TECHNIQUE CONSIDERATIONS FOR THE ANALYSIS OF MINERAL SPECIMENS BY SINGLE REFLECTION DIAMOND ATR SPECTROSCOPY

Figure 1. Meridian™ with modified pressure applicator and new powder cup.

Figure 2. Microscope with camera.

ABSTRACT

A previous work[7], using the Harrick Meridian™ accessory, has demonstrated the advantages and potential of single reflection diamond ATR FTIR spectroscopy for the analysis of geological specimens. In that paper it was shown that, in order to obtain reproducible spectra on such samples, it is necessary to reduce the solids to powdered material.

In this report, two analysis technique details will be explored. The first is the size of the particles required for ATR analysis. Both the absorbance of peaks and the reproducibility of measurements increase when the particle size is reduced. The exact nature of these relationships will be investigated. An attempt will be made to determine the optimum practical particle size and a method will be described to reduce samples to that size. The relationship between the ATR sampling size and reproducibility will also be discussed. The second detail is the amount of pressure that must be exerted on the sample to obtain reproducible spectra. The hard samples are essentially incompressible. Hence, the amount of pressure required is small, presumably only that which is required to compress a loosely filled sample holder. In this current work, the exact minimum amount of pressure required will be determined.

For this study, two natural mineral samples, with a wide hardness difference, are chosen: gypsum ($CaSO_4 \cdot 2H_2O$) with a Knoop hardness of 32 psi and milky quartz (SiO_2) with a Knoop hardness of 820 psi. Both samples have several peaks in the 1700 to 400cm^{-1} range, the heights of which will be monitored as the particle size or the pressure is changed.

OBJECTIVE

The purpose of this work is to quantify the effects of particle size and pressure on the sample in the diamond ATR analysis of powdered mineral samples. Two naturally derived samples, of widely different hardness, are used. The effects on sensitivity and reproducibility will be monitored.

EXPERIMENTAL

All spectra were taken with a Nicolet Nexus™ 670 FTIR spectrometer equipped with a DTGS detector and a standard mid-IR beamsplitter and using Nicolet EZ Omnic™ 5.1 software. All spectra were run at 4000cm^{-1} to 400cm^{-1}, 100 scans, and 4 cm^{-1} resolution.
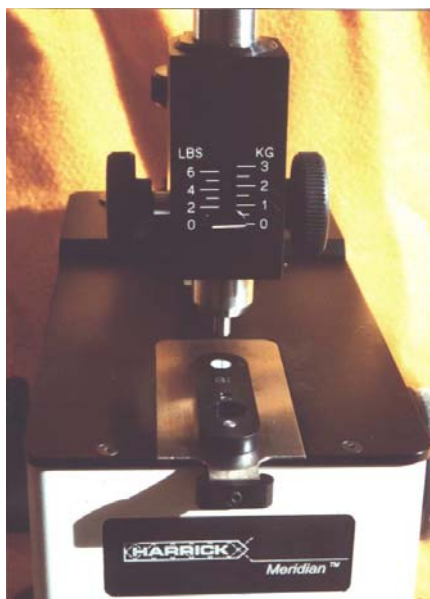
Technique Considerations for the Analysis of Mineral Specimens by Single Reflection Diamond ATR Spectroscopy

The aperture was set to 100 and the gain was set to 8. A background spectrum (air) was taken prior to each sample spectrum in all cases except for the pressure tests, described below. Here, only one initial background spectrum was taken for each sample run. The purge input of the spectrometer was connected to dry nitrogen at 25 SCFH.

