

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Diamond spectra of diamond micro-ATR sensor

Figure 4.1 shows transmittance spectra of flat tip and sharp tip diamond micro-ATR sensors. The spectra obtained from the two configurations of diamond tips are almost the same. Both spectra clearly reveal three principal absorption bands (three-phonon ($3900\text{-}2650\text{ cm}^{-1}$), two-phonon ($2650\text{-}1500\text{ cm}^{-1}$), and one-phonon ($1400\text{-}900\text{ cm}^{-1}$)) of diamond [25]. In addition, weak absorption bands in the high wavenumber region are clearly observed. A sharp peak at 3107 cm^{-1} in Figure 4.1 (A) is attributed to the hydrogen impurity in crystal structure of diamond. The over absorption band in the two-phonon and one-phonon regions are due to the high absorption coefficient in these spectral regions, concentration of nitrogen impurity in crystal structure and size of the diamond sample. Diamond with high nitrogen content always shows high absorption in the one-phonon region.

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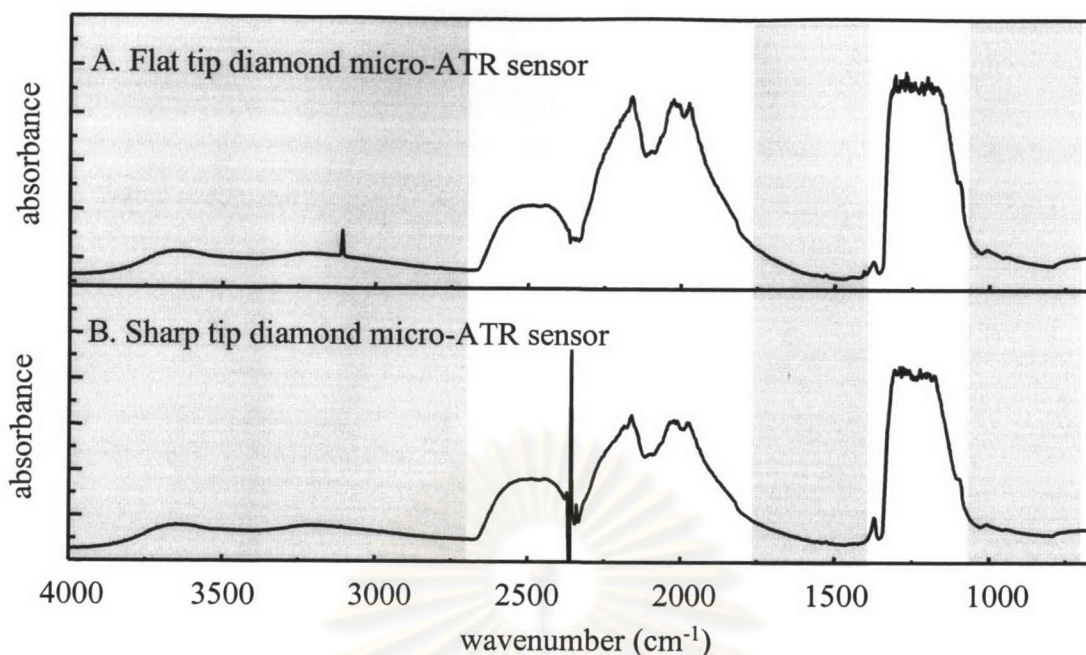


Figure 4.1 Infrared spectra of diamond micro-ATR sensor: flat tip diamond (A) and sharp tip diamond (B)

To use a diamond as an IRE in micro-ATR sensor, the spectral regions useful for the analysis of samples are the regions without high absorption bands of diamond, which are the between $3000\text{-}2800\text{ cm}^{-1}$, $1800\text{-}1400\text{ cm}^{-1}$, and $1000\text{-}650\text{ cm}^{-1}$.

4.2 ATR spectra of soft polymers

4.2.1 Flat polyethylene film

Figure 4.2 demonstrates spectra of polyethylene sample. Figure 4.2 (A) shows a spectrum obtained via ZnSe IRE. The spectrum clearly reveals characteristic absorption bands of poly(ethylene) film. Since the sample is flexible, a good contact between the sample and the surface of the IRE can be obtained. The spectra obtained from the diamond micro-ATR sensors are similar to that obtained from the conventional ATR technique. It can be seen from Figures 4.2 (B) and (C) that the characteristic feature of PE can be observed in the spectral region. It should be noted that their spectral intensities are not so much different. This implies that the contacts

between the flat tip and sharp tip diamonds with the sample are not different. Since PE film is flexible, its flat surface can be easily put into an optical contact with both types of diamond sensors.

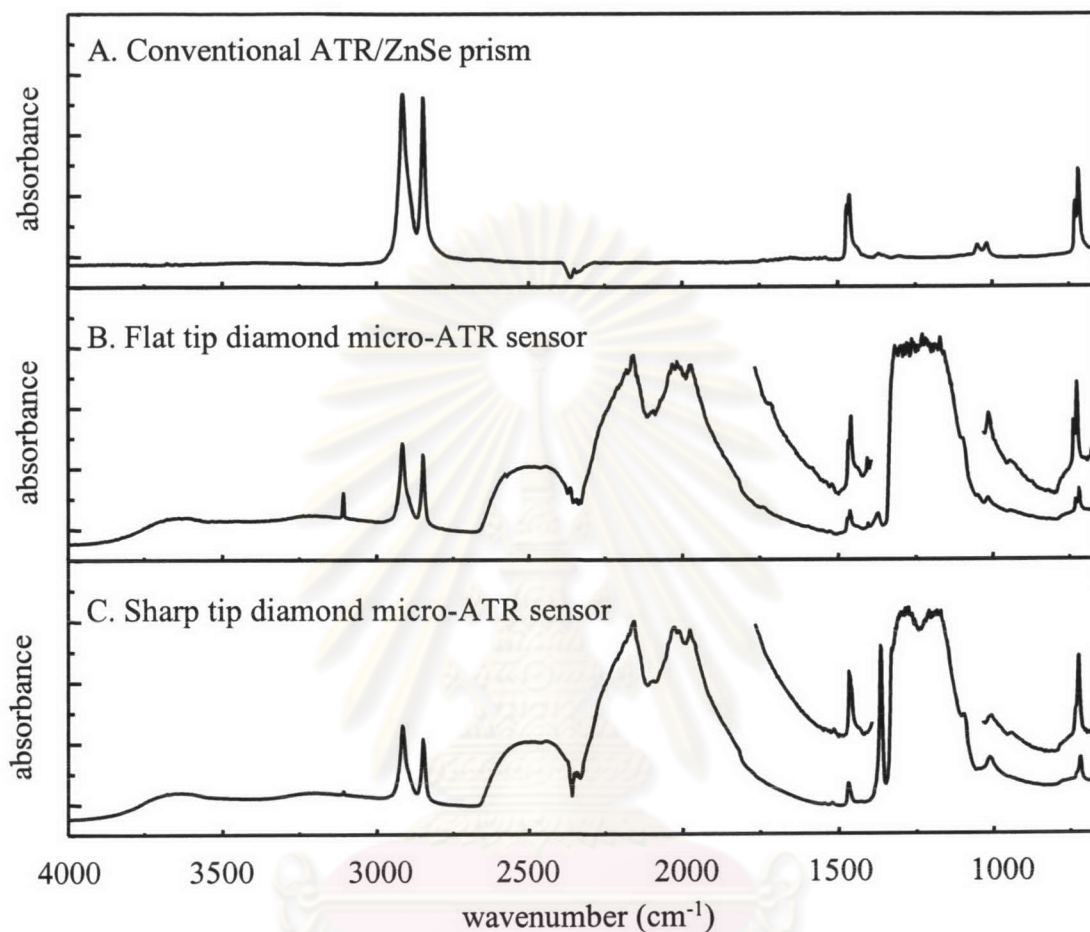


Figure 4.2 ATR spectra of Flat polyethylene film obtained via ZnSe prism (A), flat tip diamond micro-ATR sensor (B), and sharp tip diamond micro-ATR sensor (C).

