

SPECTROSCOPY

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Spectroscopy

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Foreign (Blue)Stones

The combination of portable XRF, Raman spectroscopy and microscopy has shed new light on Stonehenge's origin – and possibly its constructors



A quick internet search about Stonehenge raises more questions than answers about the origin and history of the Neolithic monument. (We are fairly certain that it was not built by aliens.)

With the power of spectroscopy, researchers from Italy, Canada, and the UK collaborated to analyze the mineralogy of the Stonehenge Altar Stone, revealing that its origin is not the same as the rest of the “bluestones” – a detail that could unveil more about the migration of the British Neolithic ancestors, their cultural and religious practices, and thus Stonehenge's history (1).

Richard Bevins, Honorary Professor at the Department of Geography and Earth Sciences, Aberystwyth University; Nick Pearce, Professor of Public Policy and Director of the Institute for Policy Research (IPR) at the University of Bath; and Sergio Andò, Associate Professor, Department of Earth and Environmental Sciences, University of Milano Bicocca discuss how spectroscopic analysis enabled them to make this significant discovery and discusses the future of miniaturized spectroscopy in geochemical research.

What makes the Stonehenge Altar Stone so special?

The majority of the Stonehenge bluestones (originally known as “Foreign Stones”) were sourced to the Mynydd Preseli area in southwest Wales by H.H. Thomas in 1923. Monoliths, like the

bluestones used in the construction of stone circles, are usually locally derived. This is not the case for Stonehenge; in fact, its bluestones represent one of the longest transport distances known from source to monument construction site anywhere in the world.

Using modern analytical techniques, we have been able to refine the provenance of the majority of the bluestones – some down to particular outcrops of igneous rocks which have been identified as Neolithic quarry sites following excavations by our archaeological co-workers. But one bluestone (Stone 80, known as the Altar Stone), is anomalous; it is not of igneous origin but is a gray-green sandstone and is clearly unrelated to the other bluestones. Thomas considered that it also came from southwest Wales, deriving from outcrops of Old Red Sandstone age in that region. Identifying the source of the Altar Stone could have important implications for understanding the migration of people in Neolithic Britain and the significance of their stone monuments.

Why did you choose spectroscopy for your analysis?

Different approaches can be used to characterize the mineralogy of a sedimentary rock – but most conventional techniques do not allow the recognition of minor minerals or other essential characteristics of the rock. Another constraint to bear in mind is that archaeological material analysis – almost always – needs to be non-destructive and

often only very small quantities are available for study. These factors mean that some standard analytical techniques cannot be applied.

In recent decades, spectroscopy has established itself as an excellent technique for the non-destructive analysis of such sensitive material in the cultural heritage domain. Because of the sensitive nature of the Stonehenge monument, we have applied largely non-destructive techniques to our in situ and laboratory-based investigations; X-ray fluorescence (both desktop and portable instrumentation), X-ray diffraction and automated scanning electron microscopy combined with energy-dispersive X-ray spectroscopy, combined with standard transmitted and reflected light microscopy.

Using a portable XRF, we have identified the geochemical signature for the Altar Stone. Raman spectroscopy (conducted at the Università of Milano, Bicocca) was especially useful in identifying minerals – baryte, apatite, zircon and, garnet – because we applied a single grain approach, directly directing the laser at grains embedded in the bonding resin, we could couple the morphological features of each single grain along with a formal species identification.

Some minerals when examined using standard transmitted light microscopy are not transparent to light and are difficult to identify. When Raman spectroscopy is combined with reflected light microscopy, however, it is possible to identify the varieties of iron oxides/hydroxides and titanium oxides present and to separate one sandstone from



Richard Bevins at Craig Rhos-y-Felin in the Mynydd Preseli area, a site identified as the source of rhyolitic debris at Stonehenge. *Photo by Christine Faulkner.*



Professor Nick Pearce using a portable XRF to analyse spotted dolerite at Carn Goedog in the Mynydd Preseli, one of the sites identified as a source for spotted dolerite bluestones at Stonehenge. *Photo by Richard Bevins.*

another. This approach was fundamental in our study and enabled us to distinguish between samples of the Old Red Sandstone sequences in Wales. Such a high-resolution approach is required to fingerprint the possible source of rocks used in archaeological monuments.

