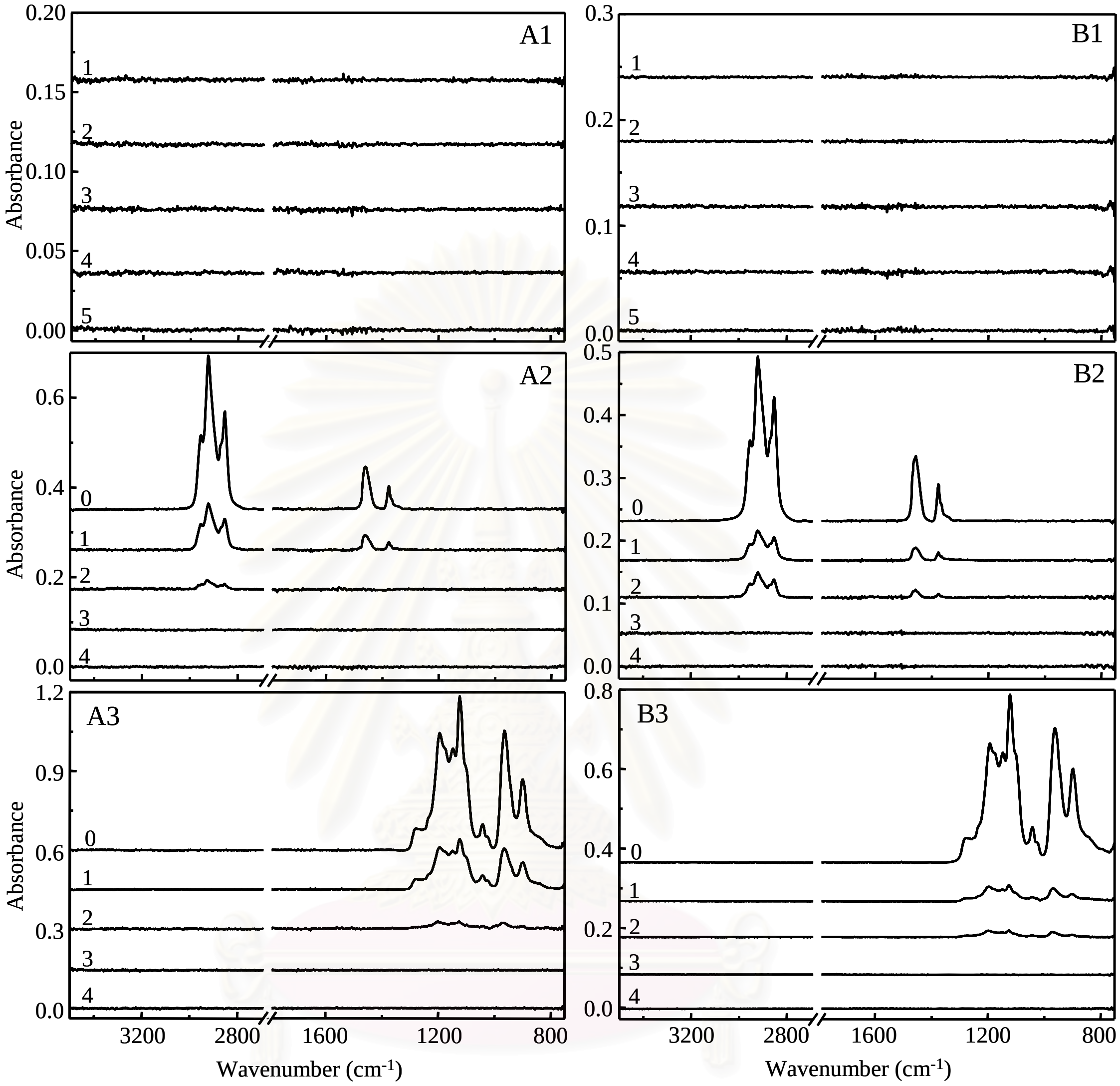


Figure 4.23 ATR FT-IR spectra of collecting residue of inside of chopstick brand name No.1: (A1, A2, A3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on diamond μIRE, and (B1, B2, B3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on Ge μIRE. The numbers indicated times of contacts between the IRE and the contaminated surface.

The spectra of the collecting residue on the surface of chopstick brand name No.2 acquired by slide-on diamond μIRE (Fig. 4.24 A1, A2 and A3) and slide-on Ge μIRE (Fig. 4.24 B1, B2, B3) are shown in Figure 4.24. The strong absorption band centered at 1014 cm^{-1} in the observed spectrum suggested that the dust on the chopstick brand name No.2 was talc. The talc powder may originate from the manufacturing process. The observed phenomenon suggested that the *"contact-and-collect"* operation with the slide-on diamond μIRE and slide-on Ge μIRE the great potential for trace analysis.