4.2.2 Thick polypropylene film

The spectrum of poly(propylene), (PP) obtained via ZnSe IRE is shown in Figure 4.3 (A). The observed spectrum clearly shows characteristic band of PP. Since PP is soft and flexible, an optical contact can be easily achieved. The spectra shown in Figures 4.3 (B) and 4.3 (C) are ATR spectra of PP sample placed into contact with flat tip and sharp tip diamond micro-ATR sensors by applying pressure. Both spectra indicate the characteristic bands of PP similar to those obtained by using ZnSe prism.

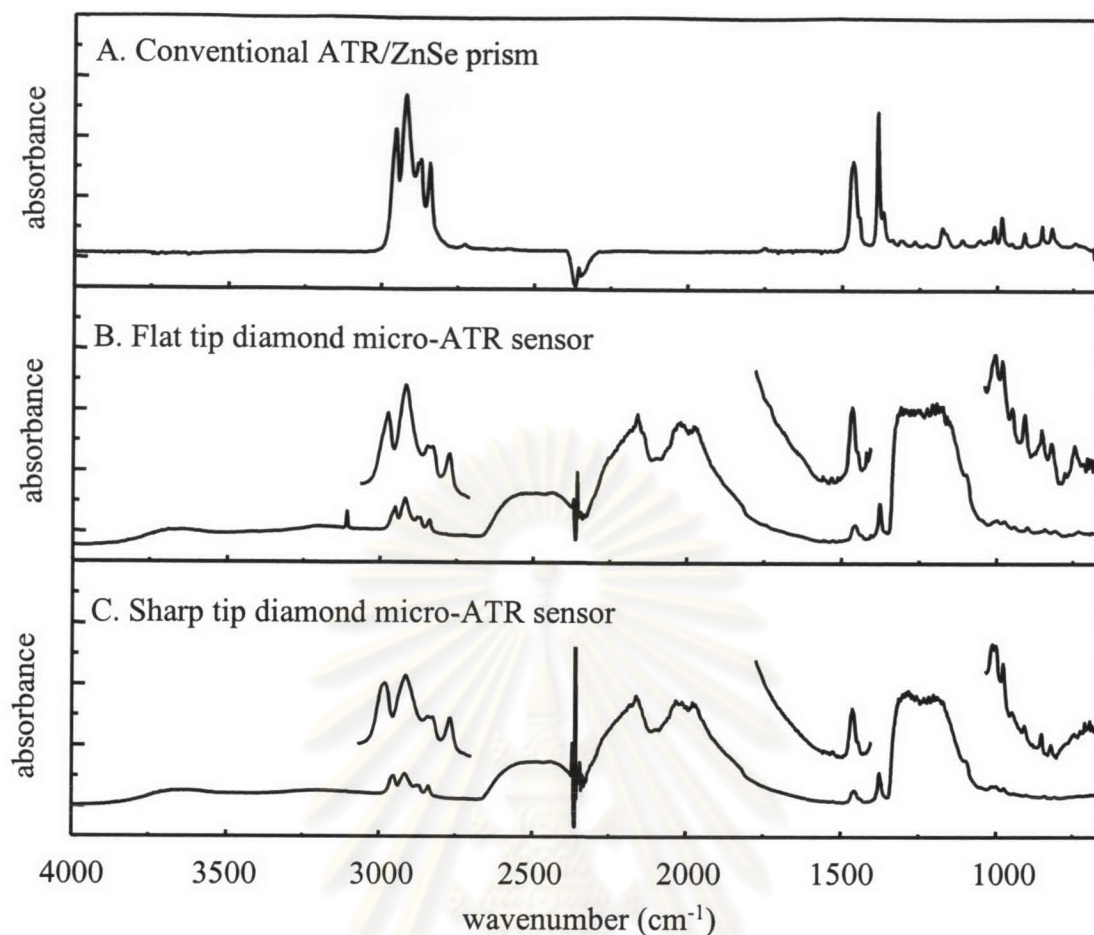


Figure 4.3 ATR spectra of thick poly(propylene) film obtained via ZnSe prism (A), flat tip diamond micro-ATR sensor (B), and sharp tip diamond micro-ATR sensor (C).

From the experiment results, it was found that an optical contact between soft sample and two types of diamond IRE is crucial for further analysis of the observed spectra. In addition, there are the same absorbance bands of sample in three regions when spectrum observed via ZnSe IRE and spectra observed via diamond micro-ATR sensors are compared. Spectra obtained from diamond micro-ATR sensors can be directly compared from ZnSe IRE.

4.3 ATR spectra of hard and rigid polymers

4.3.1 Thick polystyrene piece

Figure 4.4 (A) shows ATR spectra of thick poly(styrene), (PS) obtained via ZnSe prism. There is no characteristic band of PS in spectrum. Because of the irregular surface of the sample, a contact between the sample and the IRE is poor.

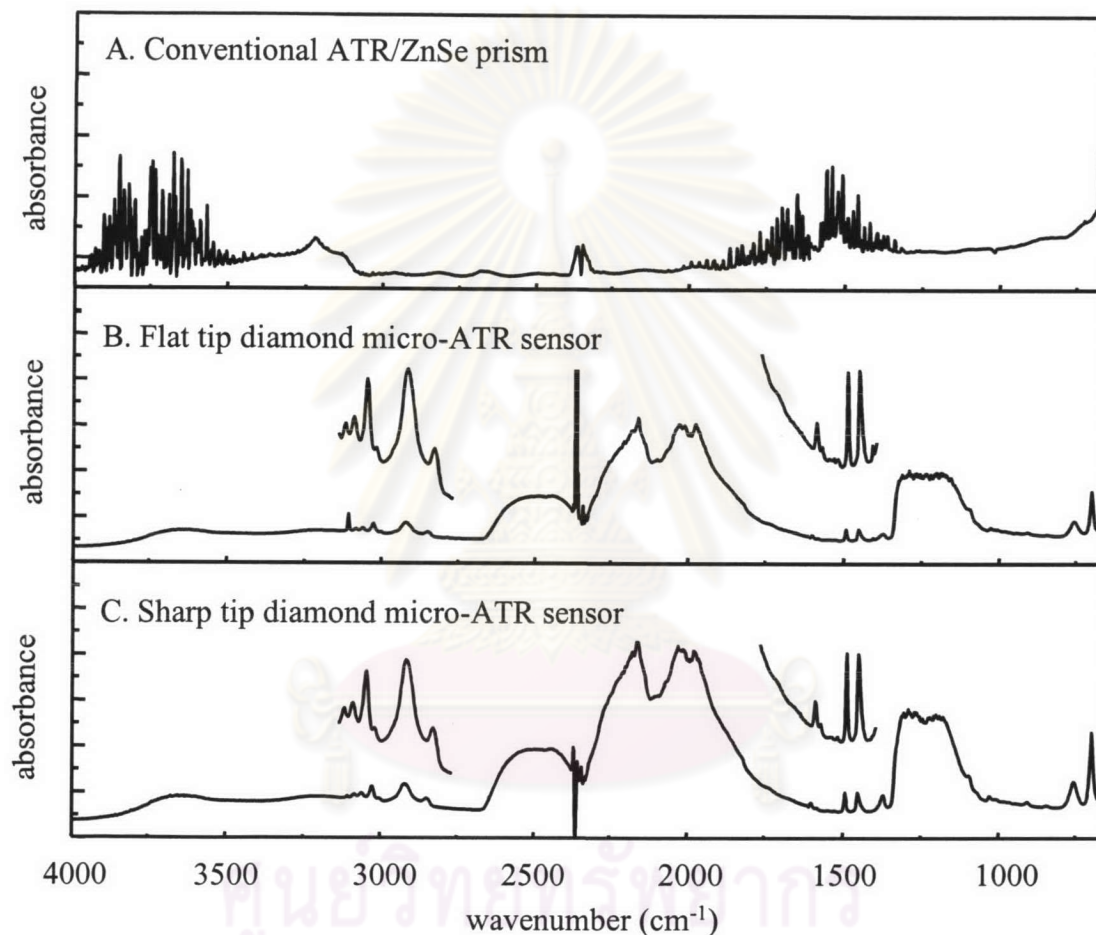


Figure 4.4 ATR spectra of thick poly(styrene) obtained via ZnSe prism (A), flat tip diamond micro-ATR sensor (B), and sharp tip diamond micro-ATR sensor (C).