The accessory used was a Harrick Meridian[TM] (diamond SplitPea[TM]). e accessory included a 40º angular mask installed in the diamond ATR cartridge to remove subcritical light rays. The special calibrated pressure applicator and the special powder holder, previously described[7], were installed in the accessory. The pressure applicator had a 4.75mm diameter cylindrical tip (17.72mm^2 area) and had installed a spring (Lee Spring Company P/N LC-050K-5S), which required less compression force than that used in the standard applicator. The force and pressure calibration data for this new applicator are given in Table I. Note that the actual measured force at the "0" marking is not 0 N, since the spring is still slightly compressed at its most relaxed position. The 0.895 x 10^{6}Nm^{-2} pressure setting was used for all samples, except where noted. The volume of the powder holder was 119mm^3. A picture

of the Meridian, pressure applicator, and powder holder is given in Figure 1. The purge input of the accessory was connected to the purge fitting inside the sample compartment of the spectrometer. The purge ears of the accessory (PermaPurge[TM]) were extended to the beam ports of the sample compartment. In this manner, samples could be run, one after the other, without breaking purge even with the sample compartment cover of the spectrometer open.

Two natural mineral samples, with widely different hardnesses, were selected for use in this study. The first was selenite, a type of gypsum (CaSO$_4$·2H$_2$O), with a Knoop hardness of 32 psi. With a Mohs hardness of only 2, gypsum is one of the soft minerals. The second was milky quartz, a coarsely crystallized quartz (SiO$_2$), with a Knoop hardness of 820 psi. With a Mohs hardness of 7, quartz is one of the harder, although not among the hardest, minerals. In addition to their wide hardness difference, these two minerals shared another advantage. For both, corresponding reference materials could be readily obtained from a chemical supplier, to verify their identification. The monolithic (natural type 2A) diamond ATR of the Meridian[TM], with a Knoop hardness of 7000 psi (Mohs 10),

Table I. Calibration for pressure applicator with reduced force spring.

Applicator Marking (kg)	Measured Force (N)	Pressure* (10^6 Nm^{-2})
2.5	15.86	0.895
2.0	13.24	0.747
1.5	9.81	0.554
1.0	7.85	0.443
0.5	5.40	0.305
0.0	2.78	0.157

*Tip of pressure applicator has an area of 17.72 mm^2.

is considerably harder than either of the two selected samples.

The following sample preparation technique was used to quickly reduce over 70g of each solid sample to a powder, with the consistency of fine sand: (a) a hammer was used to produce pieces approximately 12mm on a side or less; (b) these smaller pieces were placed between two stainless steel plates and crushed with a hammer; and (c) the resultant particles were ground with a mortar and pestle until no larger particles were evident. Approximately 0.09g of gypsum and approximately 0.15g of quartz are required to fill the sample holder.

The particle size resulting from the above procedure has been previously estimated to be 420 to 590 microns (-40 to –30 mesh). This size has been shown to be too large for adequate sensitivity and reproducibility with the Meridian

Technique Considerations for the Analysis of Mineral Specimens by Single Reflection Diamond ATR Spectroscopy

diamond equipment. To further refine the prepared samples, type 340 stainless steel 6" x 6" mesh screens were used. Two identical screen sets (McMaster-Carr P/N 92405T17), one for each sample type, were obtained, in order to avoid inter-sample contamination. See Table II. Using these screen sets, one to three grams at each of the listed mesh sizes were obtained for each of the two samples. During sample pre-paration, it was found that the 250 and 400 mesh sizes were the practical limits for the gypsum and quartz samples, respectively. To obtain sufficient sample at these sizes, a large amount of additional grinding with the mortal and pestle was required. Also with the gypsum sample, the 250 mesh screen became clogged frequently and had to be cleared with compressed air. With finer mesh sizes, it was essentially impossible to accumulate sufficient sample of either type, regardless of the amount of additional grinding.

In order to verify the screen sizes as well as the particle sizes derived from them, the equipment shown in Figure 2 was employed. This consists of a microscope with illuminator and graduated stage (Edmund Scientific #C31147-00). The 10X objective of the microscope was used with its 10X eyepiece, yielding a magnification of 100X. The system was adapted

Table II. Screen opening sizes.