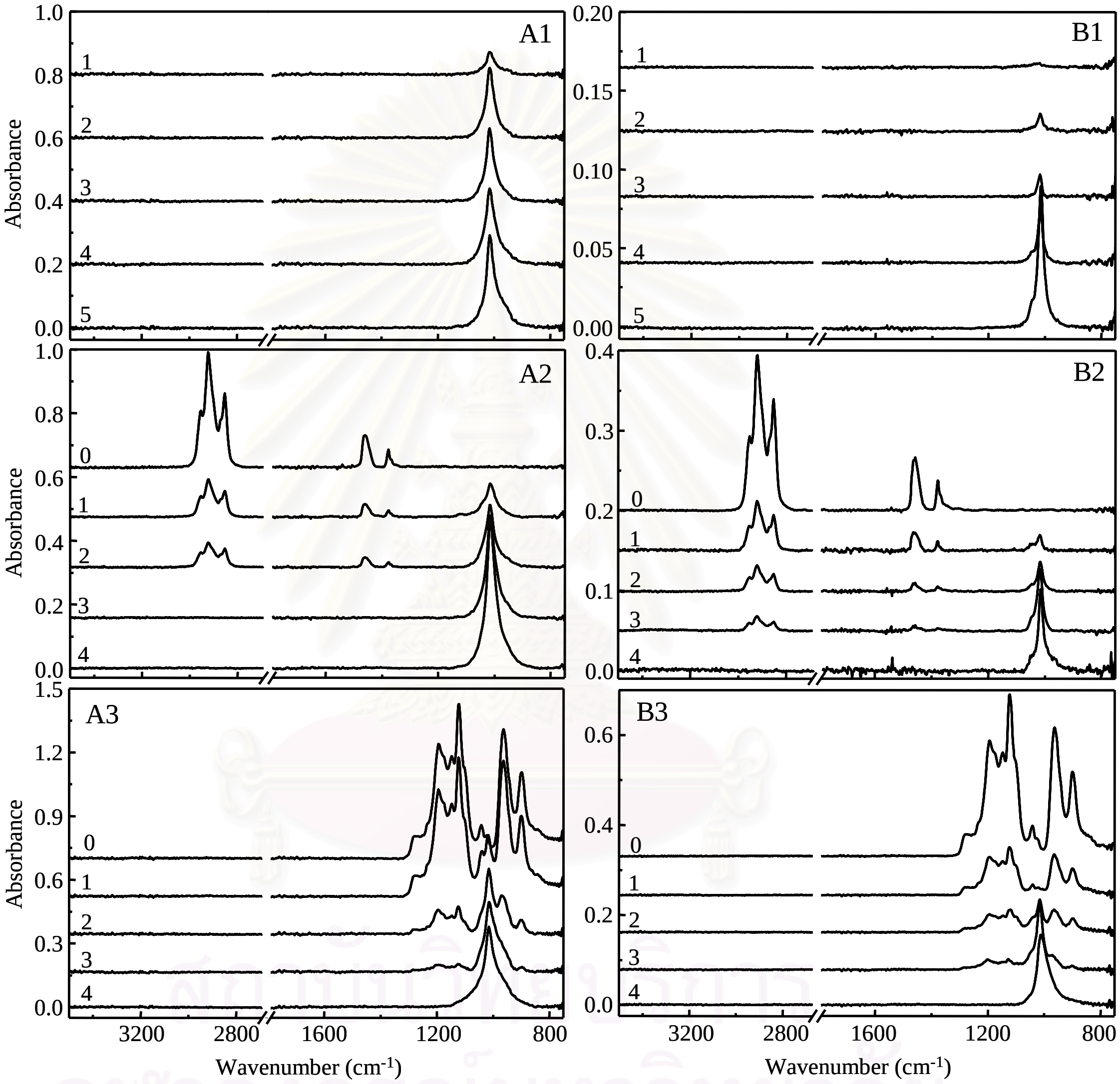


Figure 4.24 ATR FT-IR spectra of collecting residue of surface of chopstick brand name No.2: (A1, A2, A3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on diamond μIRE, and (B1, B2, B3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on Ge μIRE. The numbers indicated times of contacts between the IRE and the contaminated surface.

Fig 4.25 shows ATR FT-IR spectra of contaminants from inside of chopstick brand name No.2 by using “*contact-and-collect*” technique with slide-on diamond μIRE (Fig. 4.25 A1, A2, A3) and slide-on Ge μIRE (Fig. 4.25 B1, B2, B3). ATR FT-IR spectra of collecting residue of inside chopstick brand name No.2 were not observed. The spectra of inside chopstick were shown free of contaminant.

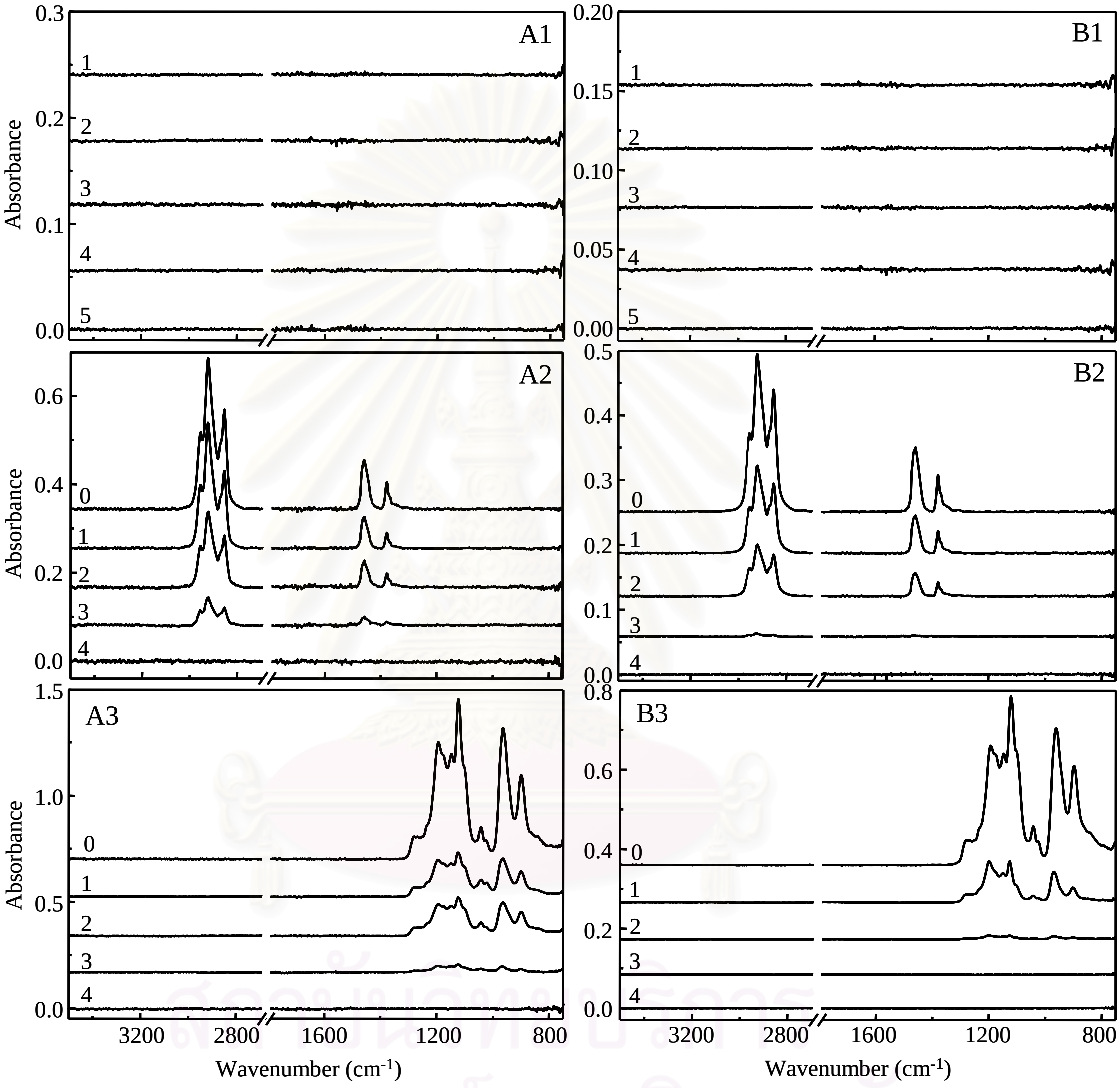


Figure 4.25 ATR FT-IR spectra of collecting residue of inside of chopstick brand name No.2: (A1, A2, A3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on diamond μIRE, and (B1, B2, B3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on Ge μIRE. The numbers indicated times of contacts between the IRE and the contaminated surface.