Figure 4.4 (B) spectrum of the PS sample acquired via flat tip diamond micro-ATR sensor. It can be seen that the spectrum shows the characteristic bands of the PS sample. Its curved surface is not a problem for analyzing the sample since the flat tip diamond possesses a good sample/IRE contact. The result is similar to the spectrum is

observed via sharp tip diamond micro-ATR sensor shown in Figure 4.4 (C). Due to small sampling area of flat tip, sample with curved and rigid surface can be analyzed using this technique. A good contact can easily be obtained.

From spectra B and C, one will quickly notice that the spectral intensities are not so much difference. This implies that the contacts between two tips of diamonds and the PS sample are not significantly different.

4.3.2 Thick polycarbonate film

Figure 4.5 shows spectra of thick poly(carbonate) (PC) film obtained via ZnSe prism (A), flat tip diamond (B), and sharp tip diamond (C). Figure 4.5 (A) shows ATR spectrum of thick PC film. The ATR spectrum of the PC film cannot be observed under the applied pressure. In order to ensure the good contact, the ATR spectra were collected with increasing applied pressure. This observed spectrum indicates the existence of an air gap between IRE and hard and rigid sample. As a result, a good contact between the sample and the IRE cannot be achieved by simply applying the pressure. Since the ZnSe prism is soft IRE, its surface can be damaged by the excessive applied pressure. In order to verify optical contact, diamond micro-ATR sensor was introduced for the analysis of hard and rigid sample.

ATR spectra of thick PC film acquired via two systems of diamond micro-ATR sensors are shown in Figures 4.5 (B) and (C). High absorption bands of PC are observed with small applied pressure. The phenomena observed in Figures 4.5 (B) and (C) indicate an improved contact between both types of diamond tips and the sample.

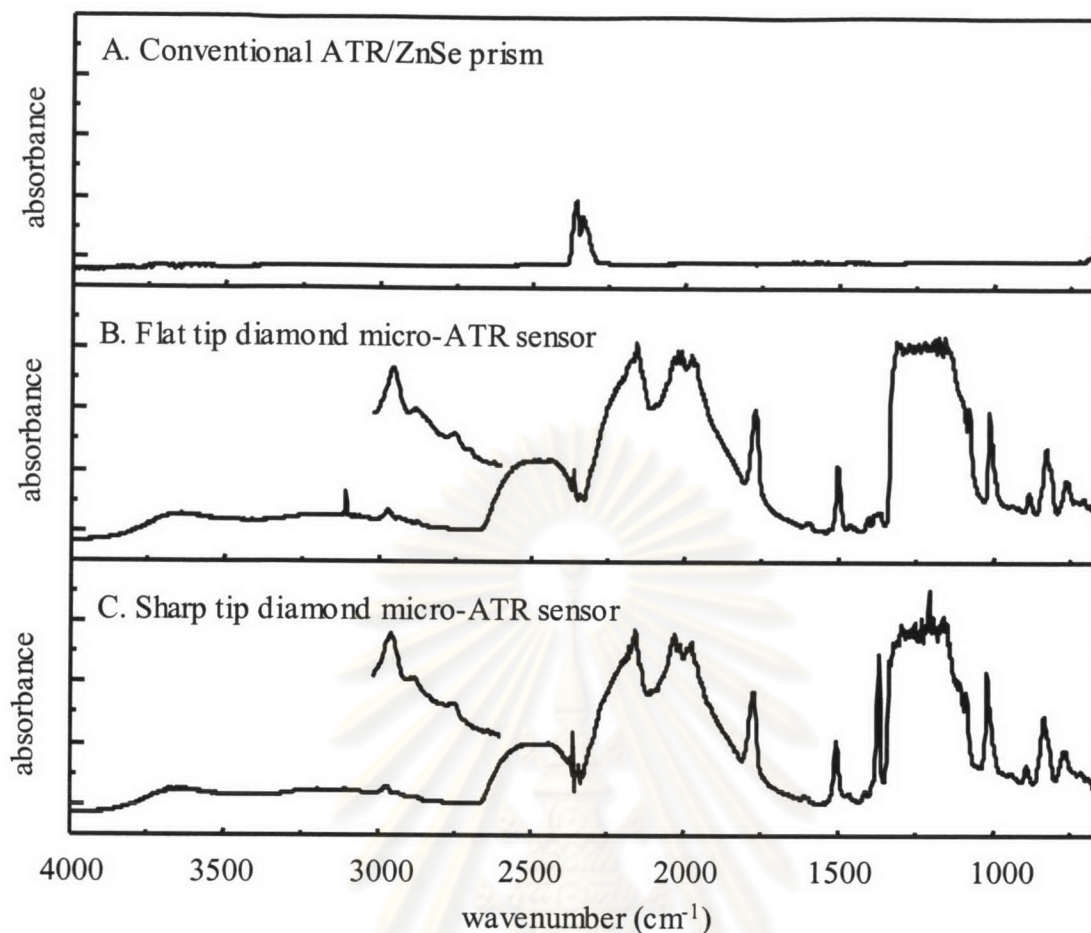


Figure 4.5 ATR spectra of thick polycarbonate film obtained via ZnSe prism (A), flat tip diamond micro-ATR sensor (B), and sharp tip diamond micro-ATR sensor (C).

From experimental results, it was found that an optical contact between hard and rigid samples and the IRE is necessary for further analysis of the observed spectrum. However, it cannot be easily achieved by simply applying pressure to the system. Different types of samples and their surface (i.e., rigid samples and rough and curved surface) make a good contact impossible. The contact improvement is required in order to acquire ATR spectrum of the sample. The diamond micro-ATR sensors are introduced into the analysis of the rigid samples in order to improve the contact. Small applied pressure seems to improve the contact significantly. Due to the hardness of diamond and small sampling area, high pressure and goodness of contact are generated.

4.4 ATR spectra of thin film polymer on metal

The spectra of a soft drink can obtained with various sensors are shown in Figure 4.6. In Figure 4.6 (A), the ATR spectrum obtained by ZnSe prism cannot be observed. For the analysis of thin film polymer on metal, sample preparation is very difficult since the ZnSe prism can be easily scratched by the edge of metal. The characterization of solid samples, especially hard and rigid samples such as a metal, normally encounters air gap problems. Severe absorbance deterioration is observed when the surface of the sample is not smooth or cannot be pressed against the IRE. This spectrum shows that when the air gap is thick enough, the characteristic absorption of the sample cannot be observed.

