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• SPECTROPHOTOMETRIC ANALYSIS

No.A261

Microanalysis by ATR Microspectroscopy

The FTIR infrared microscope has become indispensable for the measurement of a microscopic area or a microscopic foreign substance. Introduced in this article is an example of mapping by ATR (Attenuated Total Reflection) with an infrared microscope and improvement of contact with the introduction of a solvent. So far, the most of the measurement of microscopic areas with an infrared microscope was centered on the measurement of a spot. For the linear analysis or superficial analysis for which other analytical method is often applied, automated sample stage was necessary.

Outline of the Mapping Method by ATR Measurement

Fig.1 shows the outline of the mapping method by ATR method. For the ATR objective, refer to Spectroscopic Analysis News No.A244. As stated above, in the ATR method, the prism is put in close contact with the area of measurement, and after the measurement is over, the contact needs to be set free, and at another area of measurement, the prism needs to be contacted. For that reason, different from the transmittance or reflectance method, the sample stage is lowered once to set free the contact after every measurement, which cannot be met by conventional type of auto stage having only the function of X and Y directions. Control of Z direction is necessary for lowering the stage. In the measurement introduced here, background was measured each time and mapping by the ATR method was carried out by standard automatic measurement mode by changing the position of measurement in turn. In Fig. 2, for the sake of explanation, line mapping was carried out by moving the prism, but in practice, the stage is moved.

Result of ATR Line Mapping of Multilayer Film

Fig.2 shows an example of line mapping of multilayer film by the ART method. It is comprehended that the sample is built up of the three layers from the front to the rear, polyethylene, ethylene-vinyl acetate copolymer, and vinylidene chloride. As regards spatial resolution, it is assumed to be several tens of um from the result of measurement of the narrowest layer of 10um of ethylene-vinyl acetate copolymer. In the transmittance method, the multiple layer film is sliced through the layers for sampling, but in the ATR method, if the cross section can be exposed, measurement of the cross section as it is possible. Furthermore, as only an area close to the surface contacted with the prism is measured, the measurement is free from the hindrance

In transmittance and reflection measurement by mapping, measurement is possible only by moving the stage, but with the ATR method, contact of the sample and the prism needs to be separated once, then the sample needs to be contacted with the prism again at another place. For that purpose, it was necessary to provide the function of auto stage capable of moving the stage in the direction of Z axis in addition to **X** and Y directions. The AIM-8000 and μIR-8000 is an infrared microscope provided with the function of moving the stage in the X, Y, and *Z* directions, and can meet the above-mentioned requirement with the standard specifications.

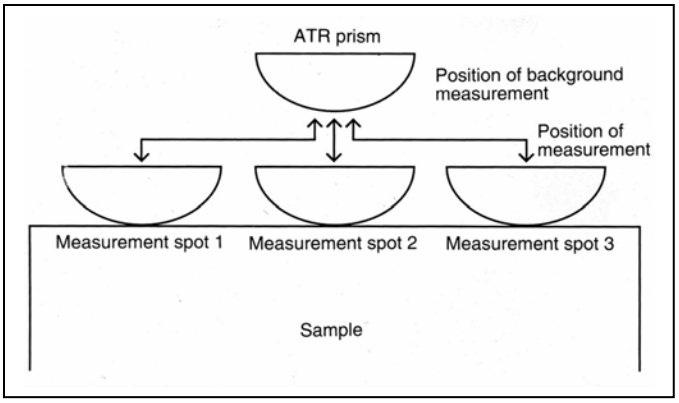

Fig. 1 Representation of ATR Mapping

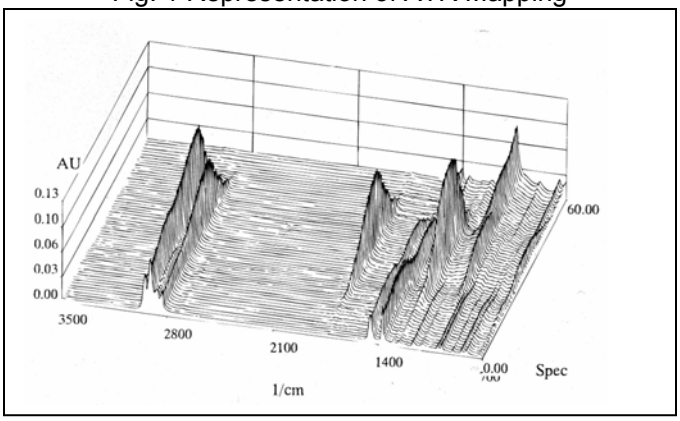

Fig.2 Line Mapping by ATR Measurement

from interference fringe which is apt to occur in general in transmittance measurement and saturation of peak does not occur. Different from the transmittance and reflectance methods, the mapping by the ATR method measures only the surface of the sample, and is calling attention a new method of surface mapping by infrared spectroscopy.

Improvement of Contact between Sample and ATR Prism

With a comparatively hard sample, peak intensity was increased by letting the prism come into contact with the area of measurement more closely. But, with a soft sample, for example, paper sample or fiber sample, in spite of any increase of pressure, the sample itself worked as a cushion, and closeness of the prism and the sample surface was hardly increased. As solution ensures the most closed contact between the two, introduction of solution between the prism and the sample has been adopted for the ATR method. This method was used for the measurement of a microscopic area. In the ATR method with the infrared microscope introduced in this article, the prism comes into contact with the sample at a very small area. For that reason, injection of a very small quantity of solution is enough. Injection of this extremely small quantity of sample is made possible by applying “micro dropping”, one of the functions of the micromanipulator.