The spectra of the contaminants on the outside and the inside of chopstick brand name No.3 acquired by the slide-on diamond μIRE and slide-on Ge μIRE are shown in Fig 4.26 and 4.27. ATR FT-IR spectra of collecting residue on the surface of the slide-on diamond μIRE (Fig. 4.26 A1, A2, A3 and Fig 4.27 A1, A2, A3) and slide-on Ge μIRE (Fig. 4.26 B1, B2, B3 and Fig 4.27 B1, B2, B3) were shown. After collecting spectra of contaminants of chopstick, there was no residue on the clean μIRE (Fig. 4.26 and 4.27 A1, B1), the mineral-oil-coated IRE (Fig 4.26 and 4.27 A2, B2), nor the fluorolube-coated IRE (Fig. 4.26 and 4.27 A3, B3). For the thin-film-coated IRE, the amount of the collecting agent was decreased after a subsequently contact. The unchanged spectral envelops suggested that the surface and inside of the chopstick brand name No.3 was free of contaminant. It implies that chopstick brand name No.3 is clean.

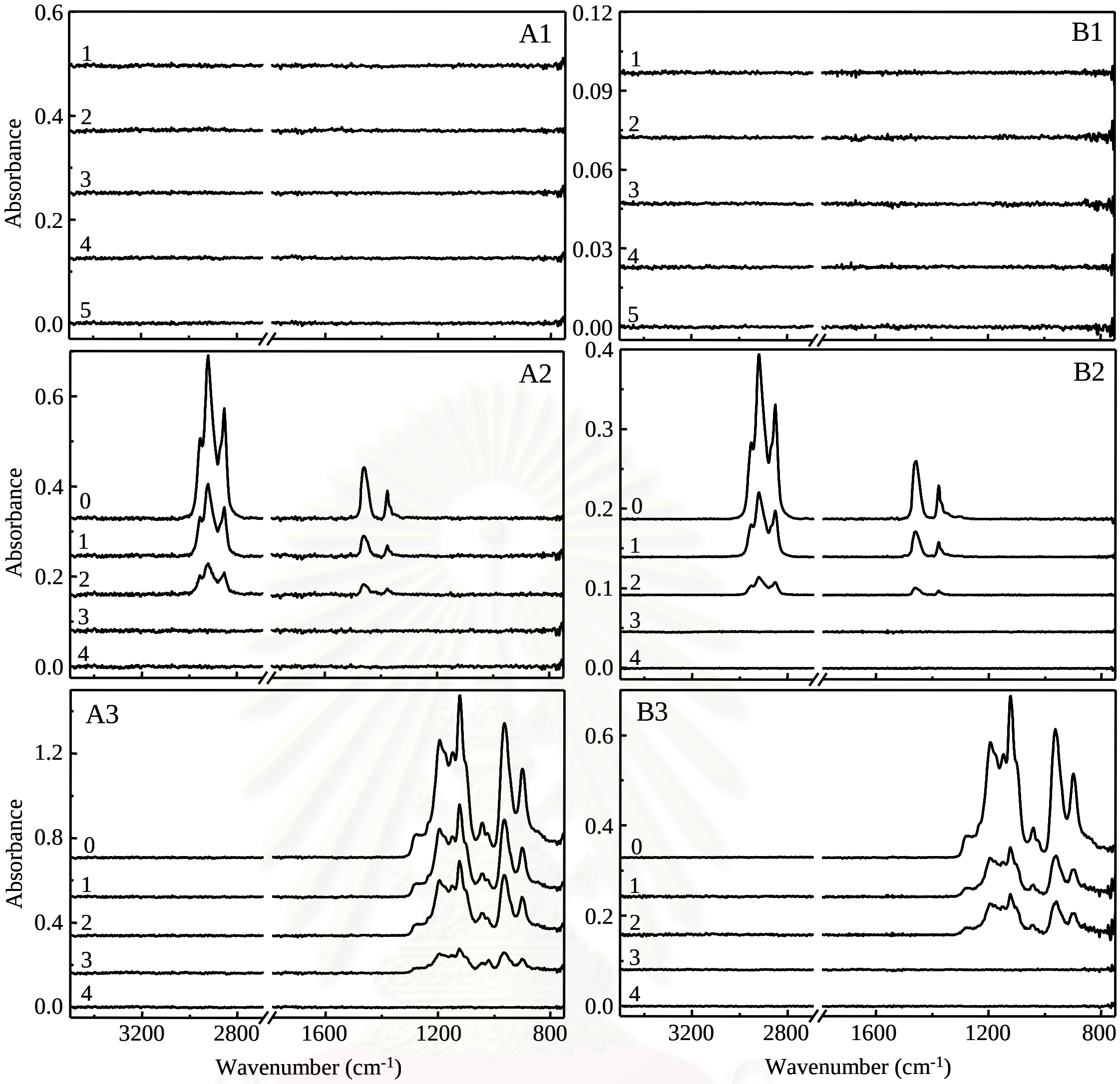


Figure 4.26 ATR FT-IR spectra of collecting residue of surface of chopstick brand name No.3: (A1, A2, A3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on diamond μIRE, and (B1, B2, B3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on Ge μIRE. The numbers indicated times of contacts between the IRE and the contaminated surface.