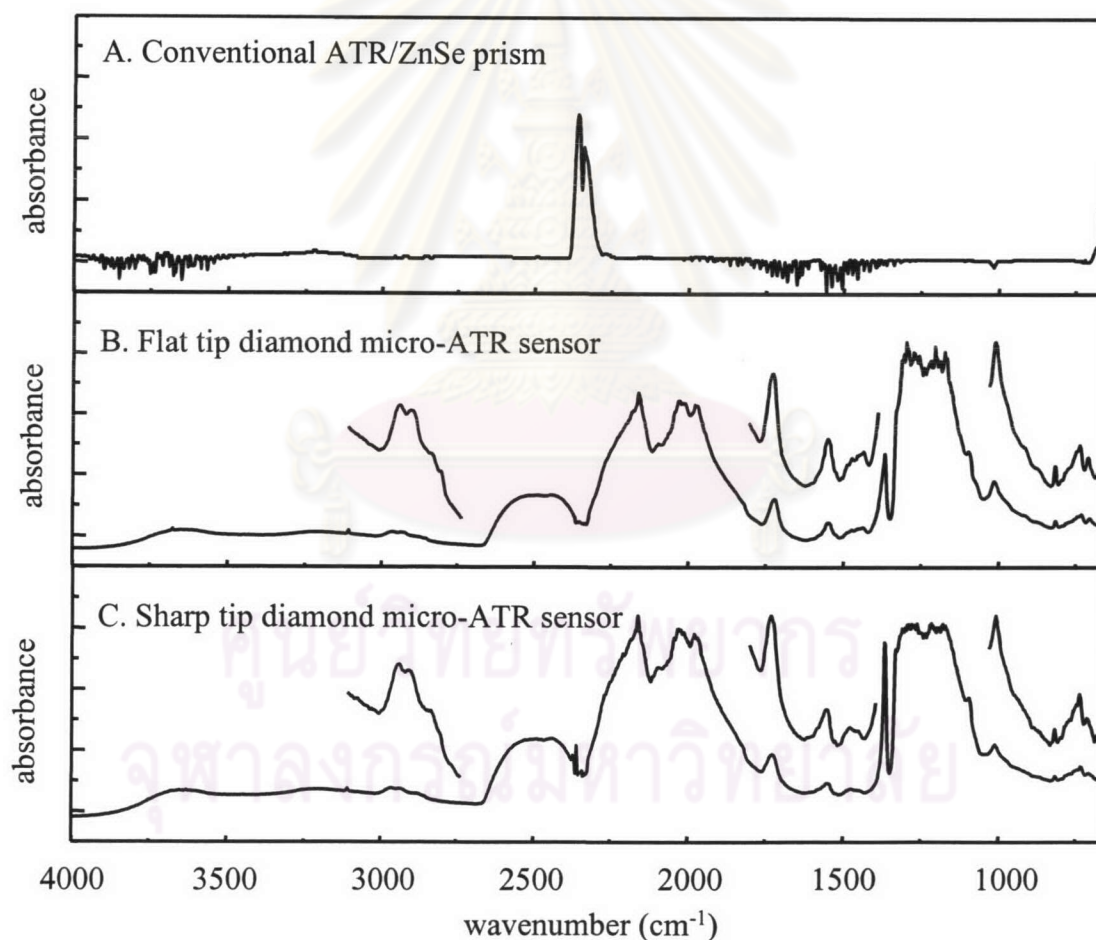


Figure 4.6 ATR spectra of a soft drink can obtained via ZnSe prism (A), flat tip diamond micro-ATR sensor (B), and sharp tip diamond micro-ATR sensor (C).

When the diamond micro-ATR sensors are employed (see Figures 4.6 (B) and (C)), characteristic absorptions of the sample can be observed. In Figures 4.6 (B) and (C), the obtained spectra show the same spectral feature although physical shapes of diamond tip are different. This is because the coating on a soft drinks can has been brought into an optical contact with diamond IREs.

The use of diamonds does significantly improve optical contact with the sample. When the air gap is eliminated, absorption bands associated with the thin polymer film coated on the metal can be observed.

4.5 ATR spectra of polymer coating on polymer

4.5.1 Compact disc

Figure 4.7 shows spectra of compact disc, (CD) acquired by ZnSe prism (A), flat tip diamond (B), and sharp tip diamond (C). The sample was a virgin compact disc with mirror-flat surface. The CD is a good example for the study of sampling depth since its surface is coated with a thin polymeric film. Figure 4.7 (A) shows a spectrum of CD sample at the point where no further intensity change was observed as pressure was increased. In order to verify optical contact, two configurations of diamond tips were employed. Consider spectra B and C, the slightly different spectral feature is observed at 1760 cm^{-1} (see Figure 4.9). This band only appears in the spectrum of PC obtained via sharp tip diamond. This is because the compact disc is consists of two components: color polymer coating and thick PC substrate. The sharp tip diamond can penetrate polymer coating on PC and collect the information both at the surface and bulk of the sample. The distinguishable absorption band appeared in Figures 4.9 and 4.10 may be identified as a characteristic peak of PC. These appearances confirm the benefit of sharp tip diamond which suitable for the characterization of coating sample since it can reveal the surface information and depth-dependent information of coating sample.

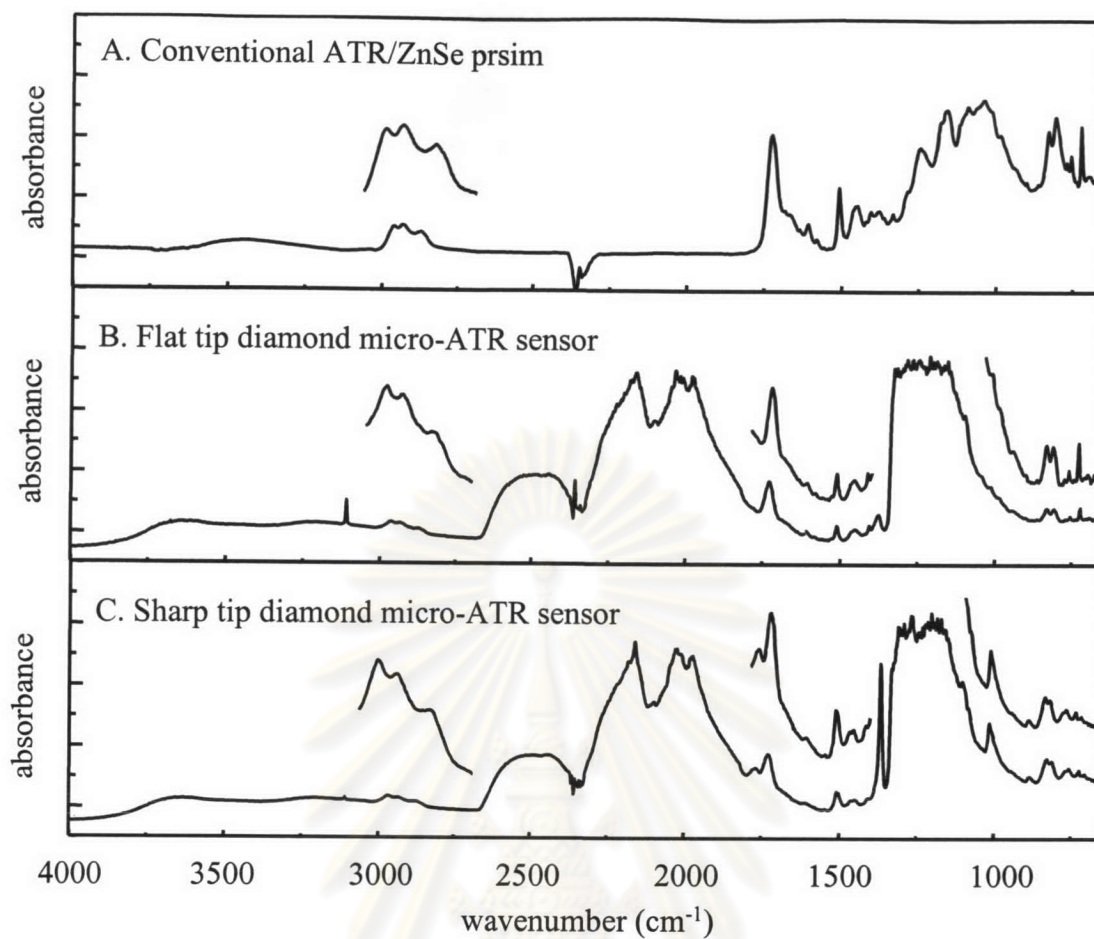


Figure 4.7 ATR spectra of CD obtained via ZnSe prism (A), flat tip diamond micro-ATR sensor (B), and sharp tip diamond micro-ATR sensor (C).

