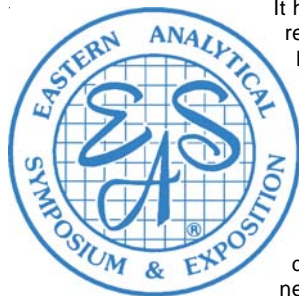


# PIKE REFLECTIONS



Information for Practicing Chemists and Spectroscopists

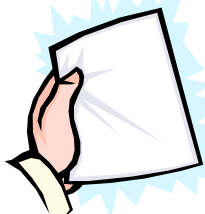
## New Products Lunched at EAS



It has been another record year at PIKE and so we are using the Eastern Analytical Symposium to show our excitement, along with a couple of our new products that could not wait for PITCON.

From November 17-20, PIKE is showing our new Three Bounce MIRacle, the Heated DiffusIR, the Automated Soil Analysis XY, and several ST Japan products now available from PIKE. We hope you are able to see them in person.

## EAS Paper



Also at EAS, a paper presented by Dr. Gabor Kemeny of PIKE Technologies and T.J. Hart of the Biodiagnostics Laboratory, Cyclin Pharmaceuticals, Inc., explores the "Comparison of Mid-Infrared and Near Infrared Technologies for the identification of pharmaceutical compounding materials".

The talk is given on Tuesday, November 18 at 9:00am as part of the On-Line Monitoring of Process Analysis Session.

The paper explores the theoretical and practical advantages and disadvantages of NIR Diffuse Reflectance and Mid-IR Attenuated Total Reflectance (ATR) for rapid analysis of incoming material inspection in the pharmaceutical industry. Examples of the same real-life sample set run on the different techniques will be used to illustrate the comparative analysis.

Contact us at sales@piketech.com to receive a copy of this paper.

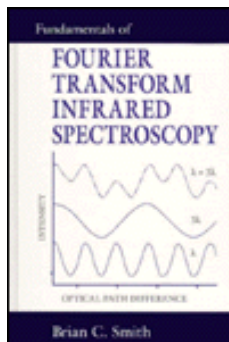
## Can you pick out the new PIKE employee??



Find the answer on page 3!

## Inorganic Analysis using the MIRacle™

By Brian C. Smith, Ph.D.



Spectros Associates,

author of

*Fundamentals of Fourier Transform Infrared Spectroscopy*

(PIKE part number 163-0690)

## Analysis of Inorganic Materials with the PIKE Diamond MIRacle™ Horizontal ATR

### I. Abstract

Traditionally, the ATR spectra of inorganic materials have been difficult to obtain for a number of reasons. With the advent of the use of diamond as an ATR crystal and the development of high pressure clamps, analyses of hard substances such as rocks and cement are now feasible. The Diamond MIRacle™ Horizontal ATR from PIKE is an excellent example of this type of accessory. High quality spectra of a variety of inorganic substances can be obtained quickly and easily using this accessory. It was found that although spectra of intact solid materials could be obtained directly, grinding of samples afforded better sample/crystal contact and better quality spectra.

### II. Experimental

All mid-infrared spectra were obtained with a FTIR equipped with an air cooled source, Ge on KBr beamsplitter, and a room temperature DTGS detector. All spectra were obtained using 32 scans and 8 cm<sup>-1</sup> resolution. The sampling accessory was a PIKE Technologies (Madison, WI) Diamond MIRacle horizontal ATR accessory equipped with a single bounce diamond crystal and high pressure clamp with LCD read out. Spectra of some materials were obtained intact or "as is". However, best results were obtained by pulverizing solids with a hammer, and then grinding the resultant dust for 1 minute in an agate mortar and pestle. All spectra were obtained with the clamp pressure set to its maximum value. The "powder funnel" arrangement of the ATR accessory was used. It was found that a minimum amount of material, just enough to cover the crystal surface maximized absorbance values.