Screen mesh size	Given Screen Opening (μm)	Measured Screen Opening (μm)
80	178	182
100	140	150
150	103	116
250	61	57
400	36	34

for photomicroscopy by using a microscope tube adapter (Edmund Scientific #C30411-00) and a Nikon camera "T" adapter (Edmund Scientific #C30428-35) to mount the body of a Nikon FG single reflex 35mm camera. The film used for this study was Kodak Elite Chrome 400 color slide film. Dimensional calibration of the system was accomplished by using a stage micrometer (Fisher Scientific 12-561-SM3) with 10 micron divisions.

Developed slide film allows the use of a projector to view images taken of the stage micrometer and the sample under identical conditions. The greatly enlarged, projected images are readily measured. Microscope pictures of the stage micrometer, one of the screens, and one screened sample are given in Figures 3, 4, and 5, respectively. It can be seen from Figure 5 that screened samples still have a wide particle size distribution, although none of the particles will be larger (at
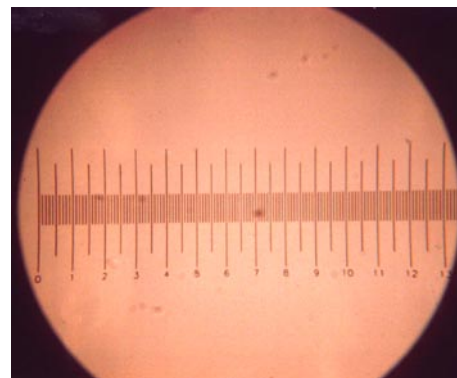

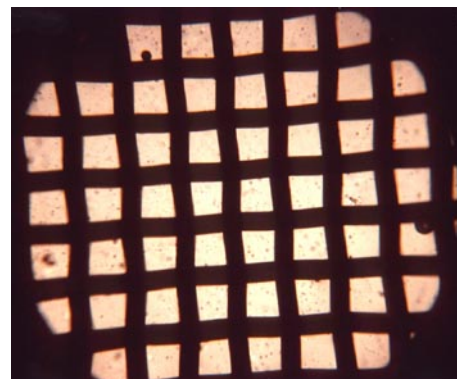Figure 3. Stage micrometer (photomicrograph at 100X magnification).

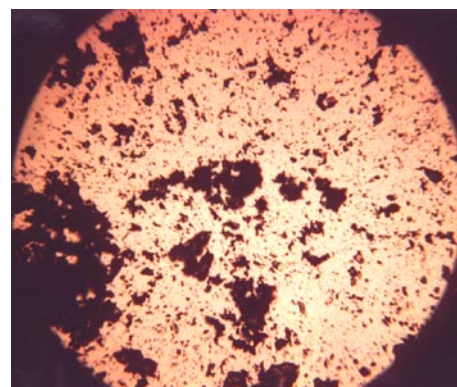Figure 4. Typical Screen, 150 mesh (photomicrograph at 100X magnification).

Figure 5. Quartz sample after filtering through 150 mesh screen photomicro-graph at 100X magnification).

Technique Considerations for the Analysis of Mineral Specimens by Single Reflection Diamond ATR Spectroscopy

least in two dimensions) than the opening of the screen.

The data in Table II for actual screen sizes were obtained using the above equipment and procedure. The microscope technique proved impractical for measuring particle size directly, due the wide size distribution obtained from the use of only one screen and the tendency of clumping. Distinguishing a clump of small particles from a single large particle is problematic. (Certainly, other, more sophisticated methods[17] for determining particle size and distribution exist, but were not available for this study.)

The gypsum and milky quartz samples were obtained from Minerals Unlimited in Ridgecrest, California. These identifications as gypsum and quartz were confirmed by comparing their spectra, after sample preparation to the -150 and -400 mesh sizes, respectively, with those obtained from the corresponding reference materials. For the gypsum sample, the reference material was calcium sulfate (Alfa Aesar P/N 33301-A1). For the milky quartz sample, the reference material was silicon (IV) oxide (Alfa Aesar P/N 13024-A3). This latter material has a stated mesh size of –400, and an average stated particle size of 2 microns. No sample preparation was performed on

either reference material. See Figures 6 and 7. The artifacts observed in the quartz sample spectrum around the Si-O-Si stretch peak ($1085\text{-}1090\text{cm}^{-1}$) are attributed to impurities in the natural material.