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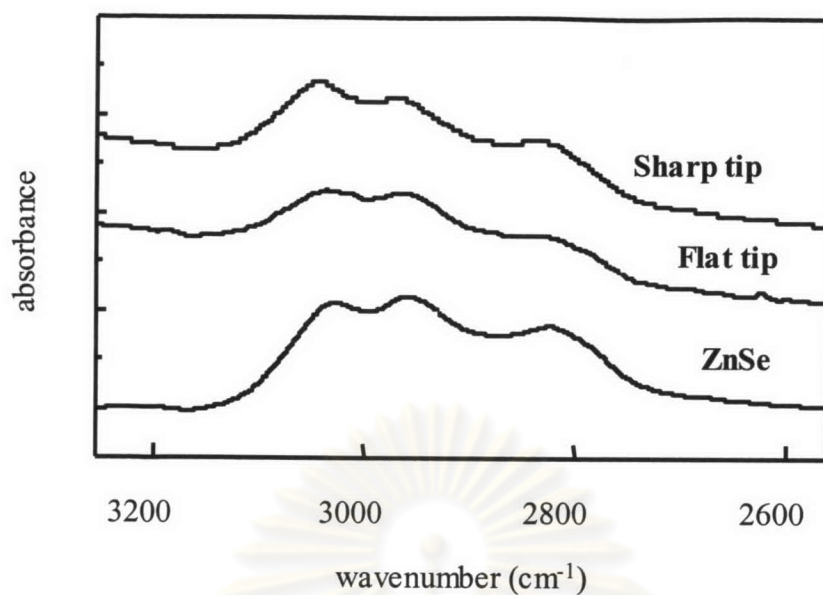


Figure 4.8 ATR spectra of CD in the spectral range of 3250-2550 cm^{-1} obtained via ZnSe prism, flat tip diamond micro-ATR sensor, and sharp tip diamond micro-ATR sensor.

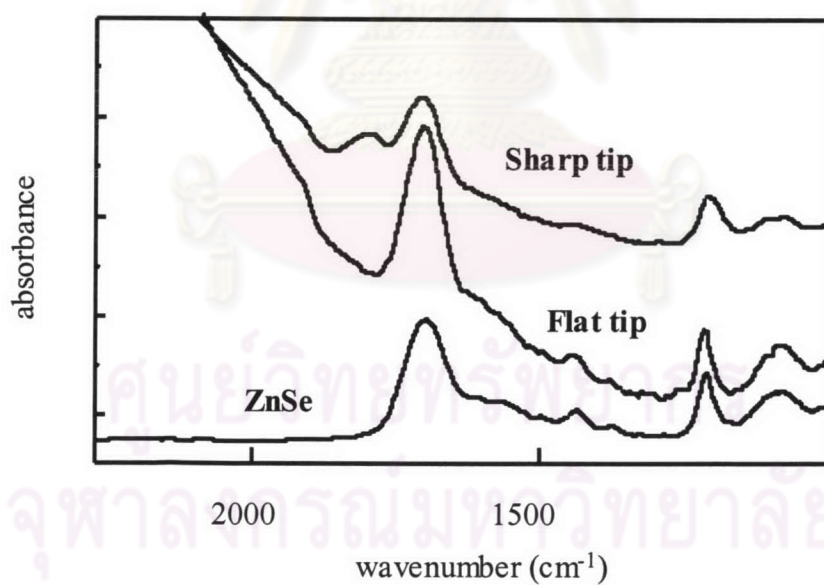


Figure 4.9 ATR spectra of CD in the spectral range of 2200-1250 cm^{-1} obtained via ZnSe prism, flat tip diamond micro-ATR sensor, and sharp tip diamond micro-ATR sensor.

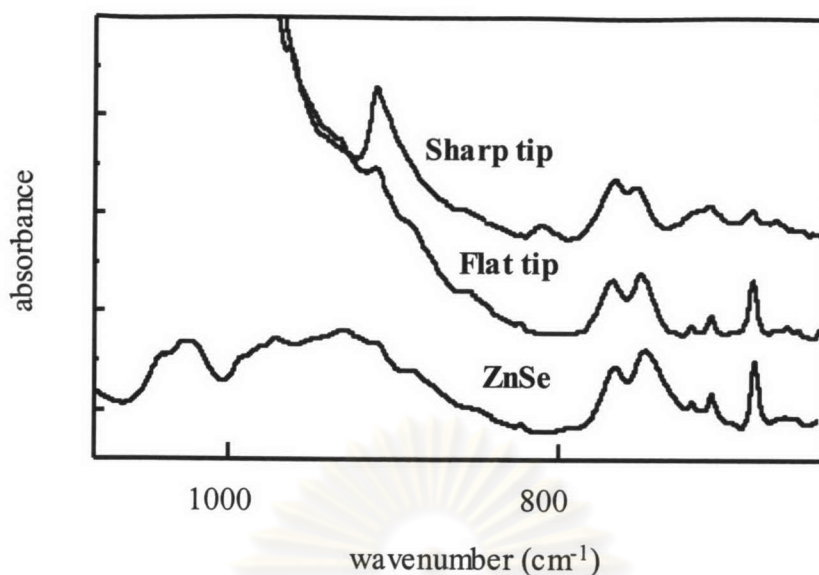


Figure 4.10 ATR spectra of CD in the spectral range of 1000-700 cm^{-1} obtained via ZnSe prism, flat tip diamond micro-ATR sensor, and sharp tip diamond micro-ATR sensor.

The observation illustrates the ATR using ZnSe prism and flat tip diamond micro-ATR sensor can provide only surface information while using sharp tip diamond contributed both the surface and depth information of sample.

4.5.2 Adhesive tape

ATR spectra of adhesive tape are shown in Figure 4.11. Adhesive tape is a polymer thin coated with an adhesive layer. Three sensors can achieve the absorption bands of sample. Moreover, three spectra observed from each sensor provide the same absorption bands (in three regions). In both ZnSe prism and flat tip diamond system, the same spectral feature is observed due to configuration of contact surface. Although, the configurations of contact surface between flat tip diamond and sharp tip diamond are quite different, similar spectra (Figures 4.11 (B) and (C)) are obtained. This is because the glue layer on the tape surface is thick hence, sharp tip diamond cannot reach the thin polymer substrate.