What was the biggest challenge during your study?

The major challenge working on these types of materials is the non-destructive analytical approach that is required because it constrains data collection. A fresh rock surface is chemically different from a weathered surface, as is a wet or dry surface because of X-ray attenuation by water. So, we developed specialized protocols to get “bulk surface” (many analyses across samples) data, ensuring that we obtained data from similar surfaces by portable XRF and maintained day-to-day instrument stability/reproducibility. Despite employing field-based equipment, there are always issues related to the weather conditions, such as those encountered when working outdoors in the UK – which affected our analysis at times. In situ analysis at Stonehenge and at the possible source sites has been extensive and time-consuming, but always detailed and non-invasive nonetheless. However, as “destructive” sampling and analysis has been allowed in the past, comparison of our study with these earlier bulk analyses can be performed, but the different approaches can make this rather challenging.

What were your key findings?

The key accessory minerals identified during this study of an Altar Stone fragment were baryte, apatite, zircon, garnet, coupled with an absence of oxides and hydroxides of iron. The varieties of garnets and

Ti-oxides and the crystallinity of zircon was established by Raman spectroscopy as a reference for future comparison with the same minerals in other samples. We also recorded that, in the Altar Stone, the apatites are all rounded – baryte is often corroded or angular, while the phyllosilicates, such as chlorite and biotite, which are larger in size than the other minerals, have very rounded rims. These are all distinctive characteristics of the Altar Stone, which are not found in samples which have a similar mineral makeup from potential source rocks elsewhere.

Our investigations have led us to the conclusion that the Altar Stone did not come from southwest Wales and in fact does not come from the geological region known as the Anglo-Welsh Basin. This was an unexpected result and means that we now need to broaden our stratigraphic and geological horizons; we must look at rock sequences from different parts of Britain, in particular northern England and Scotland where similar rock types occur. Identification of a source in one of these two regions would have important implications for understanding communications between Neolithic populations in Britain, as well as their trading and migration.

How would further miniaturization or other technological advances help in future geochemical studies?

Miniaturization would make portable XRFs lighter – carrying one all day with a few spare batteries in rugged terrain is physically demanding! I’m sure we can also expect better performance – better detectors with better signal/noise characteristics perhaps, more intense X-ray generators to provide better signals. Nonetheless, there are physical issues that cannot readily be overcome so easily, such as the attenuation of light X-rays in air, so some aspects of methods like pXRF will always have some physical limits upon them.

For studies like the Altar Stone work, we still need to study bulk surface analysis of coarse-grained rocks, so making things that can analyze smaller areas on the surface of a sample (akin to the move to microanalysis in geochemistry, for example) would be of no benefit. The recent innovation of transportable Raman spectrometers has made it possible to take the instrumentation to field locations. Further miniaturization could give portable Raman devices the same level of data acquisition (e.g. the same resolution) as current, heavier laboratory-based instruments – and that would enable more comprehensive analysis of many rocks in other situations, where invasive sampling is prohibited.

What is next for you and your research?

Our research is still on-going and the next phase of work will involve fieldwork in northern England and Scotland to see if we can identify gray-green sandstone with the same overall mineralogy and geochemistry as the Altar Stone. We’ve already conducted desktop reviews of geologically-relevant areas to establish a sample collecting strategy, and fieldwork is planned for March–April 2024. After that, we’ll conduct further analytical investigations; again the combination of portable XRF and Raman spectroscopy techniques will help verify the presence or absence of diagnostic minerals (baryte, carbonates, K-feldspars in the case of the Altar Stone) – providing a mineralogical fingerprint without the need for extracting chips of stone from archaeological monuments.