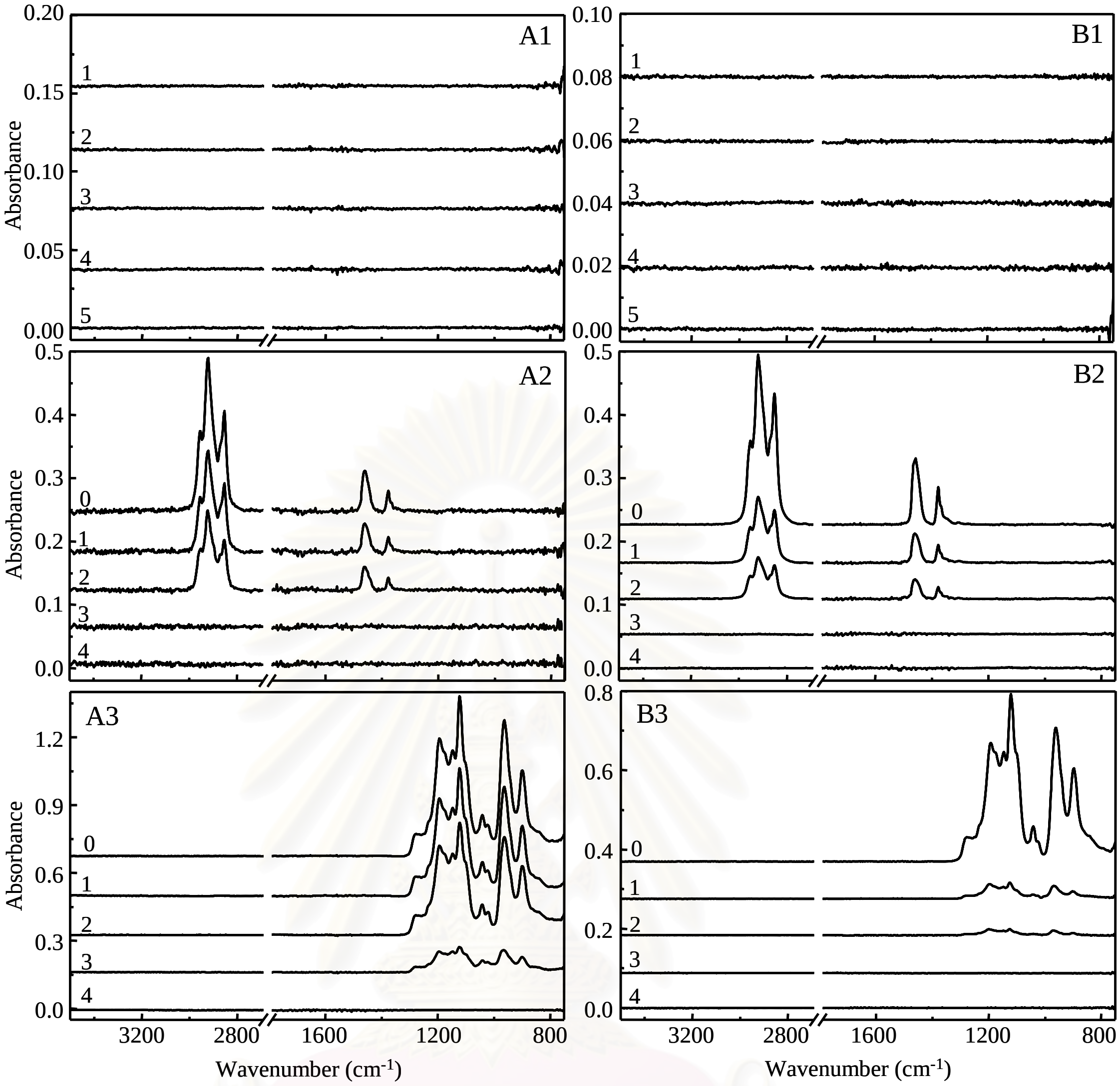


Figure 4.27 ATR FT-IR spectra of collecting residue of inside of chopstick brand name No.3: (A1, A2, A3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on diamond µIRE, and (B1, B2, B3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on Ge µIRE. The numbers indicated times of contacts between the IRE and the contaminated surface.

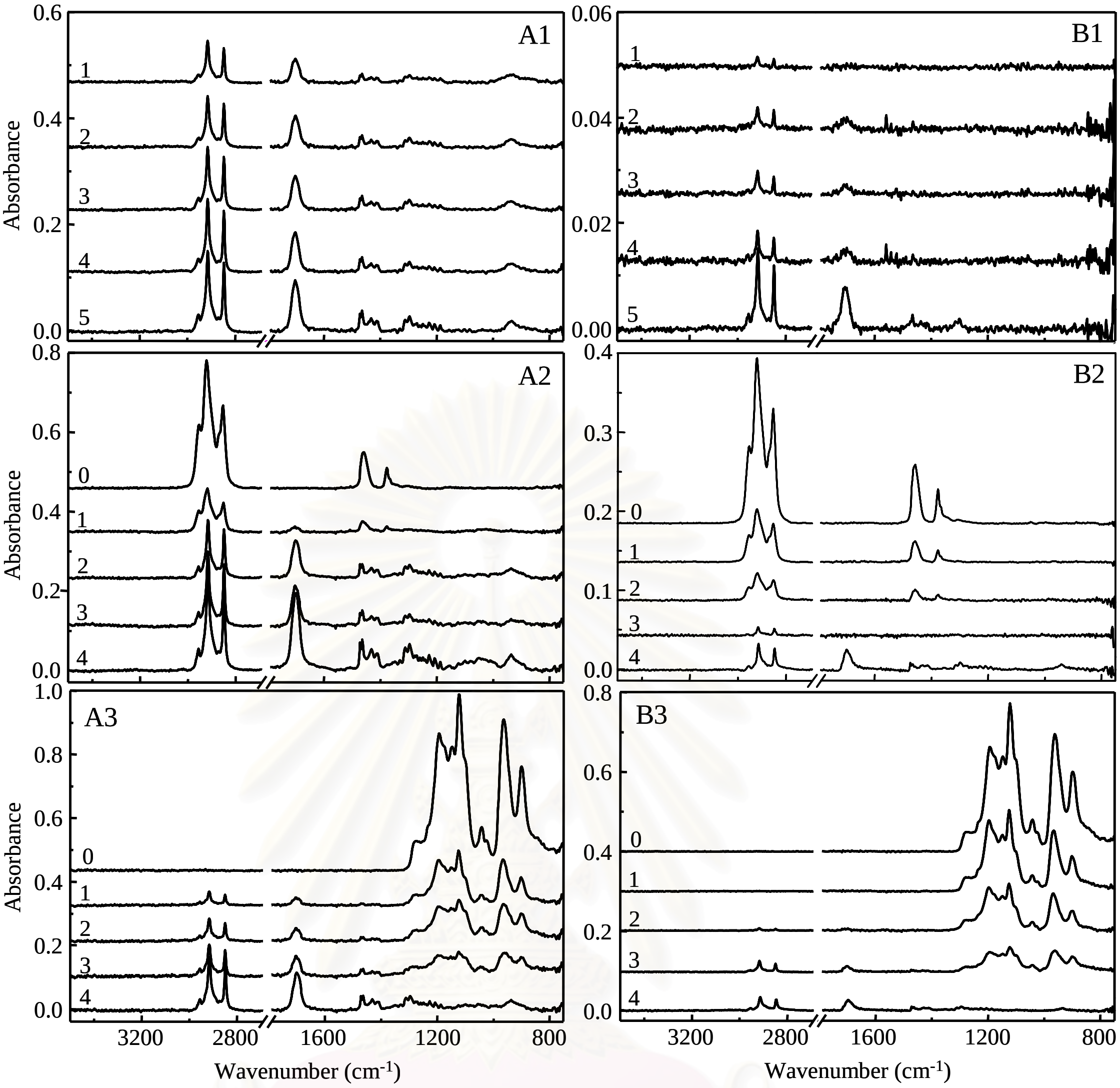


Figure 4.28 ATR FT-IR spectra of collecting residue of surface of chopstick brand name No.4: (A1, A2, A3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on diamond µIRE, and (B1, B2, B3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on Ge µIRE. The numbers indicated times of contacts between the IRE and the contaminated surface.