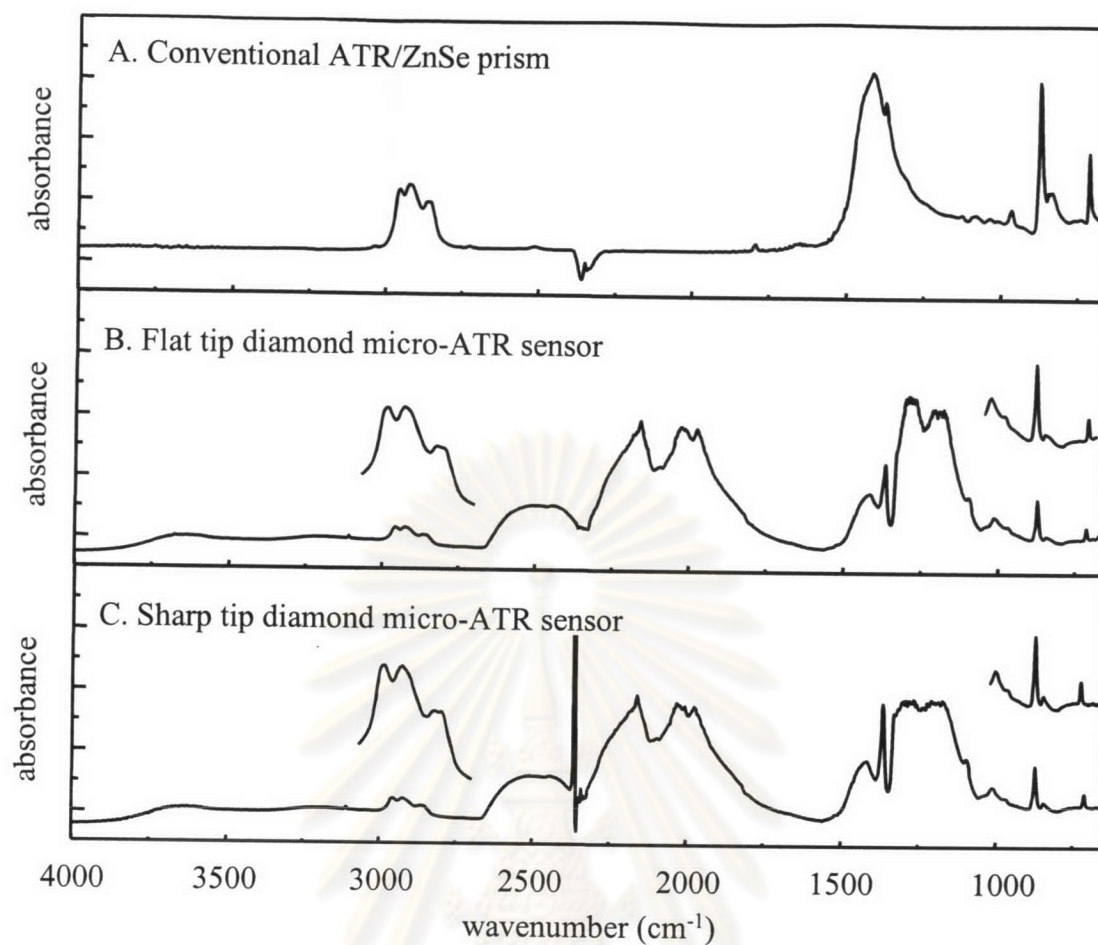


Figure 4.11 ATR spectra of adhesive tape obtained via ZnSe prism (A), flat tip diamond micro-ATR sensor (B), and sharp tip diamond micro-ATR sensor (C).

In case of using various configurations of diamond heads (i.e., flat and sharp tip diamonds) for analyzing coating, when the coating is thick, the spectra observed from flat tip diamond and sharp diamond provide only the information associated with the thick coating layer.

4.6 ATR spectra of the small sampling area

4.6.1 50 baht bank note on blue region

Figure 4.12 shows ATR spectra of 50 baht bank note obtained via various ATR systems in blue color area. In Figure 4.12, three regions in the spectra obtained via ZnSe prism and flat tip diamond micro-ATR sensor provide the same absorption bands (see Figures 4.12 (A) 4.12 (B)). This is due to the same configurations of surface contact in the IREs (i.e., flat surface). In Figures 4.12 (A), (B), and 4.12 (C), absorption bands of the sample obtained via sharp tip diamond provide significantly different absorption bands from ZnSe prism and flat tip diamond sensor. This is because the sharp tip diamond can penetrate color polymer coating on the bank note and collect the information both at the surface and bulk of the sample.



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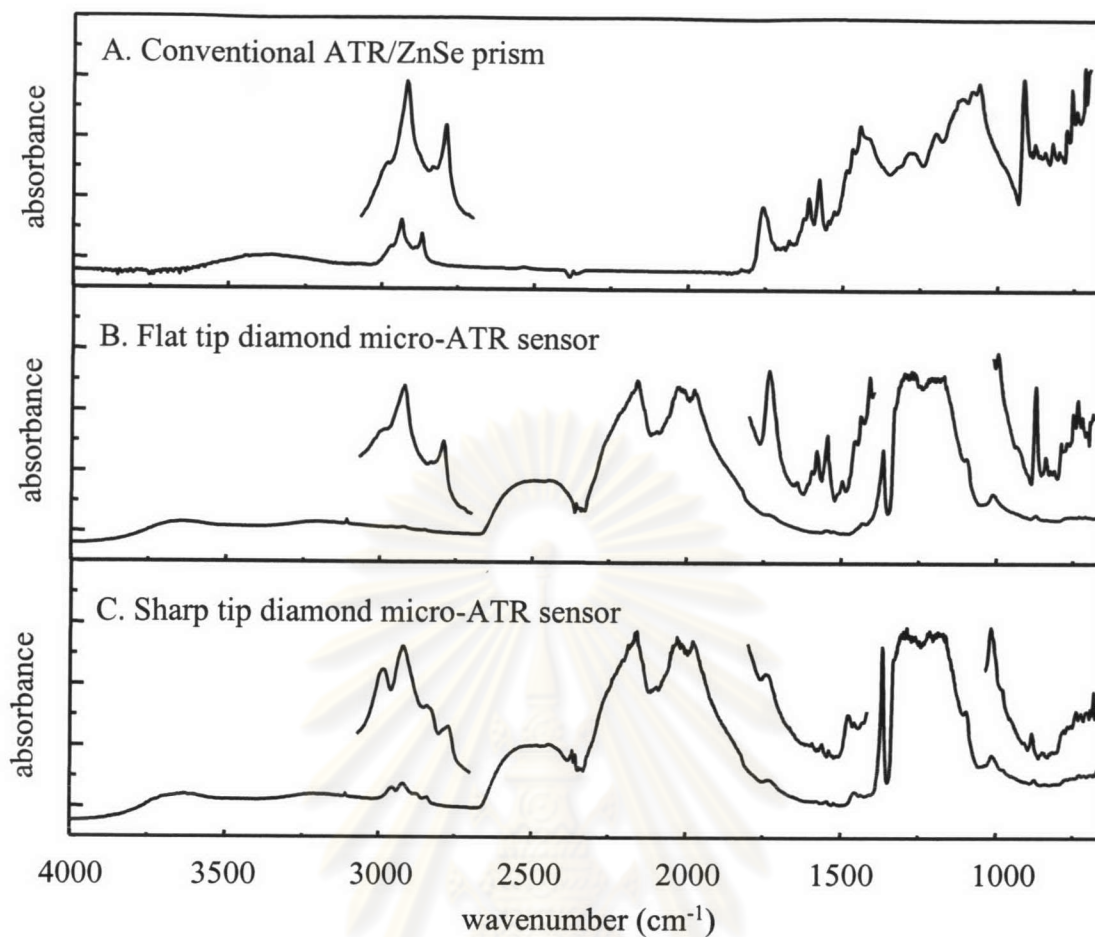


Figure 4.12 ATR spectra of 50 baht bank note on blue color area obtained via ZnSe prism (A), flat tip diamond micro-ATR sensor (B), and sharp tip diamond micro-ATR sensor (C).

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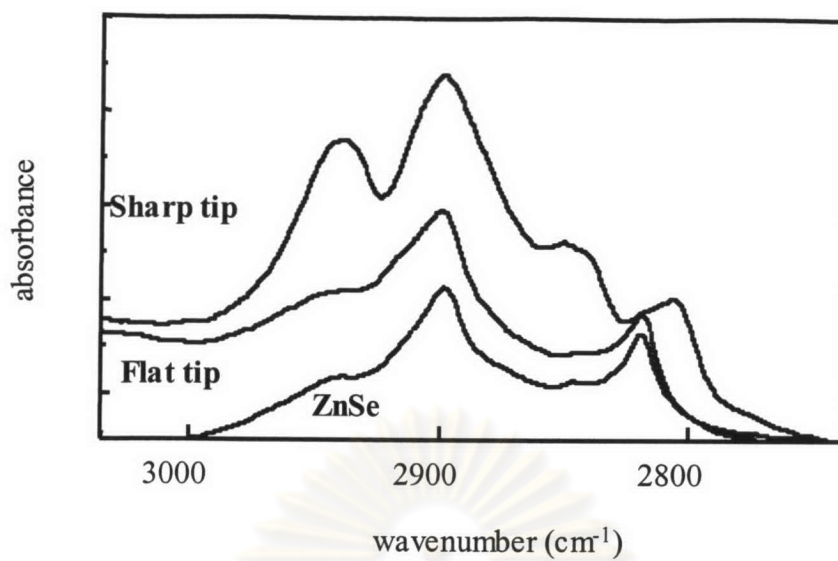


Figure 4.13 ATR spectra of 50 baht bank note on blue color area in the spectral range of 3050-2750 cm^{-1} obtained via ZnSe prism, flat tip diamond, and sharp tip diamond.