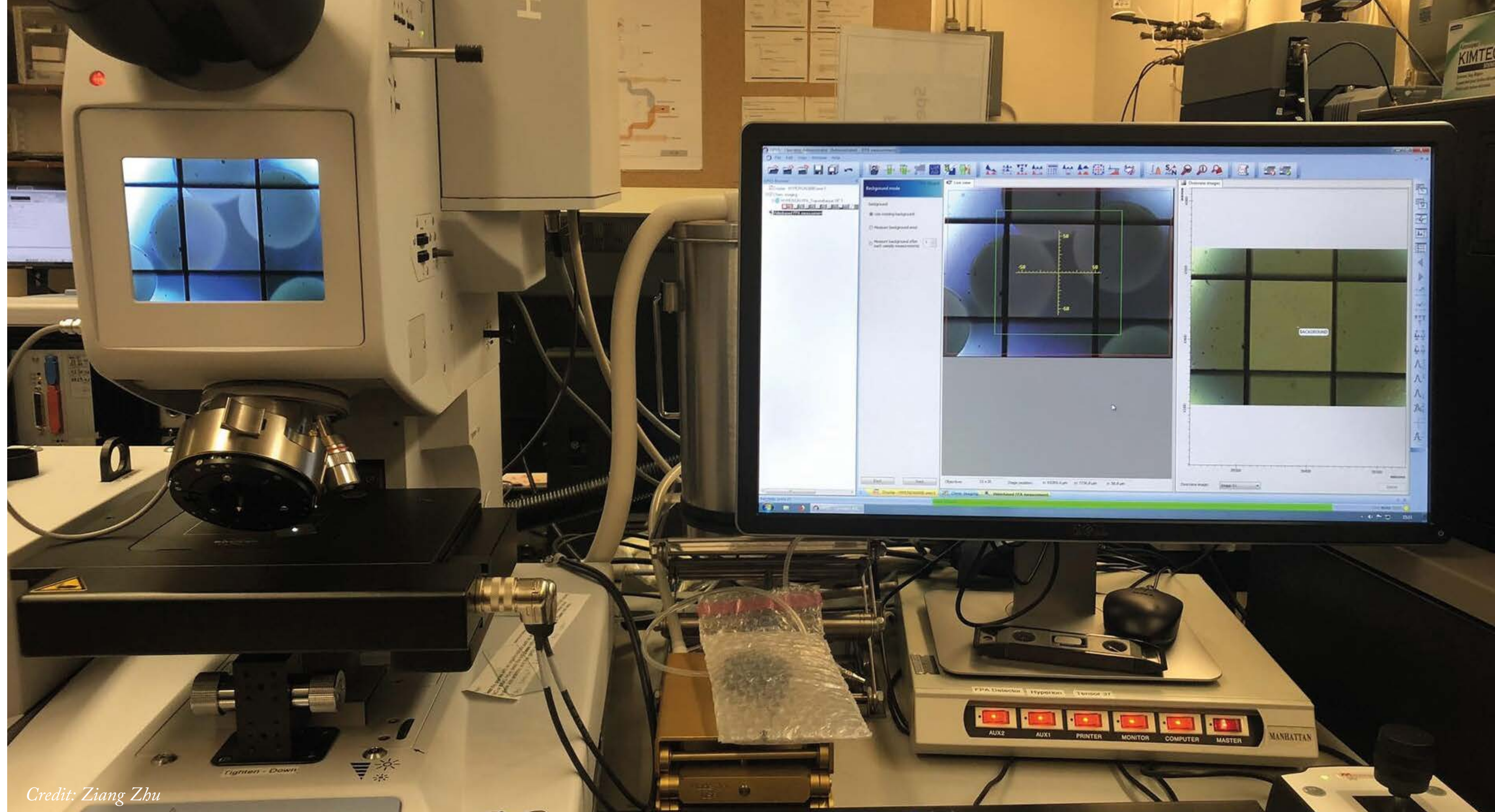
Reference

1. R.E. Bevins et al., *J Archaeol Sci Rep*, 51 (2023). DOI: doi.org/10.1016/j.jasrep.2023.104215.

UPFRONT

An Automated Avenue for Microplastic Detection

An AI-spectroscopic synergy could be the key to identifying microplastics faster and with more accuracy



Credit: Ziang Zhu

An AI-based microspectroscopy imaging identification system, PlasticNet, can detect microplastics with high accuracy – and could be used in wastewater treatment and food production plants (1). The tool, developed by researchers at University of Waterloo, Canada, uses a deep learning convolutional neural network architecture to automatically detect images generated by focal plane array (FPA)-based micro-fourier transform infrared (FT-IR) microscopy.

