

Microanalysis Made Easy: Attenuated Total Reflectance (ATR)

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Reflection microscopy techniques are typically the easiest to employ for routine sample analysis, as they require little or no sample preparation. Included in these methods are reflection-absorption spectroscopy (RAS), which emulates transmission spectroscopy, diffuse reflection infrared spectroscopy (DRIFT), specular or external reflectance, and attenuated total reflectance (ATR). For RAS, DRIFT, and specular reflection, the nature of the resultant spectra is determined by the nature of the sample. These techniques will be discussed in future articles. ATR is primarily a surface technique which provides a high quality absorbance-like infrared spectrum and can be used to readily analyze almost any liquid or solid sample.

For ATR measurements, the sample is brought into direct contact with an internal reflection element (IRE) attached to the bottom of an objective such that the IR beam focus is at the sample/IRE interface. The angles of light incident at the IRE contact surface exceed the critical angle and thus produce total internal reflection. Upon reflection, the light penetrates into the surface of the sample allowing collection of the sample infrared spectrum.

The ATR objective has a slide for analysis selecting the proper light rays as show in Figure 1. Typically, the specimen is centered visually, using the survey mode of the ATR objective. An example of a paper sample as seen through an ATR objective is shown in Figure 2. The sample/IRE contact is then observed directly using the contact mode (middle slide position). A darkening or wetting of the crystal in the shape of the sample is evident when contact is made, Contact with the paper sample is also shown in Figure 2. Lastly, the slide is moved to the ATR mode for infrared data collection.

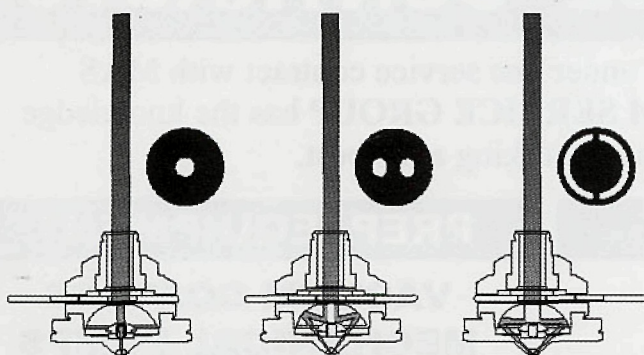


Figure 1

Sample contact can also be monitored through the integrated Contact Alert system on the sample stage. The Contact Alert is a force-sensing device used to monitor IRE/sample contact. Background spectra are acquired through the crystal without the sample in contact. The reproducibility of the ATR measurement is dependent upon IRE insertion alignment and contact force. The mechanical design of the ATR objective and contact alert allows better than 5% spectral variance.

The IRE itself reduces the spot size to increase the effective magnification of the optical system. The spot size reduction is dependent upon the IRE refractive index. The zinc selenide element reduces a spot size to approximately 40%,

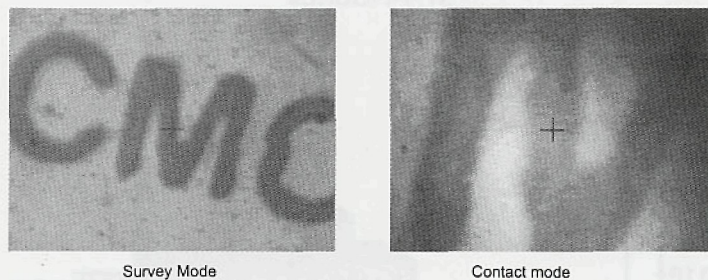


Figure 2

whereas silicon and germanium IRE's yield 30% and 25%, respectively. Use of the internal reflection mode serves to further improve spectralsampling performance and yields greater spatial discrimination. Lastly, the resultant spectra are absorbance-like, suitable for analysis and the sample is analyzed in a non-destructive manner.

The depth of penetration of the incident light into the sample is dependent upon the wavelength of radiation, the incident angle at the sample-IRE interface and the ratio of the refractive indices of the sample and IRE. These factors are related mathematically and are described by the following equation:

$$d_p = \lambda / 2 \pi n_o \sqrt{(\sin^2 \theta - n^2/n_o^2)}$$

Where λ is the wavelength, θ is the angle of incidence and n and n_o are the refractive indices of the sample and the IRE, respectively. Zinc selenide, diamond, silicon, and germanium crystals are available for use and easily exchanged to allow depth profiling of the sample. These elements have refractive indices of 2.4, 2.2, 3.4, and 4.0, respectively and yield depths of penetration of about 2.0, 2.0, 1.0, and 0.5 microns, respectively. The spectra depicted in Figure 3 show the relative effect of the IRE refractive index on spectral data. Note the increase in band intensity, as the refractive index of the IRE is smaller, indicating greater depth of penetration.