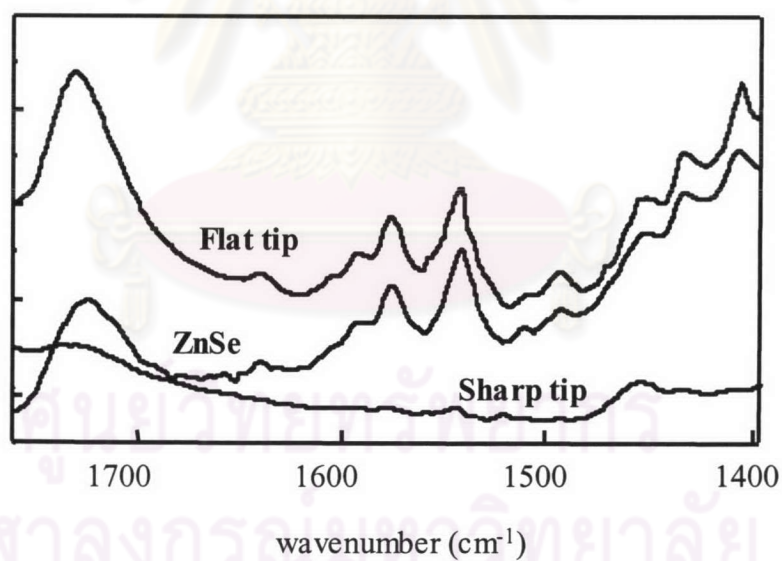


Figure 4.14 ATR spectra of 50 baht bank note on blue color area in the spectral range of 1760-1400 cm^{-1} obtained via ZnSe prism, flat tip diamond, and sharp tip diamond.

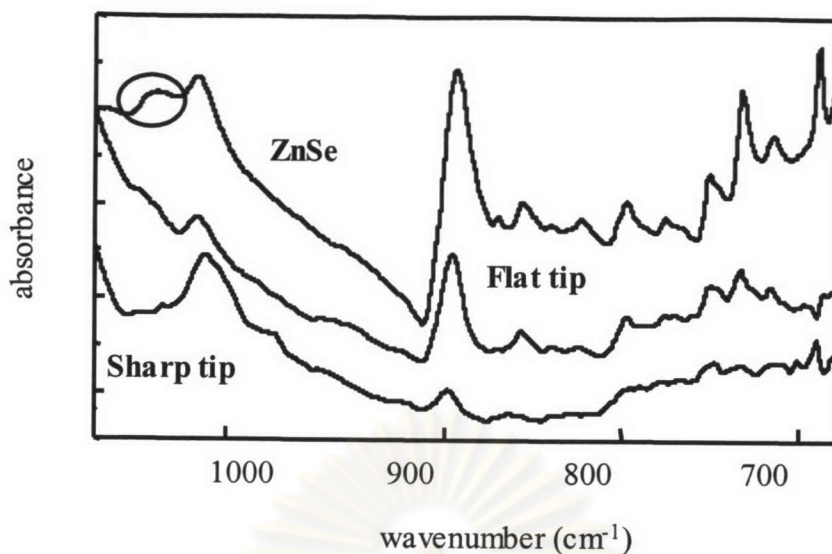


Figure 4.15 ATR spectra of 50 baht bank note on blue color area in the spectral range of 1070-650 cm^{-1} obtained via ZnSe prism, flat tip diamond, and sharp tip diamond.

In Figure 4.15, ATR spectrum shows absorption peak at 1041 cm^{-1} while the others disappear. This is because ZnSe prism covers area larger than flat tip and sharp tip diamond micro-ATR sensors hence, spectrum observed from this sensor provides average sampling area, which is in contact with ZnSe prism.

4.6.2 50 baht bank note on white area

Figure 4.16 shows ATR spectra of 50 baht bank note in white color area obtained via various ATR systems. Figures 4.16 (A), (B), and (C) show spectra of the sample obtained via ZnSe prism, flat tip diamond micro-ATR sensor, and sharp diamond micro-ATR sensor, respectively. Three spectra observed via various sensors provide different absorption bands in each range (see Figures 4.17, 4.18, and 4.19). The spectra obtained via ZnSe prism and flat tip diamond micro-ATR sensor provide the same major absorption bands while the sharp tip diamond micro-ATR sensor is different. This is due to the different configurations of contact surface. The configurations of contact surface in ZnSe prism and flat tip diamond micro-ATR sensor are the same therefore the same major absorption bands can be observed. On

the other hand, the spectrum observed via sharp tip diamond provides different absorption bands from both ZnSe prism and flat tip diamond micro-ATR sensor. This is because the sharp tip diamond can penetrate polymer coating on the bank note and observe the information both at the surface and bulk of the sample.

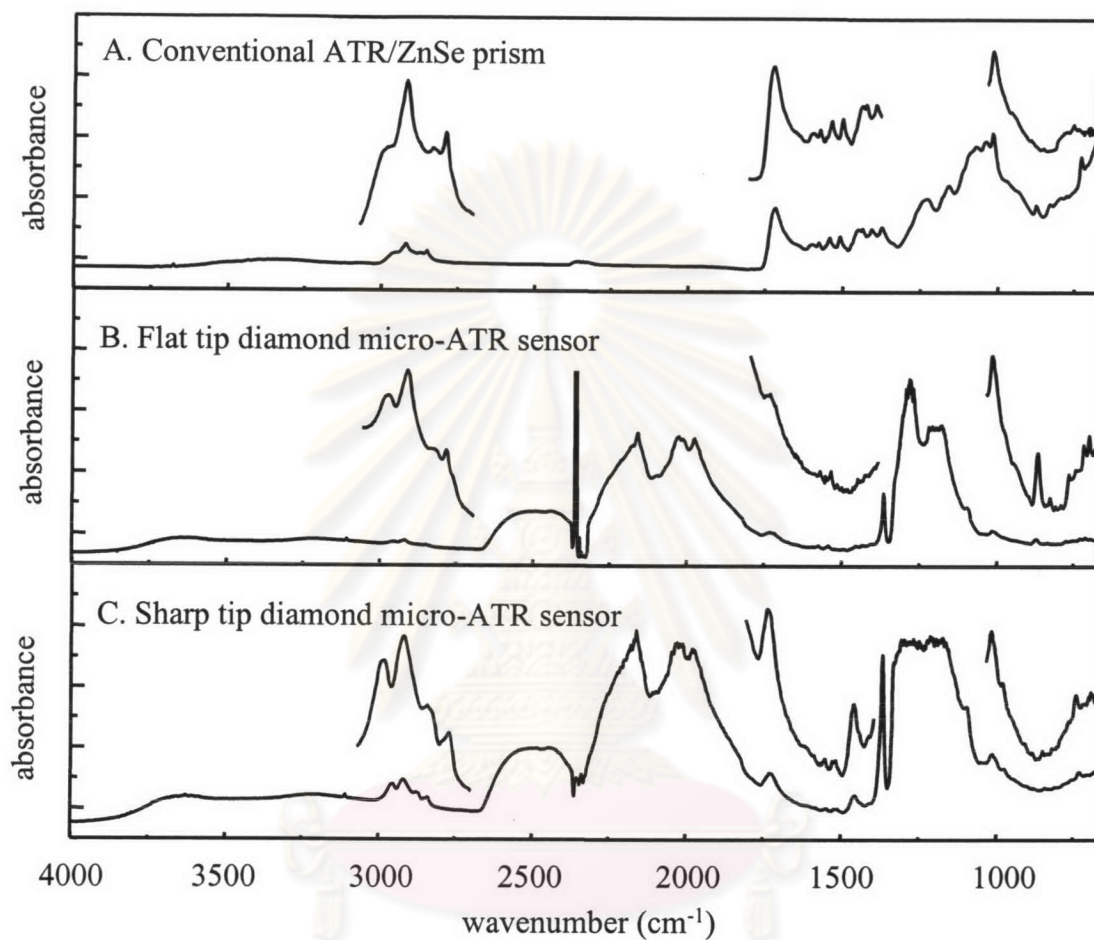


Figure 4.16 ATR spectra of 50 baht bank note on white color area obtained via ZnSe prism (A), flat tip diamond micro-ATR sensor (B), and sharp tip diamond micro-ATR sensor (C).