After training PlasticNet with over 8,000 spectra of virgin plastic, and then retraining the tool using non-virgin plastics, PlasticNet was able to successfully classify 11 types of common plastics with 95 percent accuracy. The team also demonstrated a 17.3 percent improvement

in identifying polypropylene microplastics compared with other environmental datasets.

“I was surprised by the efficiency of deep learning in this context,” says lead author Ziang Zhu. “With PlasticNet, we received precise and reliable results in a field that is known for often dealing with complex and variable data. It’s really opened up avenues for future investigations in environmental science.”

After trailing PlasticNet at a local wastewater treatment plant, the team are confident in taking their discovery to the next step. “Our findings mark a significant step forward in environmental research,”

says Zhu. “PlasticNet’s ability to rapidly and accurately recognize microplastics could pave the way for a standardized method in micro and nano pollutant detection.”

Zhu is hopeful that environmental researchers will embrace AI for detecting microplastics – as well as other pollutants and applications: “Without acceptance of this technology, we’re unable to apply it to the complex criteria involved in different areas of environmental science.”

Reference

1. Z Zhu et al., *ScienceDirect*, 337 (2023). DOI: 10.1016/j.envpol.2023.122548.

DKD Detection

ATR-FTIR spectroscopy combined with machine learning can help detect early stage diabetic kidney disease – and it could be implemented into point-of-care settings

Albumin excretion in urine is a common biomarker of diabetic kidney disease (DKD). Current routine screening methods not only have point of care limitations, but only identify patients in the late disease stages. Recently, a group of Australian researchers have combined ATR-FTIR spectroscopy with machine learning to rapidly profile proteins – such as albumin – in urine to detect DKD in its early stages (1). To gain more perspective, we asked the lead authors of the study – David Pérez-Guaita, Bayden Wood, and Karin Jandeleit-Dahm – a few questions.

Could you please introduce your work and its importance?

Our work focuses on the development of an infrared-based spectroscopic method that combines machine learning for the quantification and characterization of proteins in urine. The presence of specific proteins in urine is indicative of a wide range of diseases – including DKD and chronic kidney disease. And so, analytical tools that can quantify proteins at low levels are fundamental for the early detection of DKD. These techniques should be simple, fast, and portable enough to be used in close proximity to the patient in pharmacies or community clinics. Our instrument is the size of a shoebox, and provides accurate results in a few minutes at a reasonable per test cost.

Could you please share some details of your research?

We measured the urine protein extract – obtained by ultrafiltration – from 22 controls and 155 diabetic patients with normo-, micro-, and macro-albuminuria. Visual inspection of the spectra indicated a strong correlation between the amide bands from proteins and the total protein

content of the samples. We applied support vector machine classification and regression models to extract the diagnostic information contained within the infrared spectra. The model was independently tested and successfully identified micro- and macro albuminuria with sensitivity of >91 percent and specificity of >99 percent. Furthermore, the regression methods predicted the amount of albumin with error values of 17 and 44 mg/L for normo- and micro albuminuric patients, respectively.

What are the advantages of using ATR-FTIR spectroscopy over conventional diagnostic techniques?

The current diagnostic test for DKD uses dipsticks for screening and can only detect albuminuria at medium levels with low sensitivity. More sophisticated techniques used in pathology labs have appropriate limits of detection (1 mg/L), but they are expensive and difficult to translate into point-of-care (POC) settings. There is therefore an urgent need to increase screening for early kidney disease – not only in the diabetic context. Early detection and treatment means less patients with end stage kidney disease that require costly dialysis and transplantation.

The main advantage of our technique is that it combines appropriate sensitivity, specificity, and POC capability for screening urine samples. Furthermore, ATR-FTIR is portable, so it may be taken to more remote, indigenous communities where DKD is far too common. We believe that – with automatization and cleaning of the spectral window – the technology can be improved and decrease the measurement time to a few minutes. The use of stable filters could also put the cost at the \$1 level. Even so,

commercialization of a technology is a long and expensive process.

What do you want diagnostic professionals to know about this type of testing?