For this study, three peaks for both gypsum and quartz were monitored for changes as a result of particle size and applied pressure. For gypsum, the peaks at $1113\text{-}1117\text{cm}^{-1}$, $668\text{-}669\text{cm}^{-1}$, and $599\text{-}600\text{cm}^{-1}$ were used. For quartz, peaks at $777\text{-}779\text{cm}^{-1}$, 694cm^{-1}, and $452\text{-}459\text{cm}^{-1}$ were used.

Full source information for the geological samples, reference materials, and special equipment used in this study is given in Table III.

DISCUSSION

A previous study[7] showed the need to grind solid mineral samples to a fine powder to assure reliable contact with the ATR sampling surface, to obtain good sensitivity and repeat-ability, and to average out crystal orientation effects, if present. That study also implied that very little pressure applied to the sample was required, since mineral samples were essentially incompressible. In this current study, data have been collected in an attempt to quantitate some of these effects.

The methodology introduced in the previous study and its

Table III. Sources

| Alfa Aesar 30 Bond Street Ward Hill, MA 01835 800-343-0660 www.alfa.com (reference materials)	Lee Spring Company 1462 62nd Street Brooklyn, NY 11219 800-426-0272 www.leespring.com (springs)
Edmund Scientific 60 Pearce Ave. Tonawanda, NY 14150 800-728-6999 www.scientificsonline.com (microscope equipment)	McMaster-Carr Supply Co. P.O. Box 440 New Brunswick, NJ 08903 732-329-3200 www.mcmaster.com (screen sets)
Fisher Scientific 2000 Park Lane Drive Pittsburgh, PA 15275 800-766-7000 www.fishersci.com (stage micrometer)	Minerals Unlimited P.O. Box 877 Ridgecrest, CA 93556 760-375-5279 mimi@ridgecrest.ca.us (mineral samples)
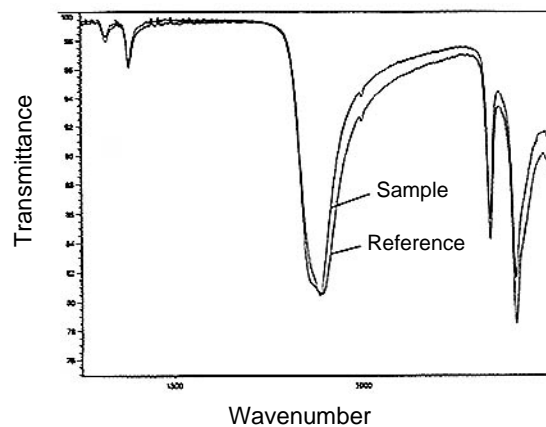
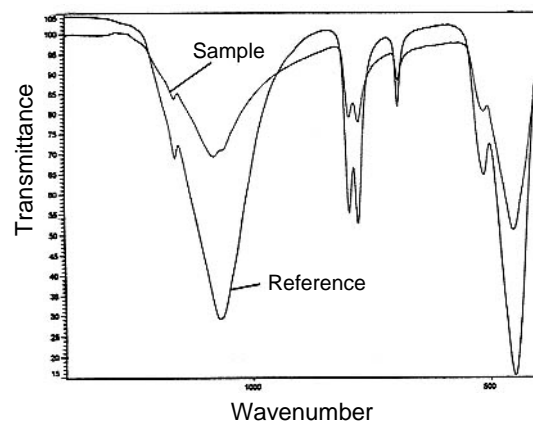Figure 6. Spectra of gypsum sample (150 mesh) and reference material.

Figure 7. Specta of quartz sample (400 mesh) and reference material.