## IN THIS ISSUE

**EAS 2003  
Paper at EAS  
MIRacle White Paper  
PIKE Expands (AGAIN!!!)  
New Ad  
Show Dates**

**MIRacle White Paper (cont.)**

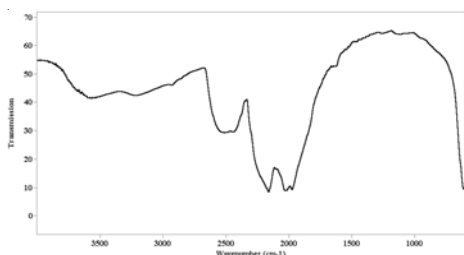
**III. Results and Discussion**

**A. Characterization of the PIKE Diamond MIRacle ATR**

An issue with ATR accessories is the amount of light that makes it through the device, called throughput. Naturally, the more light that makes it to the detector, the better the signal to noise ratio of the resultant spectrum.

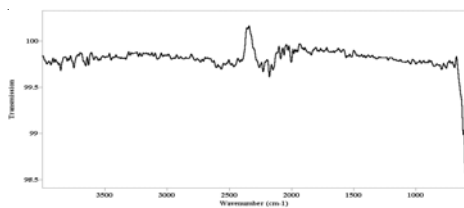
To measure the throughput of an ATR accessory, a background spectrum with an open beam and a "sample" spectrum with the ATR accessory in place are measured and then ratioed to obtain a transmittance spectrum. The transmittance spectrum of the PIKE Diamond MIRacle ATR, plotted from 4000 to 600  $\text{cm}^{-1}$  is plotted in Figure 1.

The accessory has greater than 40% transmission throughout much of the mid-infrared. The only problem area is between 2500 and 2000  $\text{cm}^{-1}$  where diamond has strong features. Fortunately, there are very few other substances other than diamond that absorb in this wavenumber region. The spectrum cuts off at 600  $\text{cm}^{-1}$  due to the absorbance of the ZnSe lenses used in the accessory.



**Figure 1** The transmission spectrum of the PIKE Diamond MIRacle ATR accessory. Note that the throughput is greater than 40% throughout much of the mid-infrared.

Another method of measuring the quality of an ATR accessory is to run a 100% line with the accessory in the FTIR sample compartment to obtain a measure of the noise level achievable with the device. The 100% line for the Pike Diamond MIRacle ATR is shown in Figure 2 plotted from 4000 to 600  $\text{cm}^{-1}$ .



**Figure 2** The 100% line spectrum of the PIKE Diamond MIRacle ATR accessory.

Traditionally, FTIR noise levels are measured between 2200 and 2000  $\text{cm}^{-1}$ . This is not appropriate with diamond ATR crystals because of the strong absorbances diamond exhibits in this region. Therefore, the region from 3200 to 2800  $\text{cm}^{-1}$  was chosen to measure the noise level.

The peak-to-peak noise in this region in the spectrum in Figure 2 is 0.06%. The peak-to-peak noise in the 100% line between 3200 and 2800  $\text{cm}^{-1}$  obtained on this instrument with an open beam was 0.02%. Thus, the presence of the ATR accessory causes only a small increase in the inherent noise level of the instrument, and the accessory promises to give good quality spectra for even poorly absorbing samples.

**B. Problems with the ATR Spectra of Solids**

Traditionally, routine ATR analysis of inorganic powders has been difficult. First, some inorganics, such as rocks and bricks, are hard substances that can scratch softer ATR crystal materials such as KRS-5 or ZnSe. Scratches on an ATR surface can interfere with the coupling of the infrared beam with the sample [1]. Another problem with inorganic powders is that they consist of small, hard crystallites that frequently will not flatten out properly to more easily couple with the IR beam. This is illustrated in Figure 3.



**Figure 3** An example of the difficulty of getting crystallites of powdered sample to make good contact with an ATR crystal surface.

