HAVE LIBS, WILL TRAVEL

Meet Dr. Richard Hark, Synthetic Organic Chemist, Conservation Scientist and LIBS Enthusiast

Handheld LIBS and Dr. Richard Hark have a long relationship that reads like an adventure series, where partnership with a company like SciAps leads to unexpected places.

"I guess you could say that I've been a bit of a beta tester for SciAps, which means that I push the instruments to their limits by using them in novel ways," Hark says. "But I'd like to think that I have assisted, through feedback, in some small way throughout the years."

Hark has contributed to important improvements, such as a software fix that prevents overheating of the laser in the SciAps LIBS units and an enhancement to how data is exported on the SciAps XRF.

Dr. Richard Hark, Yale's Institute for the Preservation of Cultural Heritage

Hark worked with LIBS while the technology matured

In the beginning, SciAps Z-500 analyzer was limited in that it only went up to 675 nanometers, which was great for a handheld, but missed the important lines for potassium, which is a significant element when identifying minerals and analyzing rocks. The existing laboratory system went well beyond that. So, Hark used the original SciAps Z-500 to focus on qualitative work, like identifying the geographic sources of minerals using the concept of a geochemical fingerprint. "The Z-500 was actually quite successful at distinguishing country of origin in many early projects," Hark says.

Over time, quantitative analysis, like measuring carbon in steel, has become one of the strongest applications for the SciAps LIBS.

"Now the handheld LIBS systems, of which the SciAps unit was the first, are comparable to lab systems for a variety of applications," says Hark. He's used LIBS to analyze seemingly everything under the sun, from hazardous materials encountered by first responders to historic silver coins, seashells, and even pottery sherds at Virginia's Jamestown historic site.

Early work — forensics and first responders

Hark trained as a synthetic organic chemist, and his first laboratory LIBS applications were associated with his interest in forensics, an outgrowth of his work with latent fingerprint developing reagents, which are used for visualizing latent prints on porous surfaces like paper, cardboard, currency, wallpaper, etc.

At that time he was working with "the U.S. Secret Service and some other three-letter agencies that saw a lot of value in the LIBS," he says, so he wrote a proposal to see if he could acquire instrumentation. Hark used his grant to build his own system, using individual components, for geological analysis and exploratory work with forensics.

When he learned the U.S. Army Research Laboratory, was focusing on hazmat detection as an extension of LIBS, providing rapid answers in the field for first responders, he utilized his training as a hazmat technician and his experience with emerging LIBS technology to support a project with funding provided by Congress. The project was fruitful for the development of LIBS and for Hark, who eventually got a nice laboratory LIBS system.

Hark analyzes the colors of the glazes and the clay body of a rare, still-intact Tongzhi porcelain plate from the Qing dynasty, early 19th century

Cultural heritage science — paintings and pigments

Still using the laboratory LIBS system, Hark then became deeply involved in cultural heritage science work. He spent an entire sabbatical year in London working at the Victoria and Albert Museum using techniques such as X-ray fluorescence spectroscopy and Raman spectroscopy to analyze pigments in manuscripts and paintings. He later continued this work using the first handhelds, from SciAps.

SciAps introduces handheld LIBS

It was ten years after his first encounter with LIBS that Hark heard of a new startup, SciAps, Inc. "I saw that SciAps created a handheld LIBS instrument, something my collaborators and I were very interested in. We could take it into the field, both for first responder type applications and for geochemical work," says Hark. SciAps agreed to loan him an instrument. "Before there was an official academic loaner program, I was the loan program," Hark says with a laugh.

Hark used the nascent handheld in conjunction with the laboratory LIBS. With his undergraduate coauthors at Juniata College, Hark published a number of papers involving both handheld and lab instruments for geochemical analysis.

"Within the terms of the comparison—for example, identifying different types of carbonate minerals—the handheld LIBS actually did a little bit better because it had slightly better resolution than the laboratory version," says Hark. In 2019, he and co-authors including Andrew Somers of SciAps reviewed expanding geochemistry applications in "Laser-induced Breakdown Spectroscopy – An emerging analytical tool for mineral exploration" in Minerals. You can read more on SciAps blog.

(continues on reverse)

HAVE LIBS, WILL TRAVEL *(continued from reverse)*

As the instruments developed and improved at SciAps, Hark was able to see more and more utility for the analyzers, sharing what he was learning through publishing. Highlights include three book chapters, and now a review article that has just been published in Spectrochimica Acta Part B; Atomic Spectroscopy on portable and handheld LIBS.