Technique Considerations for the Analysis of Mineral Specimens by Single Reflection Diamond ATR Spectroscopy

elaboration here represent an advance in reduced analysis time in the measurement of powdered inorganic substances in the mid-infrared when compared to the technique employed by Miller and Wilkins[9]. Once powdered samples are obtained, they are simply placed on the ATR element, the pressure applicator is applied, and the spectrum is taken. Since the ATR element is diamond, it is not subject to scratching by the relatively hard mineral samples and it is easy to clean for the next sample.

The results shown in Figures 8 and 9 show the expected increase in sensitivity with decreased particle size. Similarly, the data presented in Figures 10 and 11 for repro-ducibility indicate the expected decrease in relative standard deviation of the measurements with decreased particle size. Some individual deviations from these trends are observed. In particular, a major deviation is noted for the 116 micron gypsum in Figure 10. These deviations are attributed to inadequate sampling (i.e., five samples were not enough to be representative) and to variations in sample size distributions, discussed below.

Unfiltered samples were run for comparison. For such samples, the sensitivities were 0.2 to 0.3 times and the relative standard deviations were 5 to 10 times those obtained for the

corresponding -250 mesh samples. Clearly, unfiltered samples should be avoided.

Figures 8 through 11 further indicate that, if smaller particle sizes were obtainable, then these would lead to even further enhancements in sensitivity and reproducibility. A set of data was collected on the quartz reference material. Here the mean particle size is specified as only 2 microns. This material yielded absorbance values that were 2 to 3 times and a relative standard deviation of approximately one-half that of the -400 mesh (34 micron) sample.

Figures 12 and 13 show the relationship between absorbance and applied pressure for gypsum and quartz, respectively. With both samples, the greatest increase in absorbance is obtained with a pressure less than 0.3×10^6 Nm^{-2}, the smallest contact setting available with the equipment in use. Figure 13, for quartz, shows the expected curve set for absorbance vs. applied pressure, where, after the initial pressure, a plateau area is reached. For the gypsum, however, there are small, but significant slopes to the curves as greater pressure is applied, as seen in Figure 12. Obviously, the initial assumption that mineral samples are completely incompressible is false. Three things are clear from this data. First, to obtain repeatable

results, a calibrated pressure applicator is required. The same pressure should be used to
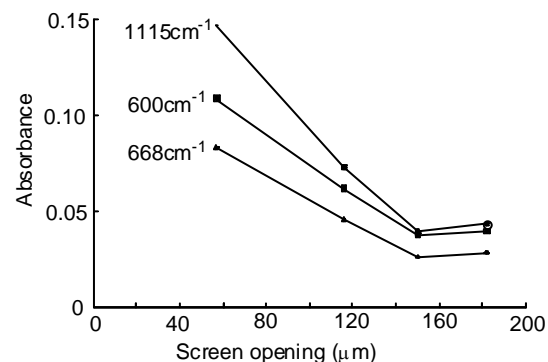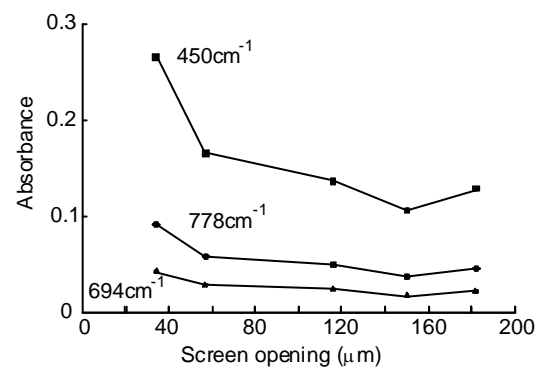
Figure 8. Absorbance vs screen opening for gypsum.