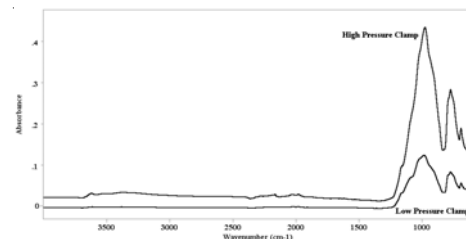
A way of getting crystallites to flatten out is to apply high pressure to them. However, softer ATR crystal materials such as ZnSe can be damaged and cracked by high pressure.

The PIKE Diamond MIRacle horizontal ATR accessory avoids these problems. The ATR crystal material used is diamond, which is the hardest substance known to man and very unlikely to be scratched by even the hardest of substances. The diamond is also tough enough to stand up to high pressure. Addition of a high pressure clamp with LED readout to the MIRacle allows application of high but reproducible pressure.

Pressure reproducibility is critical in reproducing conditions from sample to sample so that legitimate comparisons of spectra can be made. Pressures high enough to flatten the crystallites of hard substances are obtainable. The clamp comes with a built in clutch that does not allow the user to apply pressure beyond a certain limit. This is to protect the integrity of the ATR unit.

An example of the utility of a high pressure clamp is seen in Figure 4. The figure shows two spectra of the same sample, powdered gray rock. The bottom spectrum in Figure 4 was obtained with a low pressure clamp. It is usable, but certainly not optimal because of the low absorbances.

The top spectrum in Figure 4 was obtained using the high pressure clamp that comes with the PIKE Diamond MIRacle ATR. Note that the maximum absorbance at 979  $\text{cm}^{-1}$  is 4 times larger with the high pressure clamp than with the low pressure clamp. Again, this is because of the flattening ability of the high pressure clamp.



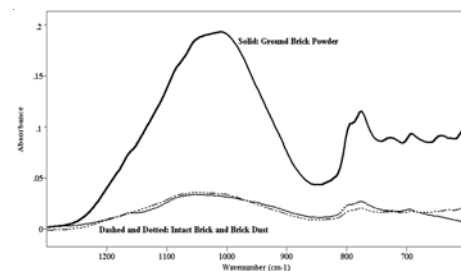
**Figure 4** ATR spectra of the same ground rock sample. Bottom: low pressure clamp. Top: high pressure clamp. Note that the high pressure clamp achieves significantly higher absorbances than the low pressure clamp.

Thus, the combination of a tough, resistant diamond ATR crystal and high pressure clamp makes the PIKE MIRacle suitable to analyze inorganic substances.

**C. Preparation of Inorganic Substances for ATR Analysis**

One of the many advantages of the ATR sampling technique is the lack of sample preparation required. For many samples quality spectra can be obtained by simply bringing the intact sample into direct contact with the ATR crystal. This applies to liquids, polymer films, and semi-solids [1].

The ATR spectra of inorganic solids can also be obtained intact without sample preparation as shown by the spectra of intact brick, brick dust, and brick powder seen in Figure 5.



**Figure 5** Overlaid mid-infrared ATR spectra of intact brick, brick dust, and ground brick powder from 1300 to 600  $\text{cm}^{-1}$ .

(continued on page 3)

(continued from page 2)

The spectrum of intact brick, seen in the bottom of Figure 5, while usable, has small absorbances and a poor signal-to-noise ratio (SNR). Brick dust was obtained by pulverizing the brick with a hammer. Its spectrum, also seen in the bottom of Figure 5, shows no improvement over that of the intact brick.

In a final attempt to improve the brick spectrum, a small quantity of brick dust was placed in an agate mortar and pestle and ground by hand for approximately 1 minute to generate what we will call brick powder. The spectrum of brick powder is seen in the top Figure 5.