The latest applications

Hark recently completed a project using solely SciAps instruments—XRF, Raman and LIBS—for JR Plumer Associates, performing soil analysis in conjunction with the Army Corps of Engineers Cold Regions Research and Engineering Laboratory in New Hampshire.

Their three goals were to upgrade the current handheld technology for chemical analysis; to design a multisensor system based on these technologies for the rapid, in situ chemical analysis of soils and other materials of military interest; and to investigate the classification/discrimination performance benefit that might be achieved through advanced signal pre-processing and data fusion. "The main point of that work was to use a combination of handheld instruments and then to use machine learning tools to fuse the results of the data," says Hark. In his role as a scientist with JR Plumer Associates, Hark is now working on a new project for the U.S. Army Research Laboratory involving analysis of composite materials.

He's also returned to cultural heritage work, in his new position as conservation scientist at Yale Universtity Institute for the Preservation of Cultural Heritage, where he continues to bring SciAps LIBS into his research. Currently, Hark is working on identifying mahogany and mahogany look-alikes in museum furniture pieces so that conservators and curators better understand their collection and the raw materials used to produce furniture.

"I've really enjoyed working with SciAps over the years. They've loaned the instruments and provided support, but they are also willing to talk about results and help me out if I'm stuck with something. I've talked with other people who have worked with SciAps, and that's a pretty consistent story," says Hark.

Selected Publications

Wingel, K., Hark, R., Schilling, K., Schwarz, C., Bezur, A. "Efflorescence on the paintings of Edwin Austin Abbey: Examination, analysis, and cleaning of surface bloom on The Spirit of Light," In Proceedings of the Conference on Modern Oil Paints. Amsterdam, Netherlands: Springer, submitted.

Harmon, R.S., Throckmorton, C. S., Hark, R.R., Gottfried, J.L., Woerner, G., Harpp, K., Collins, L.M., "Discriminating volcanic centers with handheld laser-induced breakdown spectroscopy (LIBS)," J. Archaeological Sci. 2018, 98, 112-127.

Harmon, R.S., Hark, R.R., Throckmorton, C.S., Rankey, E.C., Wise, M.A., Somers, A.M., Collins, L.M. "Geochemical Fingerprinting by Handheld Laser-induced Breakdown Spectroscopy (LIBS)," Geostand. Geoanal. Res. 2017, 41, 563-584.

The Art & Science of Portrait Miniatures, Jennifer L. Streb and Richard R. Hark, Juniata College Press: Huntingdon, PA, 2015.

Harmon, R.S., Russo, R.E., Hark, R.R., "Applications of laser-induced breakdown spectroscopy for geochemical and environmental analysis: A comprehensive review," Spectrochim. Acta B 2013, 87, 11-26.

Clark, R. J. H., Hark, R.R., Salvadó, N., Butí, S., Pradell, T. "Spectroscopic study of mural paintings from the Church of Saint Eulàlia of Unha," J. Raman Spectrosc., 2010, 41, 1128-1134.

Hark, R.R., Clark, R. J. H. "Raman microscopy of diverse samples of lapis lazuli at multiple excitation wavelengths," AIP Conference Proceedings 2010, 1267, 315.

Burgio, L., Clark, R. J. H., Hark, R.R. "Raman microscopy and x-ray fluorescence analysis of pigments on medieval and Renaissance Italian manuscript cuttings," Proc. Natl Acad. Sci. USA, 2010, 107, 5726-5731.

Burgio, L., Clark, R. J. H., Hark, R.R. "Spectroscopic investigations of modern pigments on purportedly medieval miniatures by the so-called 'Spanish Forger,'" J. Raman Spectrosc., 2009, 40, 2031-2036.

Burgio, L., Clark, R. J. H., Hark, R.R., Rumsey, M. S., Zannini, C. "Spectroscopic investigations of Bourdichon miniatures: masterpieces of light and colour," Appl. Spectrosc., 2009, 63, 611-620.

HAVE AN ACADEMIC APPLICATION?

SciAps is a fast growing, Boston-based handheld analytical instruments company. Founded in 2013, it continues to innovate three core technologies — X-ray, laser, and Raman — for portable, in-field measurements of elements, minerals and compounds. See more Independent Studies at SciAps.com/studies.

SciAps

SciAps, Inc.
7 Constitution Way
Woburn, MA 01801
sciaps.com
339.927.9455