When the term “machine learning” is used, professionals often assume that analysis is complex and can only be used by experts. We want people to know that the methodology is simple and can be performed in user-friendly software, cloud-based systems, or even interfaced through a mobile phone! Such apps have already proved successful for other IR-based clinical applications – including malaria diagnosis. These methods simply require the press of a button to input the spectra and, in a few seconds, test results are returned.

What about applications in other disease areas?

We would like to test the potential of the technique for diagnosing other diseases that modify the composition of proteins in urine (for example, hemoglobinuria). But, before tackling other diseases, we want to work on automatizing the protein extraction and cleaning process to improve the techniques POC capabilities. We are also studying the robustness of our method and plan to perform multicenter studies with different hospitals in Europe and Australia so that our method can hopefully – in the future – be implemented in a real-world setting.

Reference

1. Z. Richardson et al., *Analysis & Sensing* (2022). DOI: 10.1002/anse.202200094



Concrete Evidence

Why are Roman buildings so durable?



Credit : Daniel Klaffke

As the world’s largest unreinforced concrete dome, the Pantheon is unequivocal proof of the excellent engineering skills of the ancient Romans. But we must also consider the exceptional nature of the construction materials. Specifically, how does ancient Roman concrete survive millenia, while often enduring harsh conditions? A team of researchers led by the Massachusetts Institute of Technology have used a handful of analytical techniques to solve the mystery – and the answer can be found in the complex process of “hot mixing” (1).

Previously, the process of slaking – where water is added to lime to form a highly reactive paste – was suspected as the culprit of durability – and the macroscopic lime clasts visible in the mixture were attributed to poor mixing practices. But Admir Masic, lead author of the study, had one nagging question: “If the Romans put so much effort into making an outstanding construction material, following all of the detailed recipes that had been optimized over the course of

many centuries, why would they put so little effort into ensuring the production of a well-mixed final product?” (2).

In the study, 2,000-year-old Roman mortar samples from the archaeological site of Privernum, Italy, were subjected to large-area scanning electron microscopy and energy-dispersive x-ray spectroscopy (SEM-EDS), powder X-ray diffraction, and confocal Raman imaging. SEM-EDS revealed the complex chemical composition of the mortar, and found the tiny clasts to be calcium carbonate. Spectroscopic techniques indicated that these were formed via an exothermic reaction – evidence of calcium oxide (quicklime) hydration.

From this, the MIT researchers deduced that Roman concrete was likely made by mixing quicklime directly with pozzolanic material (such as volcanic ash) and water at extremely high temperatures.

“The benefits of hot mixing are twofold. First, when the overall

concrete is heated to high temperatures, it allows chemistries that are not possible if you only used slaked lime, producing high-temperature-associated compounds that would not otherwise form.” said Masic in the press release. “Second, this increased temperature significantly reduces curing times since all the reactions are accelerated, allowing for much faster construction.”

The hot mixing process also gives rise to lime clasts with a brittle nanoparticulate architecture that not only preferentially fractures but also enables “self-healing” of those cracks on exposure to more water.

The team hope that their findings will be considered in future cementing formulations to develop more sustainable architecture.

Reference

1. LM Seymour et al., *Science Advances*, 9 (2023). DOI: 10.1126/sciadv.add1602
2. MIT News (2023). Available at: bit.ly/3K4Jk8r

UPFRONT

Ultra-Tiny but Ultra-Mighty

Where ultra-mini spectrometers fit in the future of testing

The components used in traditional spectrometers to filter and disperse light take up space, limiting the potential to miniaturize the technology and open the door to applications that demand total mobility.

And that's why researchers from Aalto University, Finland, designed a spectrometer that fits on a microchip. But it's not just small – the team were able to achieve a performance comparable to benchtop systems, replacing certain key components with novel semiconductor materials and using the power of artificial intelligence (AI). Here, we interview Hoon Hahn Yoon, first author of the study, to find out more.

Tell us about your ultra-mini spectrometer...