This spectrum has absorbances approximately 10 times of those of intact brick and brick dust. This is probably due to the following. Since pressure is force/area, large crystallites will require more force to flatten than small crystallites. Grinding reduces crystallite size, making it easier to flatten the crystallites and obtain good coupling with the infrared beam. Also, it was found that a small amount of powder just covering the ATR crystal surface produced larger absorbances than filling the powder funnel with material.

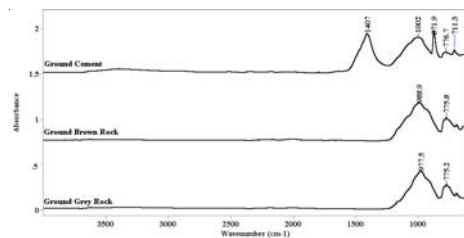
Again, this can be understood in terms of pressure. With a small amount of material, the clamp is pressing directly against the crystallites on the ATR surface that are absorbing the IR beam, maximizing crystallite flattening and sample/beam coupling. With the powder funnel full, the pressure must be transferred through many layers of material before it reaches the crystallites actually absorbing infrared radiation. Some of the pressure is simply lost in the process, and flattening ability is not as good as when using a small amount of powder.

In conclusion, although it is most convenient to analyze inorganic solids "as is" using HATR, pulverizing and grinding these solids before analysis will result in greatly improved spectra. The extra work of grinding is typically worth the improvement in spectral quality. In the rest of this paper, all spectra are of inorganic materials ground for 1 minute before taking their spectra.

**D. Representative Spectra of Inorganic Solids**

Although inorganic substances are known for being hard, which is one of the reasons they were not traditionally analyzed using ATR, there are soft inorganic materials as well. Two examples are gypsum,  $\text{CaSO}_4 \cdot (2\text{H}_2\text{O})_2$ , and dolomite limestone,  $\text{CaMg}(\text{CO}_3)_2$ . The spectra of these relatively soft inorganic solids taken with the PIKE MIRacle AG diamond ATR are seen in Figure 6. The spectra of these materials are typical of inorganics. There are no C-H stretches around  $3000 \text{ cm}^{-1}$ , the sure sign that these are inorganic compounds. The spectrum of gypsum has peaks around  $3500$  and  $1650 \text{ cm}^{-1}$  due to waters of hydration.

It is not unusual for inorganics to have multiple water peaks due to water molecules that are part of the chemical structure of the material, or are adsorbed on the surface. The gypsum spectrum has peaks typical of inorganic sulfates, a  $(\text{SO}_4)^{2-}$  stretching band at  $1100 \text{ cm}^{-1}$ , and an  $(\text{SO}_4)^{2-}$  bending band at  $666 \text{ cm}^{-1}$ .



**Figure 6** Spectra obtained using the PIKE Diamond MIRacle ATR accessory of the soft inorganics gypsum and limestone. Samples were ground manually for 1 minute before analysis.

(continued on page 4)



***PIKE Technologies welcomes a new employee and puts him right to work !!!***

Join us in a big welcome to the newest member of the PIKE spectroscopy support team, Mr. Ken Kempfert, who brings to us over 25 years of spectroscopy experience. As evidence to the importance of our customers and the continued success of PIKE, we are continuing to staff up our sales and applications area for your benefit. Note in the picture above, the graduation ceremony for Ken, where he has passed his extensive training on PIKE products with flying colors. Conferring his certificate of graduation are his colleagues in the PIKE sales and applications department: Kent Gundlach, Irene Brierley, Dr. Gabor Kemeny, Krista Garcia, Scott Little, Dennis Shanks, and Dave Engerman. We at PIKE take customer support very seriously and strive to ensure that we provide a broad range of applications experience for your sampling requirements.

Ken is a graduate in chemistry from the University of Minnesota, Duluth and comes to us with many years of FT-IR sampling experience with the Environmental Protection Agency, PerkinElmer, Wisconsin State Crime Laboratory, Nicolet Instruments, Mattson Instruments and Thermo Electron. His responsibilities will include product support, marketing, applications and product development.

