Attenuated total reflectance (ATR) has become a prominent FTIR sampling technique due to its ease of use, and its accommodation of diverse materials such as liquids, solids, pastes, gels, and powders within a single platform. In some cases having the ability to obtain a magnified view of the sampling surface enhances user efficiency and data quality because it is possible to easily find and position the sampling point, and to document the sample image. Application examples include fiber analysis, sample contamination evaluation, and small sample analysis. This article illustrates the value of FTIR-ATR with sample viewing through the analysis of an ink source on paper. Viewing capabilities assured proper sample positioning on the ATR crystal. The infrared chemical signature of three different inks on paper were compared, and the inks were differentiated.

In forensic science, it is often necessary to determine whether or not ink used within a document is the same. Adulteration may be caused by adding extra text thereby changing the meaning of the wording or altering monetary value.

Primary constituents within ink include a mixture of dyes providing the coloring matter, and resinous material serving to bind the ink to the paper. Ballpoint inks are not based on an aqueous solvent but on quick-drying pastes or gels; hence, they are only partly absorbed into the paper. Therefore, the quantity of ink deposited on paper is far less than its appearance suggests. Suitable analytical techniques for investigating inks on paper consequently need to handle very small amounts of ink material in addition to a great deal of paper matrix.

FTIR spectroscopy is a powerful analytical technique for obtaining a chemical “fingerprint” of samples under investigation. In combination with modern designed attenuated total reflectance accessories, the handling of samples has become very quick and simple yet provides reliable results. In the case of document analysis and many other applications, it is highly desirable to have the evidence or samples preserved by using a non-destructive technique such as FTIR-ATR.

In this work, the GladiATR Vision accessory was used to analyze the infrared spectral characteristics of ballpoint inks on white writing paper. This accessory was chosen due to its magnified sample viewing capabilities.

**Experimental Conditions**

A writing sample from three ball point pens containing black ink from different manufacturers were made on white paper. Spectra were collected using an FTIR spectrometer equipped with a DTGS detector, and the GladiATR Vision sampling accessory with integrated video microscope capabilities. This accessory features a monolithic diamond crystal, and all reflective optics for a virtually unlimited spectral range. The integrated miniaturized CCD camera, focused through the bottom of the diamond crystal, offers video microscope quality with a magnification of 110X. With an optional USB image capture interface, images may be electronically stored. A single reflection diamond crystal serves as the sampling interface with a dimension of 3 x 2 mm.

**Figure 1.** Optical viewing of the GladiATR Vision diamond plate; IR beam and visible illumination meet at the sample position.
For carrying out the experimental data collection, the paper sample with or without ink markings was placed face down onto the diamond. The integrated video microscope allowed for verification of the desired sample area. The opted wavenumber region was 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) with a spectral resolution of 4 cm\(^{-1}\). One minute background and data collection times were used. Three replicate measurements were made at different locations within the samples.

**Results**

A criterion for successful FTIR-ATR sampling is to apply sufficient pressure to obtain intimate contact between the sample and the ATR crystal. In this study, flattening the rough paper surface of the sampling area was successfully accomplished using the GladiATR Vision high pressure clamp, delivering up to 30,000 psi. Figure 2 shows the spectra of pure paper collected from three different locations. Despite the relative size of the sampling area, the spectra are very uniform even though paper is to be known a very heterogeneous material made from pulped fibers, minerals such as kaolin, and various binding agents, just to mention a few components.\(^1\) Specifically, cellulose and hemicellulose related absorbance bands are located around 1000 cm\(^{-1}\), and OH vibrations with hydrogen bonding is observed near 3300 cm\(^{-1}\).\(^2\)

The GladiATR Vision is ideal for the analysis of ink markings, because the sample area is easily determined through the LCD viewer. Captured images of the sampling area are shown in Figure 3. The ink stroke diameter under evaluation was approximately 460 microns for ink #1 and 2, and 560 microns for ink #3.

Considering the primary spectral contributions from ink occurred at wavenumbers less than 1800 cm\(^{-1}\), the subsequent analysis focuses on this region. Reproducibility between repeat ink measurements similar to that observed with paper was found. Therefore, the average of 3 spectra for each ink sample and for the paper only is reported for visual clarity. No additional spectrum manipulation was performed.

As expected, all spectra from the ink samples show a strong influence from the paper matrix. However, when comparing ink spectra with those from pure paper and against each other, spectral differences for all ink sources are observed. Spectral regions attributed to ink include 1725, 1584, 1366, and 695 cm\(^{-1}\). Kher et al. suggest the band around 1584 cm\(^{-1}\) is carboxylate acid salts and polymeric non-dye.
constituents such as resin within ink. No two inks evaluated in this work exhibited the same chemical fingerprint. Visually evident bands are presented here; further differences could be extracted through the application of statistical methods such as discriminate analysis.

Summary
This study was conducted to illustrate a rapid and convenient technique for the comparison of different inks on paper. The technique uses the GladiATR Vision ATR accessory capable of viewing the sampling surface. The method is non-destructive, and requires no sample preparation. Besides the study of micro-scale samples, the GladiATR Vision can analyze standard samples such as liquids, powders, granules, polymers, and other more compact solids without changing any parameter.

References