We're proud to say we've designed a miniaturized spectrometer that breaks all current resolution records – in an ultra-tiny footprint of 22 μm by 8 μm . To do so, we replaced optical and mechanical components with a combination of AI algorithm and the electrically tunable sensor's spectral response – eliminating the need for detector arrays, dispersive components, and filters. We hope that this all-in-one, miniaturized device will revolutionize the field, enabling portable, low-cost, high-performance spectrometers.

What makes this so interesting is that it offers performance comparable to benchtop systems – whilst being thousands of times smaller than those same commercial systems. In other words, these new spectrometers will provide portable alternatives to uncover otherwise invisible information without even going into the lab.

The device is also entirely electrically controllable, so it has enormous

potential for scalability and integration. For example, it could give us a next generation of smartphone cameras with hyperspectral capability.

Which areas will benefit most from this technology?

By integrating on-chip spectrometers into portable devices, such as smartphones and drones, we could open up a whole host of analytical possibilities in quality inspection, security, biomedical analyzers, environmental monitoring tools, and space telescopes. To give you a concrete example, people with food allergies could verify their food is safe. Such devices could also enable monitoring of crop health, pollution, food quality, and even the progression of some diseases.

What do these findings mean for the future of spectroscopy?

Ultra-miniaturization is definitely the way forward. Our spectrometers offer high performance with high wavelength accuracy, high spectral resolution, and broad operation bandwidth, using only a single microchip-sized detector in ambient conditions.

Until now, there has been a trade-off between spectrometer performance and size because traditional systems use light dispersion over distances or spectral filter and detector arrays to achieve a high resolution. Our technology eliminates this trade-off, making portable, low-cost, high-performance spectrometers a reality.

Can further improvements be made?

We are expanding our work to improve spectrometer performance

and further fit complementary metal-oxide semiconductor (CMOS) compatible technology. More advanced AI or machine learning algorithms and different combinations of materials could soon provide even better spectrometers.

We used the van der Waals heterostructure by stacking two-dimensional materials. Since these are so-called emergent materials, there is still room for engineering advances in their large-area synthesis, uniformity, and yield. Our idea can also combine with any emergent optoelectronic devices other than two-dimensional materials. There are numerous promising candidates for the material platform to realize our demonstration with better performance.

Furthermore, if a semiconductor foundry company, such as Samsung Electronics, wants to implement our spectrometer technology into their own products – such as smartphones or drones – I expect that it might take only a few years. The chip fabrication technology used for our miniaturized spectrometer belongs to the basic foundry technology widely used in the semiconductor industry. Thus, there are no fundamental barriers to overcome for commercialization.

Overall, I am excited about what the future holds – hopefully it will link to the future of next-generation smartphone cameras evolving from conventional color cameras to hyperspectral cameras!

Reference

1. HH Yoon et al., "Miniaturized spectrometers with a tunable van der Waals junction," *Science*, 378, 296 (2022). DOI: 10.1126/science.add8544



IN MY VIEW

Forget Me Not

Poorly understood and rarely emphasized by instrument manufacturers, is a lack of respect for microscopy holding back the microspectroscopy field?



Microscopy is the science – and art – of creating, recording and interpreting magnified images; spectroscopy is the science of qualitatively analyzing the chemical composition of physical and biological matter based on light emission, scattering, and absorption (1). Microspectroscopy (MSP) combines the fundamentals of both – enabling the study of microscopic materials through light–matter interactions (2).

Commercially available microspectroscopy instruments have been sold since the mid-1900s – IR microscopes have been staples in pharmaceutical, forensic, industrial and other scientific laboratories for decades.

The ability to correlate chemical and morphological features of samples is key for many MSP applications; for example, UV-Vis MSP has solved numerous problems in a variety of industries – most

notably in investigations involving the dyes and pigments commonly researched in industrial chemistry and forensic science.

The ability to see the sample before spectroscopic analysis is another clear advantage of MSP; for example, analyzing microscopically-sized samples ensures that the target is effectively analyzed. In addition, different microscope contrast techniques (for example, PLM, DIC, Phase Contrast) make different characteristics visible in a sample, which can be used to correlate changes in spectral data with sample microstructure. And when using a microspectrometer, smaller areas of analysis – or spot size – are achievable.