Fig 4.28 shows ATR FT-IR spectra of collecting residue on the surface of the slide-on diamond µIRE (Fig. 4.28 A1, A2, A3) and slide-on Ge µIRE (Fig. 4.28 B1, B2, B3). For ATR FT-IR spectra of surface of chopstick brand name No.4, spectral fingerprint of the contaminant can be observed by the "*contact-and-collect*" technique. The contaminated material can be picked up by the clean IRE (Fig. 4.28 A1, B1). These contaminants can be cumulatively collected on the tip by repeating contacts at various positions on the surface of chopstick. It clearly reveals that the strong band at 2800-3000 cm^{-1} which is the characteristic of C-H stretching vibration, the one strong absorption band at 1700 cm^{-1} is the characteristic of the C-O stretching vibration of wax and CH_3 asymmetric deformation at 1467 cm^{-1}, respectively. The observed spectrum indicated that the contaminant was wax. The obtained spectrum shows the dominant peaks of contaminants that can be assigned to octadecanoic acid or stearic acid which was employed as lubricant or softener for making chopsticks for softening up. It can be found in many foods, such as beef fat, and cocoa butter and is widely used as a lubricant i.e., in soaps, cosmetics, food packaging, deodorant, toothpastes, and as a softener in rubber.

The ATR FT-IR spectra of contamination on inside chopstick brand name No.4 obtained by the slide-on diamond µIRE and slide-on Ge µIRE are illustrated in Figure 4.29. After spectral acquisition, ATR FT-IR spectra showed the collecting residue of inside chopstick brand name No. 4 which was not observed because inside chopstick was not contaminated.

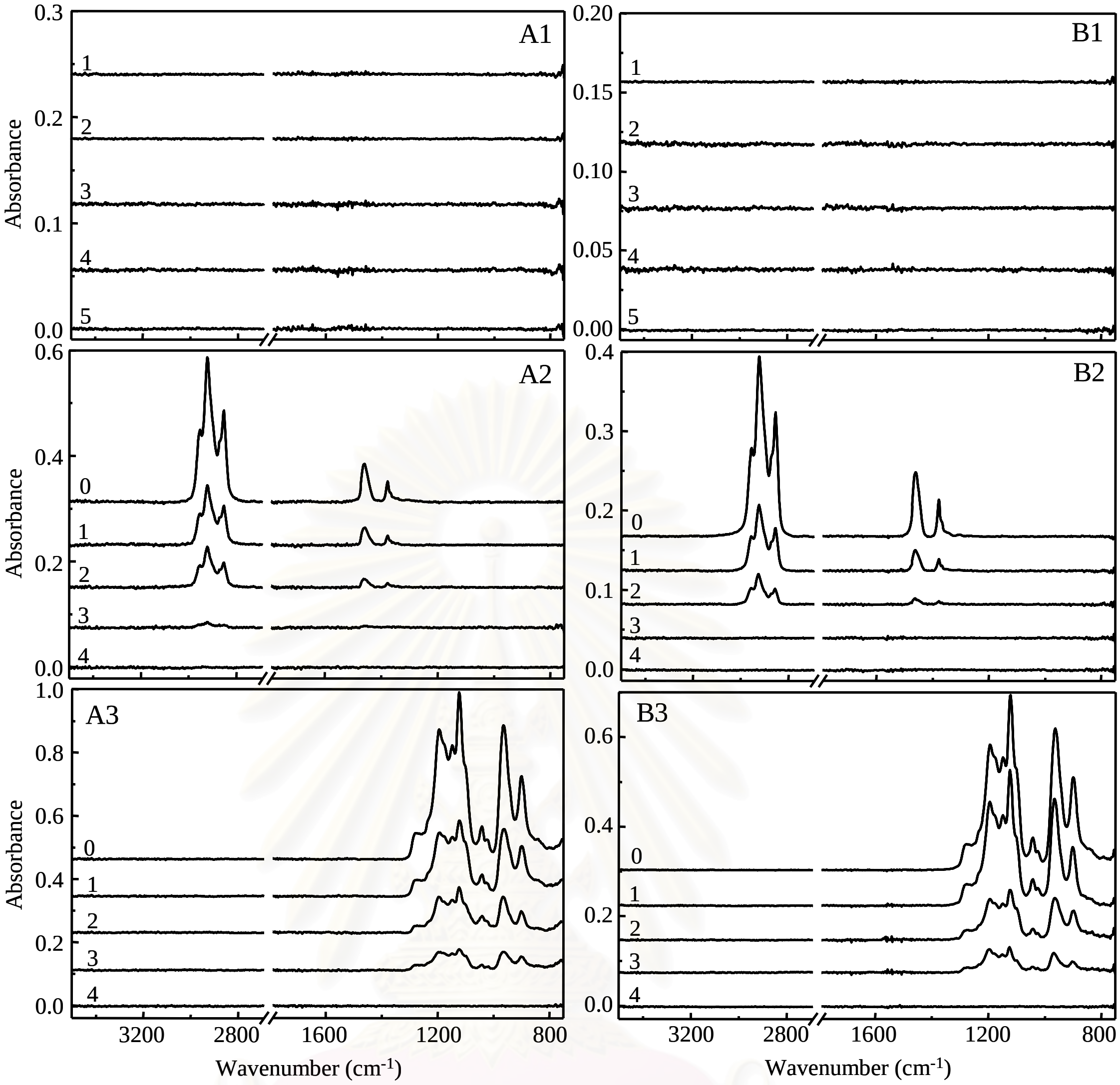


Figure 4.29 ATR FT-IR spectra of collecting residue of inside of chopstick brand name No.4: (A1, A2, A3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on diamond μIRE, and (B1, B2, B3) spectra of contaminants contacted with clean IRE, mineral-oil-coated IRE, fluorolube-coated IRE by using slide-on Ge μIRE. The numbers indicated times of contacts between the IRE and the contaminated surface.