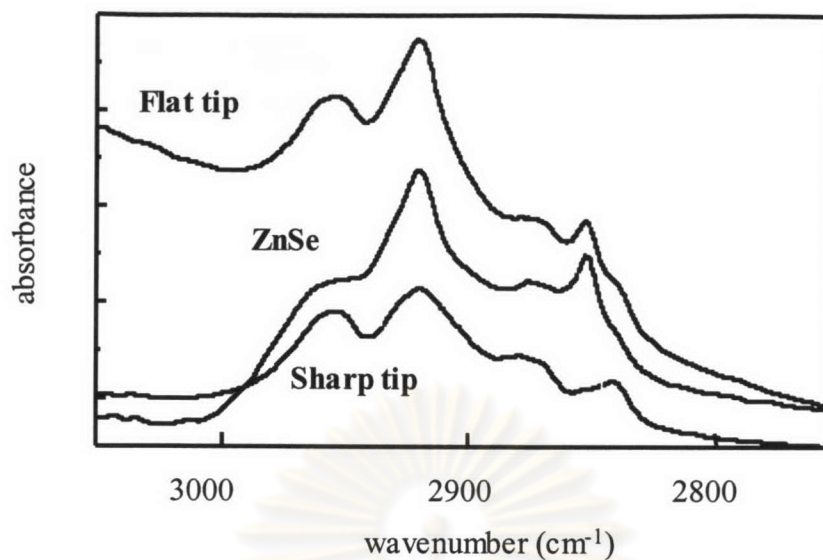


Figure 4.17 ATR spectra of 50 baht bank note on white color area in the spectral range of 3050-2750 cm^{-1} obtained via ZnSe prism, flat tip diamond micro-ATR sensor, and sharp tip diamond micro-ATR sensor.

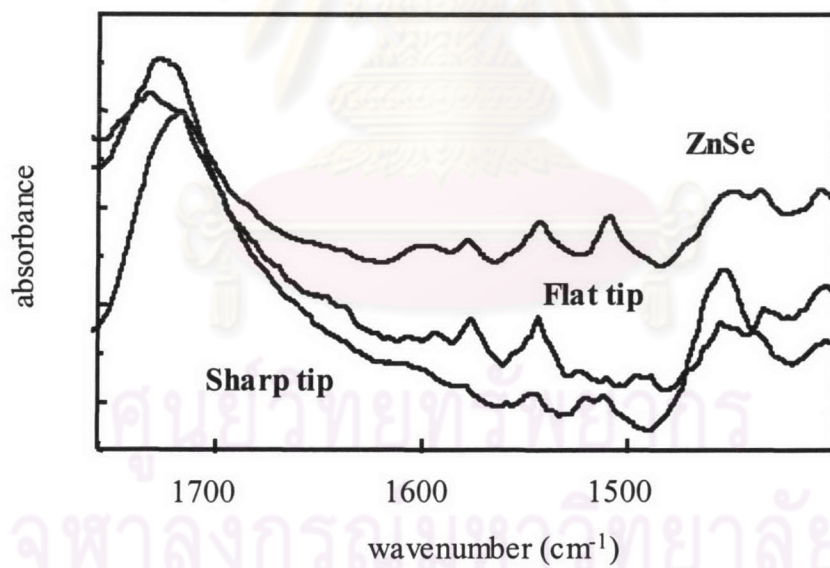


Figure 4.18 ATR spectra of 50 baht bank note on white color area in the spectral range of 1760-1400 cm^{-1} obtained via ZnSe prism, flat tip diamond micro-ATR sensor, and sharp tip diamond micro-ATR sensor.

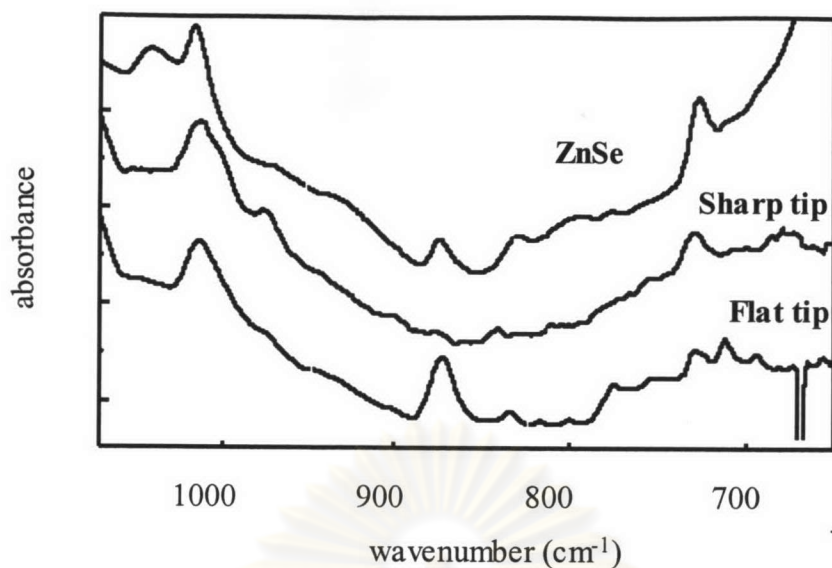


Figure 4.19 ATR spectra of 50 baht bank note on white color area in the spectral range of 1070-650 cm^{-1} obtained via ZnSe prism, flat tip diamond micro-ATR sensor, and sharp tip diamond micro-ATR sensor.

For the samples with small sampling area (i.e., 50 baht bank note), various sampling areas of IREs can affect on the spectral information. Selection of appropriated size in sampling area is important. The sharp tip diamond micro-ATR sensor provides the same spectra with blue and white area. This is because the sharp tip diamond can penetrate polymer coating on the bank note when applied pressure is increased in order to ensure the good contact. The observed spectrum provides both the information both at the surface and bulk of the bank note. The spectra observed from ZnSe prism provide spectral feature almost the same. This is due to sampling area of ZnSE prism is large. On blue color and white color areas, the ZnSe prism provides average spectral color information, which is contacted. The flat tip diamond micro-ATR sensor provides different spectra both blue color and white color. This is because there are flat surface and small sampling areas. In this study, flat tip diamond micro-ATR sensor is appropriated for analyzing printed inks on bank note.

The results illustrate that the diamond micro-ATR sensor is useful for solving the optical contact problem. Spectral information obtained from diamond micro-ATR sensor is the same as that obtained from a commercial ATR accessory. Moreover, a small sample with small sampling area can be easily analyzed.

4.7 Drawbacks of the diamond micro-ATR sensor

The problems encountered via the diamond micro-ATR sensor include:

1. For analyzing multi-coating sample, it is difficult to collect surface information from sharp tip diamond micro-ATR sensor.
2. The large sample cannot be analyzed via using diamond micro-ATR sensor since the size of the sample holder of diamond micro-ATR sensor is small. The large polymer sample should be cut into small piece before being analyzed by diamond micro-ATR sensor.
3. In the spectral range of $2500-1850\text{ cm}^{-1}$, spectral information of sample is loss. This is because this region is interfered by high absorption of diamond. For some organic compounds or polymers, there are absorption bands in this region.

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