Ken and all of the technical support staff at PIKE look forward to serving you. Remember, we want to be your favorite spectroscopy company!

By the way, Ken is the guy on the right side of the photo on page one. The other guy is "Charlie", who obviously has been around PIKE for a long time. Ken's plan is to be at PIKE even longer!

- EAS 2003
- Paper at EAS
- MIRacle White Paper
- PIKE Expands AGAIN
- Show Dates

# PIKE

## TECHNOLOGIES

*Spectroscopic Creativity*

2901 Commerce Park Drive  
Madison, Wisconsin 53719

Prsrt Std  
U.S. Postage

PAID

Permit No. 1547  
Madison, WI

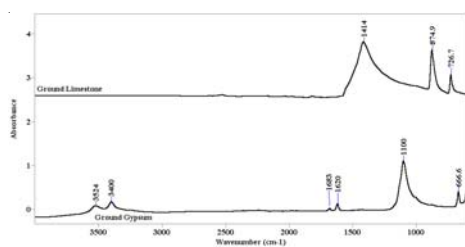
## PIKE Reflections

Page 4

(continued from page 3)

The limestone spectrum is a good example of a spectrum of an inorganic carbonate, with a  $(\text{CO}_3)^{2-}$  stretching feature at  $1414 \text{ cm}^{-1}$  and carbonate bending features at  $875$  and  $726 \text{ cm}^{-1}$ .

Lastly, we need to show that the PIKE Diamond MIRacle ATR accessory can work on hard inorganics besides brick. Figure 7 shows the infrared spectra of several typical inorganic specimens obtained using this accessory.



**Figure 7** The infrared spectra of several hard inorganics obtained using the PIKE Diamond MIRacle ATR accessory. Samples were pulverized and ground for 1 minute before analysis.

Note the overall high absorbance level and low noise level in the spectra in Figure 7. The bottom two spectra are of everyday rocks harvested from a yard in New England, distinguished by their color. Many rocks, and much of the earth's crust, are made up of silicate minerals. The absorbances in the rock spectra are easily assigned as Si-O-Si stretching modes at  $980$  and  $775 \text{ cm}^{-1}$ . The top spectrum in Figure 7 is of ground cement. This material is composed of, amongst other things, silicate rocks and limestone.

One would then expect the spectrum of cement to be a combination of silicate rock features and carbonate features. This turns out to be the case. The features at  $1407$ ,  $871$  and  $711 \text{ cm}^{-1}$  in the spectrum of cement are the carbonate stretching and bending bands of limestone, and fall almost at the same place as these bands in the spectrum of dolomite limestone seen in Figure 6.

The other two major features in the cement spectrum at  $1002$  and  $776 \text{ cm}^{-1}$  line up nicely with the silicate rock spectra seen in the lower part of Figure 7.

### IV. Conclusion

The PIKE Diamond MIRacle ATR accessory is capable of obtaining quality spectra of a wide variety of inorganic solids and powders. An accessory equipped with a lower pressure clamp may be able to analyze some of these samples, but would not give the same quality or ease of analysis given by the high pressure clamp.

Although usable spectra were obtained with intact samples, better results were obtained by pulverizing solid samples, grinding them into a powder, then using a minimum amount of powder to obtain the spectrum.

### References

[1] Brian C. Smith, *Fundamentals of FTIR*, CRC Press, Boca Raton, 1996

*This article has been written and printed with permission of Brian C. Smith, Ph.D. Spectros Associates, 175 North St, Shrewsbury, MA. 01545, bcsmith@spectros1.com*

Have you seen our new ad?

Call us for lab supplies and accessories

### PIKE Show Calendar

**Eastern Analytical Symposium and Exposition (EAS)** Garden State Convention Center, Somerset, New Jersey  
November 17-20, 2003 - **Booth # 116**

**Pittsburgh Conference 2004**  
McCormick Place, Chicago, Illinois  
March 7-12, 2004