4.5 Forensic Analysis of Medicine

From the point of view of forensic scientists, there are three important requirements for the analysis of drugs. Firstly, the method should be widely used to various samples; secondly, the method should be sensitive for a small amount of sample; and finally, the method should be accurate and rapid method for the actual needs. Above all, sample preparation should not be difficult because the pre-treatment processes may cause sample loss and can be contaminated from glassware, solvents and the labor atmosphere.

4.5.1 ATR FT-IR Spectra of Medicine Tablet (Acetominophen)

The structural formula of aspirin is shown in Figure 4.30. The observed spectra of drug tablet revealed high absorptions in the N-H stretching at 3320 cm^{-1} and plentifully absorption of drug at lower wavenumber in range 1700-750 cm^{-1}. This drug used for reproducing the investigation for forensic analysis of addicting thing in many incidents.

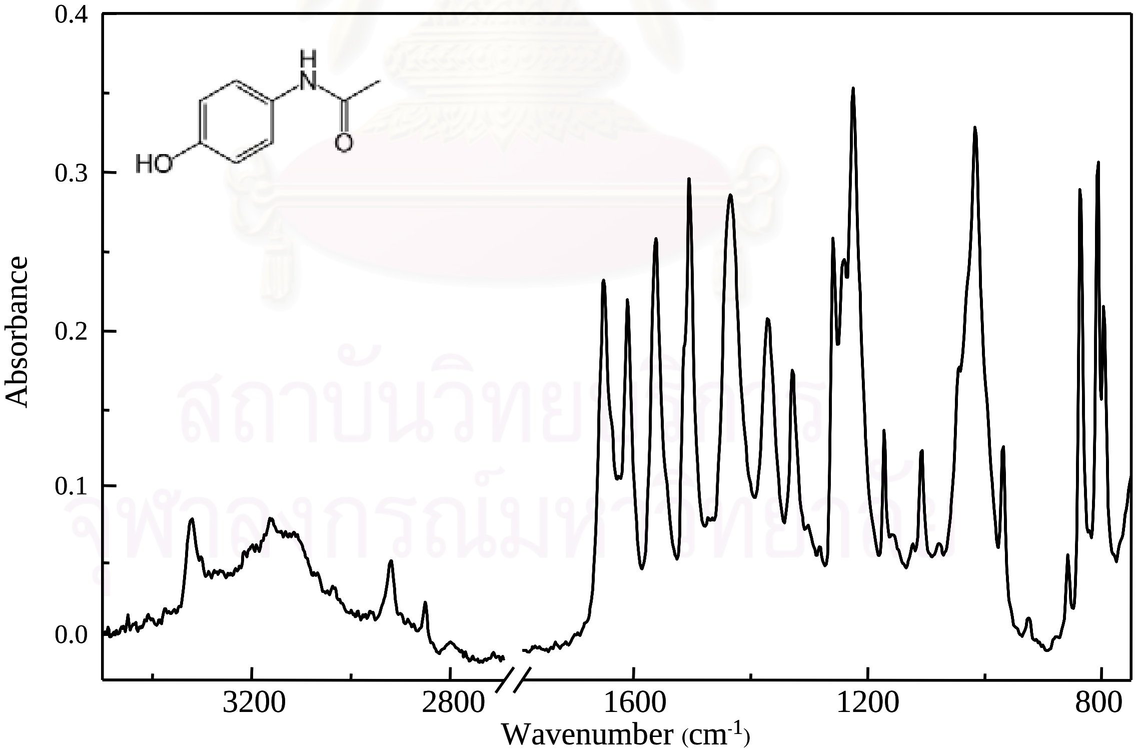


Figure 4.30 ATR FT-IR spectrum of drug tablet (acetaminophen) by using slide-on Ge μIRE.

Table 4.4: ATR spectral bands and corresponding assignments for acetominophen

Wavenumber (cm^{-1})	Assignments
3320	N-H stretching
3163	O-H stretching
1651	C=O stretching
1563	N–H in-plane bending
1610, 1505, 1435	C=C stretching of ring mode
1329	O–H bending
1259	C–O stretching
1225	C–N stretching

4.5.2 ATR FT-IR Spectra of Drug on Zip Lock® Bag

In case of forensic analysis, demonstrating the applicability of ATR FT-IR spectroscopy with the "*contact-and-collect*" technique for the analysis of surface contamination and its potential for forensic analysis were shown, and trace analysis of drug residues on surfaces were performed. Five paracetamol tablets (Acetominophen) were placed in a LDPE Zip lock® medicine bag. The bag was kept in a woman handbag for one day, so the drug tablets were contaminated on the Zip lock® bag. Fig 4.31 showed ATR FT-IR spectra of the collecting residue on the surfaces of clean and drug-contaminated Zip lock® bag. For the clean bag in Fig. 4.31 A, there is no residue or removable contaminant on the slide-on Ge µIRE although several contacts were made. When the same operation was performed on the surface of the drug-contaminated bag, the unique spectral feature of the drug was observed. The absorption increased after subsequently contacts (Fig. 4.31 B). The observed phenomenon was implied that the powder of drug on a surface can be transferred onto the slide-on Ge µIRE by a simple contact. A contact between the Ge µIRE and a drug trace, a portion of drug was left on the Ge tip. The collecting efficiency of the powder contaminant can be increased by a thin liquid film on the slide-on Ge µIRE (Fig. 4.31 C and D). This technique proved to be a very simple, rapid, sensitive and reproducible method for determining trace of drug. This novel technique can apply for forensic analysis of drug.