The elimination of sample preparation for ATR data acquisition often supplants the need for transmission or reflection-absorption measurements on most samples. Zinc selenide is particularly effective in measuring bulk constituents, due to its large depth of penetration. Germanium is most effective in the analysis of opaque samples such as carbon-filled rubbers and thin films typically under one micron thick. Diamond is particularly useful for hard or brittle samples that may damage other materials. ■

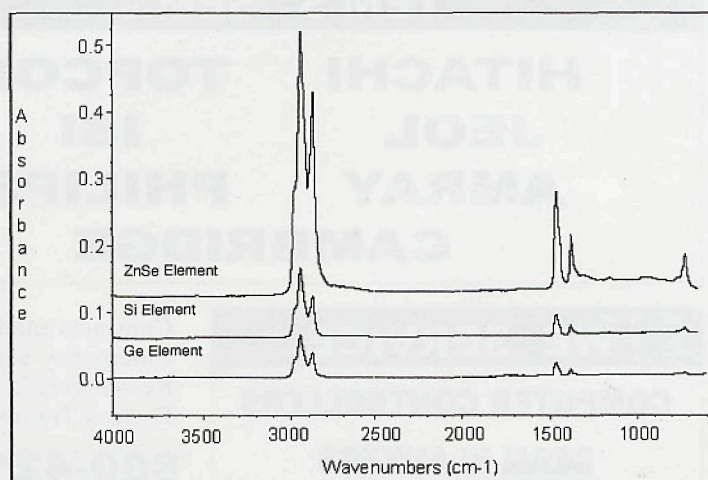


Table 3

One Beam

Many Answers

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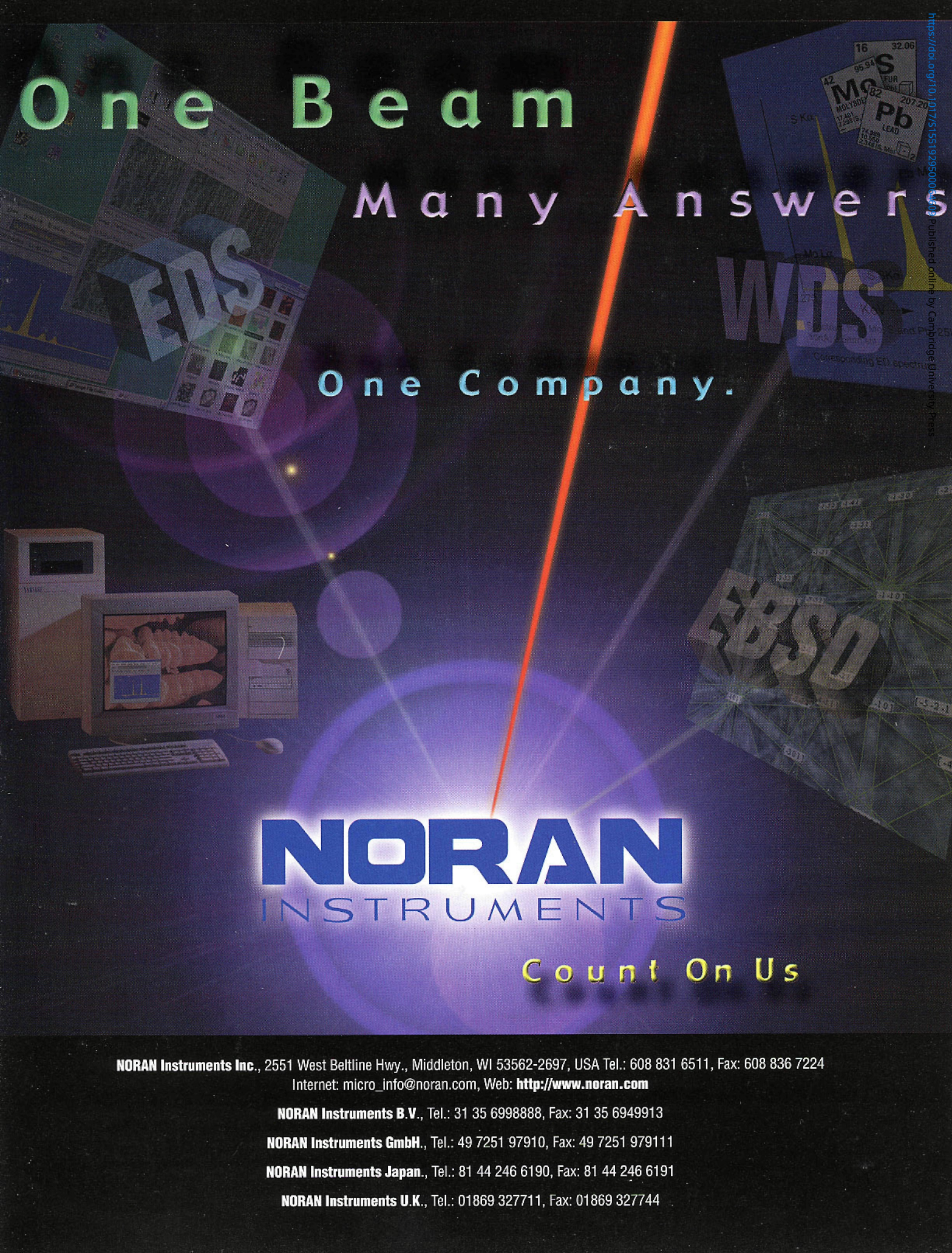
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