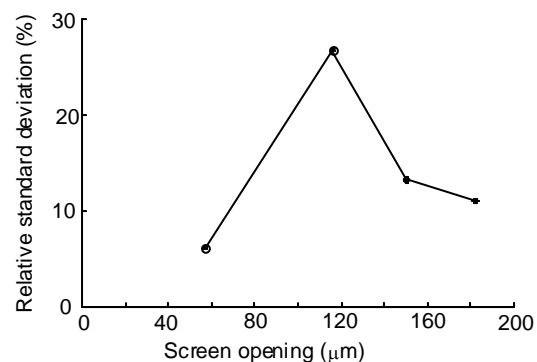Figure 9. Absorbance vs screen opening for quartz.

Figure 10. Standard deviation vs screen opening for gypsum.

obtain all data in a given procedure. Second, the applied pressure should be greater than 0.3×10^6 Nm^{-2}. Third, the highest pressure calibration setting may be used for all samples. The sensitivities with softer samples will be increased. Although the results with harder samples may not be significantly enhanced, neither will they be harmed.

The screen mesh technique employed only restricts the upper limit of particle size. There can be a wide distribution of particle sizes that go through, say, a 250 mesh screen, and it is this wide distribution that can decrease reproducibility. One method to improve repro-ducibility would be to use a diamond ATR device with a larger sampling area than that of the Meridian^{TM}, which is approximately 500 microns. The newly released Harrick MVP Star^{TM}, with a larger 1500 micron sampling area, is a candidate. (An additional approach to increasing repro-ducibility would be to mechanically control particle size distribution by using two screens with different mesh sizes, and capturing the material between the two sizes. The time to obtain sufficient material by this approach could be problematic.)

With the methodology employed here, practical considerations allowed particle sizes no lower than –250 to –400 mesh. Furthermore, the smallest particle size obtainable was sample dependent. The smaller the particle size, the more efficiently packed is the effective pathlength volume above the ATR element sampling surface. More efficient packing of this space will yield higher absorbance values. A small laboratory grinder which would produce sub –400 mesh samples, in small (1-3 gram) amounts after a short time period would be ideal for further work.

RESULTS

To determine the effect of particle size on sensitivity, the absorbances at the previously specified wavelengths were monitored for each of the filtered samples. Five runs on each mesh sample were made. These results are plotted in Figure 8 for gypsum and in Figure 9 for quartz.

To determine the effect of particle size on reproducibility, the same data sets used for the sensitivity results, above, were employed. Here, the average relative standard deviations for all three wavelengths were plotted vs. screen opening size. Figures 10 and 11 present the data for gypsum and quartz, respectively.

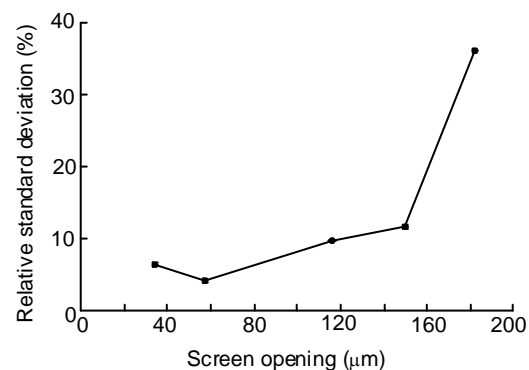For the pressure tests using gypsum and quartz, five runs

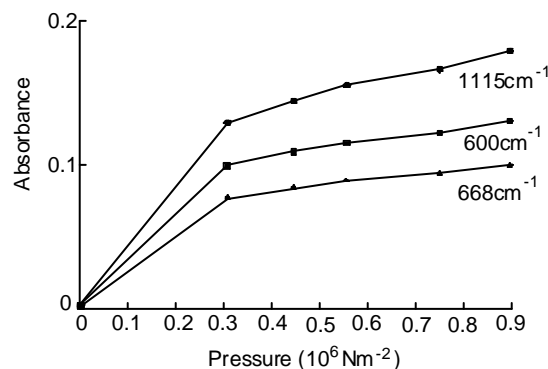Figure 11. Standard deviation vs screen opening for quartz.