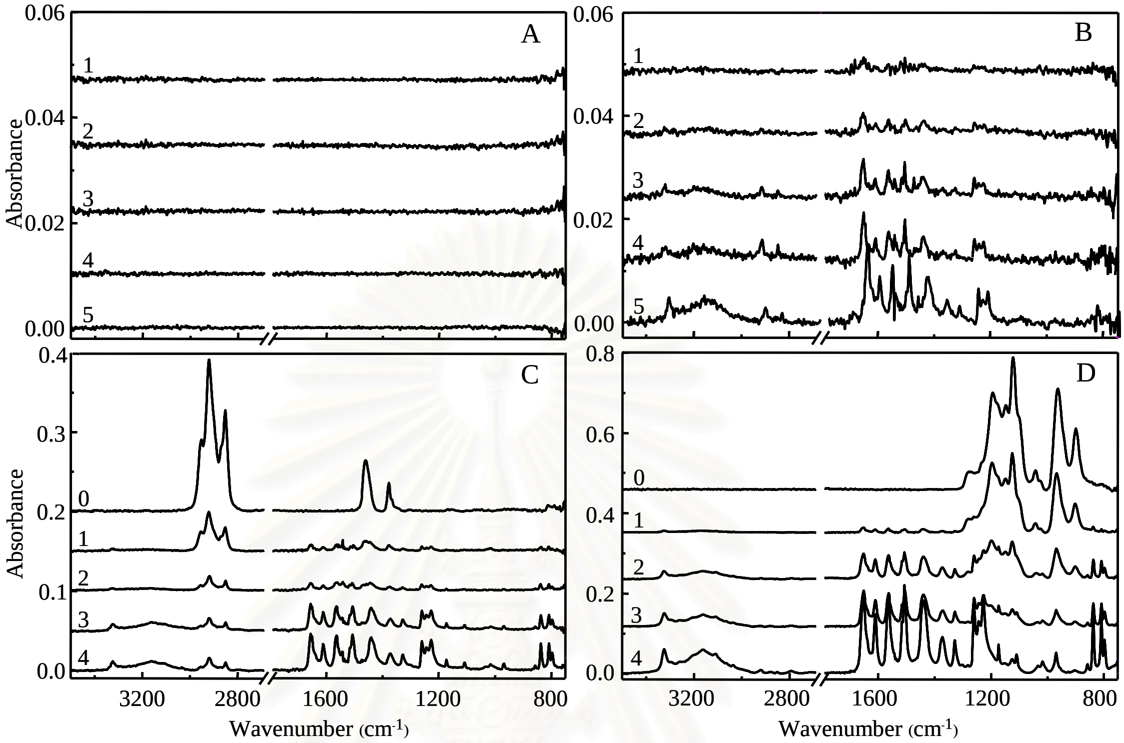


Figure 4.31 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge µIRE: (A) spectra of clean Zip lock® bag contacted with clean IRE, (B) spectra of drug-contaminated Zip lock® bag contacted with clean IRE, (C) mineral-oil-coated IRE, and (D) fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

4.5.3 ATR FT-IR Spectra of Drug on Banknote

After the banknote was used, the characteristics of the banknote fibers are changed and giving the appearance of holes which might contain the small particle [61] such as wax, drug, talc, etc. In case of drug trafficking, the drug dealers or the drug victims have a highly chance to contact banknotes. It is possible that drug may contaminate the banknote. Thus drug contamination on the banknotes may provide the evident clues and may be useful as legal evidences in court.

To solve this problem, the small tip of slide-on Ge μIRE was performed in similar phenomena from drug on Zip lock® bag. Outside the touching of contaminating of drug finger area, there was no removable contaminant on the surface of the clean-banknote (Fig. 4.32 A). A trace residue or contaminant was not observed even after a large numbers of subsequently contacts. A contact at the finger-touched area, spectral fingerprint of the drug was observed on a clean slide-on Ge μIRE. The absorption increased with the number of contacts (Fig. 4.32 B). Since the contacts were made at different positions, the contaminated drug powder was collectively transferred onto the slide-on Ge μIRE. A numbers of contact can be made in order to collect a sufficient amount of drug trace.

From these data, an experienced analyst can readily discern money closely associated with drug dealing or trafficking. The collecting efficiency of the drug powder was greatly enhanced when collecting agent were employed (Figure. 4.32 C and D). Similar to those observed in Fig. 4.31, the amount of drug powder on the slide-on Ge μIRE was increased with the number of contact while that of the collecting agent decreased. The novel technique for determining the contamination of banknotes can be used in forensic investigation.

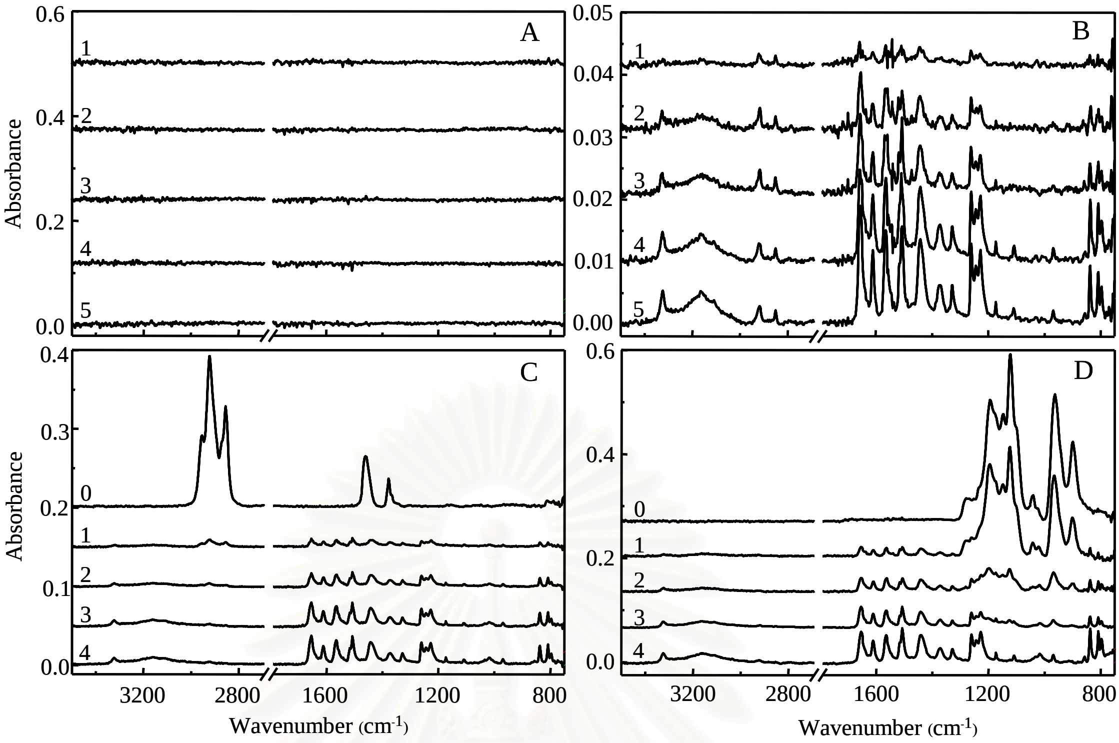


Figure 4.32 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge µIRE: (A) spectra of clean banknote contacted with clean IRE, (B) spectra of drug-contaminated banknote contacted with clean IRE, (C) mineral-oil-coated IRE, and (D) fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

4.6 Case Study for Forensic Analysis

Forensic analysis of drug is a problem in many evidences. The evidence can frequently provide useful information about the linkage between a victim, a suspect and a scene. In this case study, contaminations on the rear surface of a mobile phone mask were observed. The principle is that if telephone has been in close proximity to drugs or in drug-contaminated hand of suspect, some substances will therefore contaminating the rear of telephone and the occurrence of the contaminant can be predicted.