Outline of the Improvement of Contact

Fig.3 illustrates the concept of contact between the prism and the sample in the ATR method. In the case of a sample of sufficient thickness and close contact ensured between the two, measurement is possible under the illustrated condition, but in the case of a thin sample and insufficient closeness of the contact between the two, good sensitivity cannot be obtained. In such a case, as shown in Fig. 3 (c), by injecting a small quantity of solvent between the sample and the prism, the closeness between the sample and the prism can be increased. Besides, by separating the base of the sample so as to let the solvent evaporate and disappear after the sample solution has adhered to the surface of the prism, only the sample remains on the prism surface, enabling the measurement to be carried out without being affected by the sample base (patent pending). In the case of a large sample solution, ATR measurement is, effected on the sample as it is.

ATR Measurement after Sample Transfer on to the Prism

Fig. **4** shows spectrum of paper; in comparison with the spectrum taken before the injection of solvent between the prism and the sample, it is noted that the peak intensity has almost been doubled. It shows the increase of closeness between the prism and the sample. Next, measurement was carried out after having separated the sample from the prism, and spectrum of only ink is obtained as shown in Fig. 5. In comparison with the spectrum of only ink obtained by transmission measurement, the consistency of the two spectra is noted. It is comprehended that only the components of ink had been solved and transferred. For your information, the ordinate has been standardized for the sake of comparison. As shown above, with respect to the measurement of a soft sample, for which close contact with the prism is difficult, the following merit is obtainable by injecting a very small quantity of solvent. 1) Improved closeness of the contact 2) By selecting an appropriate solvent, only dissolved component can be transferred on to the prism and measured. As explained above, the ATR with an infrared microscope permits mapping of the sample surface as well as selective measurement of the sample by applying a suitable method, and is expected to be applied in various fields.

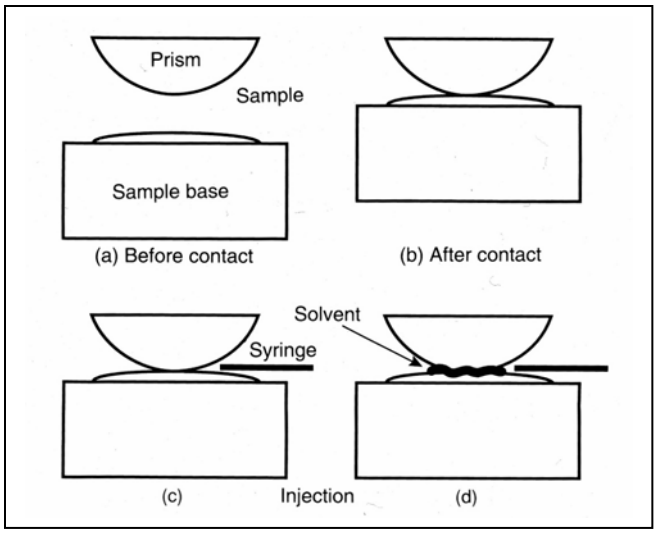

Fig.3 Representation of Improved Contact by Solvent Injection and Sample Transfer

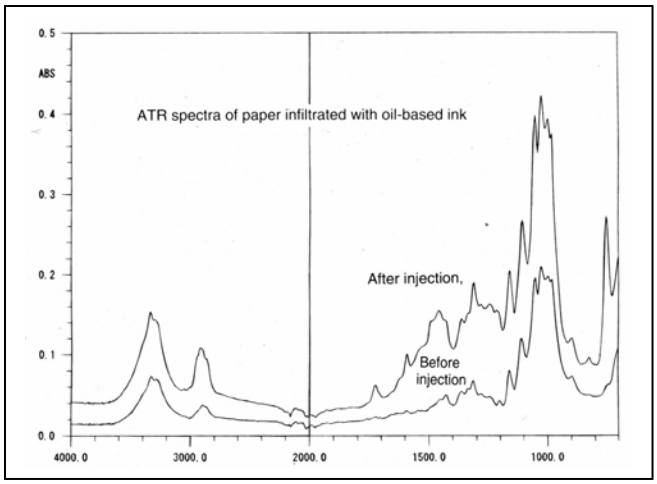

Fig.4 ATR Spectra before and after Solvent Injection

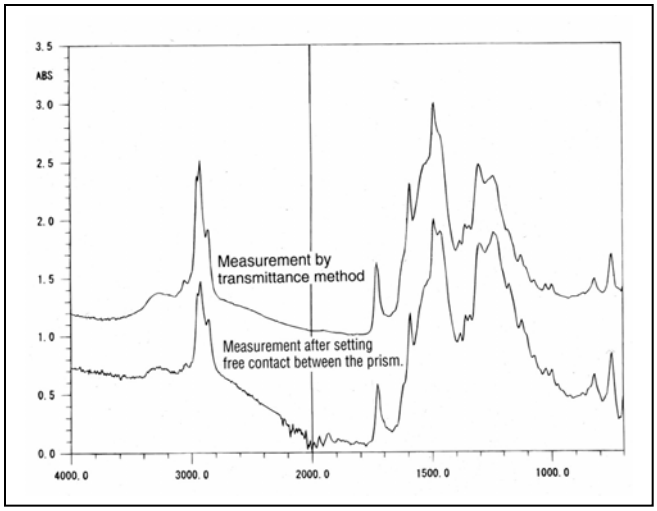

Fig.5 ATR Spectra of Ink Transferred on to the Prism