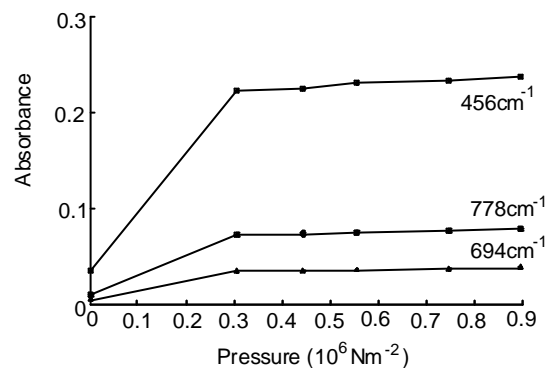Figure 12. Absorbance vs pressure of –250 mesh gypsum.

Figure 13. Absorbance vs pressure for –400 mesh quartz.

Fig. 1

...ique Considerations for the Analysis of Mineral ...mens by Single Reflection Diamond ATR Spectroscopy

were made with each sample type. For gypsum, the -250 mesh sample was used. For quartz, the -400 mesh sample was used. Within each run, six pressure settings were employed. These six pressure settings are identical to those listed in Table I, with the following exception: the zero pressure data were collected with no contact of the sample applicator on the sample. At each pressure setting, the absorbances at three wave-lengths were monitored. The results of these tests for gypsum are given in Figure 12 and those for quartz are given in Figure 13.

REFERENCES

[1] Alfa Aesar Catalog, 2001-2002, Alfa Aesar, 30 Bond Street, Ward Hill, MA 01835.

[2] S. S. Ballard, K. A. McCarthy, W. L. Wolfe: *Optical Materials for Infrared Instrumentation*, University of Michigan Willow Run Laboratories, Ann Arbor 1959.

[3] N. B. Colthup, L.H. Daly, and S.E. Wiberly: *Introduction to Infrared and Raman Spectroscopy*, 2nd ed., Academic Press, New York (1975).

[4] J. G. Delly: *Photography Through the Microscope*, 9th ed., Eastman Kodak, New York 1998.

[5] E. V. Grave: *Discover the Invisible (A Naturalist's Guide to Using the Microscope)*, Prentice Hall, New Jersey 1984.

[6] N. J. Harrick: *Internal Reflection Spectroscopy*, Harrick Scientific Corp., Ossining, New York 1987.

[7] J. P. Lucania, S. L. Berets, M. Milosevic, H. Gremlich, and J. Schmidt: *The Identification of Geological Samples Using Single Reflection Diamond ATR FTIR Spectroscopy*, Paper 2079P, 2002 Pitttsburgh Conference.

[8] McMaster-Carr Supply Company Catalog 102, McMaster-Carr Supply Company, 473 Ridge Road, Dayton, New Jersey 08810.

[9] F. A. Miller and C. H. Wilkins: *Infrared Spectra and Characteristic Frequencies of Inorganic Ions (Their Use in Qualitative Analysis)*, Analytical Chemistry 24, 1253 (1952).

[10] MystiCrystals, Kernersville, NC, www.mysticrystals.com.

[11] K. Nakamoto: *Infrared and Raman Spectroscopy of Inorganic and Coordination Compounds, Part A: Theory and Applications in Inorganic Chemistry*, 5th ed., J. Wiley & Sons, New York 1997.

[12] Olympus America, Melville, NY, www.olympusmicro.com.

[13] Photran, Amherst, NH, www.photran.com.

[14] F. H. Pough: *A Field Guide to Rocks and Minerals*, 3rd ed., Houghton Mifflin Company, Boston 1960.

[15] G. Stehli: *The Microscope and How to Use It*, Dover, New York 1970.

[16] University of Waterloo, Waterloo, Ontario, www.science.uwaterloo.ca.

[17] P. A. Webb and C. Orr (ed.): *Analytical Methods in Fine Particle Technology*, Micrometrics Instrument Corp., Norcross, Georgia.