Fig. 4.33 shows ATR FT-IR spectra of contaminants on the rear surface of a mobile phone mask. The phone belonging to a female volunteer was kept in her handbag during traveling or when it was not in use. For the clean mobile phone mask in Figure 4.33 A, there is no residue or removable contaminant on the slide-on Ge µIRE although several contacts were made. The same operation was performed on the contaminated surface of mobile phone mask, the unique spectral feature of stretching Si-O-Si peak at 1014 cm^{-1} was observed. The observed spectrum is namely talc. The collecting efficiency of the powder contaminant can be increased by a thin liquid film on the slide-on Ge µIRE. The absorption of the contaminant increased while that of the liquid film decreased (Figs. 4.33 C and D). Thus, the observed contaminants represented the dust or powder with in her bag. The talc powder may originate from her facial cosmetics that always have been kept in the handbag. The *"contact and collect"* technique are suitable for analysis of the evidence in many crime scenes because the evidences are non-destroying and rapid to analysis and the results are accurate and reliable.

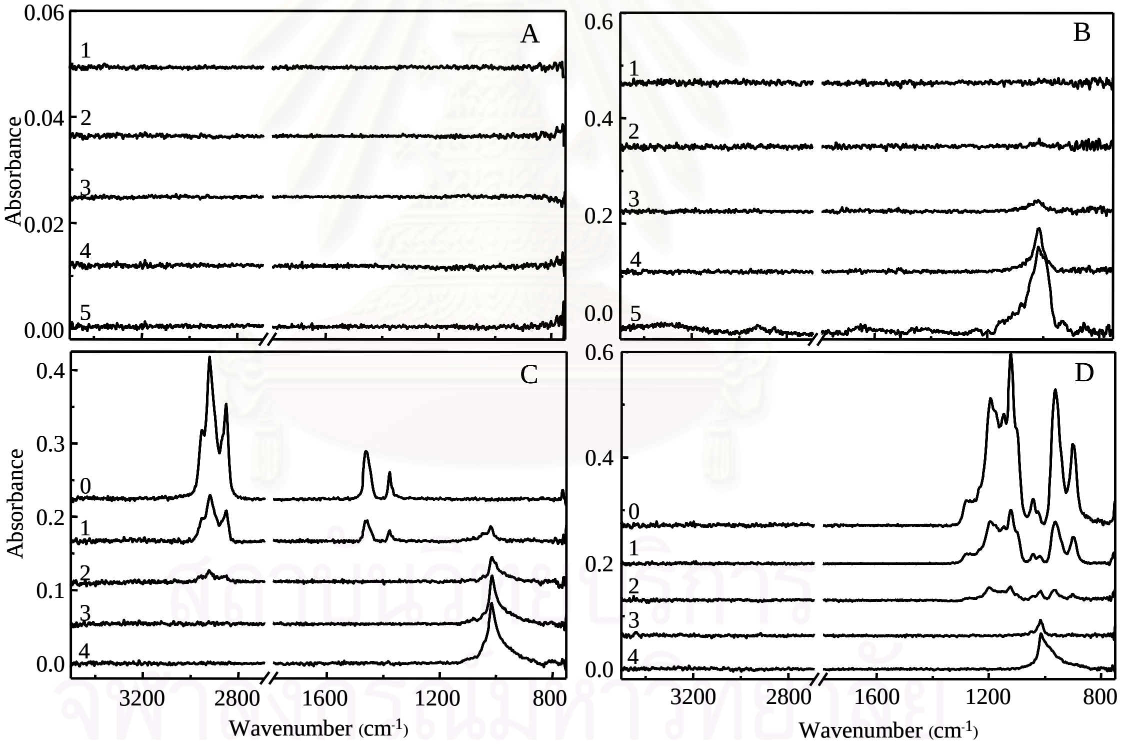


Figure 4.33 ATR FT-IR spectra of collecting residue on the surface of the slide-on Ge µIRE: (A) spectra of clean mobile phone mask contacted with clean IRE, (B) spectra of contaminated mobile phone mask contacted with clean IRE, (C) mineral-oil-coated IRE, and (D) fluorolube-coated IRE, respectively. The numbers indicated times of contacts between the IRE and the contaminated surface.

CHAPTER V

CONCLUSIONS

Attenuated total reflection Fourier transform infrared (ATR FT-IR) microspectroscopy is one of the suitable techniques for the characterization of surface contamination. Even through the contamination is widely fined in a few amount, the infrared microscope can be described the chemical information of the contaminants. Since infrared spectrum is directly related to chemical structure and the composition of the materials, the observed spectra of contaminants can be analyzed.

The homemade slide-on diamond μIRE and slide-on Ge μIRE were employed for ATR FT-IR spectral acquisition by using an infrared microscope. With the easy operation of the microscope, a specific area can be selectively analyzed and verified. Both accessories successfully employed for the investigation of the very small sample size such as dust and trace of drug. The trace amount of the contaminants on both IREs can be separated from the substrate and characterized under the ATR mode without any interference of the substrate. Several contacts between IREs and specimen were performed for collecting the trace contaminants on the tip of both IREs and gave a good quality spectrum.

The advantages of the novel *"contact-and-collect"* technique accompanied with slide-on diamond μIRE and slide-on Ge μIRE were discussed. For the excellence of this technique, the unique spectral feature can be acquired without any influence of the substrate and the increasing amount of the contaminants was collected (by making a large number of contacts). The analysis process is very simple, rapid, does not require additional sample preparation and the result is accurate and reliable. Moreover, the technique is non-destructive, does not induce a cross-contamination into the system, and the measured specimen can be kept as a reference and employed for further analysis. The ATR FT-IR spectra of contaminants can be indicated the specific information at very low levels, which is the major advantage of the slide-on diamond μIRE and the slide-on Ge μIRE.

From the studies, it is concluded that almost all of the observed spectra acquired by the slide-on diamond μIRE were similar to that acquired by the slide-on Ge μIRE. Both IREs show the potential for the characterization of surface contamination and forensic analysis, but the slide-on Ge μIRE is suitable for smooth surface such as polypropylene bag and banknote. For the slide-on diamond μIRE, due to the small culet and the rigid of the diamond μIRE, the spectral acquisition of the small contaminants on the roughness sample surface such as powder on wood chopstick gave a more highly spectrum quality than that of the slide-on Ge μIRE.

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