The present

Manufacturers are continually making advances in microspectroscopy, enabling novel research. Some of these advances are small incremental

improvements (better optics or lasers, for instance), but there have been other more revolutionary developments in the pairing of microscopy with spectroscopy, such as the recent invention of optical photothermal infrared microspectroscopy + simultaneous Raman (O-PTIR+R) by Photothermal Spectroscopy Corp.

Recent advancements in dichroic mirrors have enabled high throughput spectral analysis and confocality when using different modalities to analyze the same sample. Such advances add new depth to the chemical interrogation of microscopic samples – particularly when using the likes of hyperspectral imaging, particle correlated Raman spectroscopy (PCRS), and morphologically directed Raman spectroscopy (MDRS).

Another trend is the pairing of different techniques with Raman microspectroscopy into instruments capable of simultaneous or

“Unfortunately, microscopy, which enables many of the aforementioned benefits and advances in microspectroscopy, is often undervalued. And we’d argue that this lack of respect for the ‘micro’ side of the duo is the biggest challenge facing the field.”

tandem analysis on the same sample. Some examples include the combination of FT-IR and Raman microspectroscopy, TERS, AFM-IR, Raman+UV, and Raman+Fluorescence microspectroscopy.

Unfortunately, microscopy, which enables many of the aforementioned benefits and advances in microspectroscopy, is often undervalued. And we’d argue that this lack of respect for the “micro” side of the duo is the biggest challenge facing the field.

One fundamental principle of microscopy that is particularly undervalued in microspectroscopy is the critical importance of sample preparation. There is no post-analysis correction or processing that can overcome poor sample preparation. To achieve optimal MSP analysis, the best microscopic image must be produced. Scientists must put the time and effort into quality sample preparation because the quality of the spectral data is directly correlated with the quality of the image.

Educating individuals about the role, function and importance of good microscopical analysis cannot be underestimated either. It’s also important to know that microscopes are not plug-and-play devices. With a benchtop instrument, optics may be set and not controlled by the analyst – but with MSP, the analyst is responsible for aligning the optics through proper set-up of the microscope. Further, there are a

variety of microscopic illumination (transmitted and reflected light) and contrast methods, which could greatly improve the information provided by MSP – if the analyst knew how to use them to produce an image.

All of these aspects appear to be poorly understood in the scientific community – and perhaps worse, they are not highly emphasized by instrument manufacturers.

The future

There are several fields that can benefit tremendously from MSP – from additional applications in forensic science, where it is already established, to new areas, such as pharmaceuticals, cultural studies, and nanomaterials. In pharma, MSP could be used to optimize the identification of small domains in complex drug mixtures and determine the conversion of polymorphic forms to study degradation products and aid the development of novel vaccines and other drugs.

But it is crucial to keep in mind current trends, like artificial intelligence. Such technology will undoubtedly make meaningful advancements in MSP – specifically in areas of hyperspectral imaging, mixture analysis, and spectral interpretation.

As research is continuously expanding, and new questions arise, researchers and manufacturers must work together to ensure these MSP instruments are reaching their potential with regard to both quality images and spectroscopic analysis.

MSP is more than just a concept. It is already established in forensic science and it is ready to expand to other fields – once we put emphasis on the microscopy aspect and understand its role.

Brooke Kammrath is Professor of Forensic Science at the University of New Haven and Co-Executive Director of the Henry C. Lee Institute of Forensic Science, Connecticut, USA.

Dale Purcell is Founder and CEO of Chemical Microscopy LLC, Indiana, USA.

Reference

1. JA Reffner, “Microspectroscopy in Forensic Science,” *Encyclopedia of Analytical Chemistry*. John Wiley & Sons, Ltd: 2017. DOI: doi.org/10.1002/9780470027318.a1117.pub2
2. S Walbridge-Jones, “9 – Microspectrophotometry for textile fiber color measurement,” *Identification of Textile Fibers*, 165. Woodhead Publishing: 2009. DOI: doi.org/10.1533/9781845695651.2.165

Ready or Not...

AI is here – and a new era for clinical Raman spectroscopy beckons

Biomedical Raman spectroscopy has developed rapidly in recent years, with numerous studies demonstrating its potential for improving medical diagnostics.

We are working on two big medical fields of application where Raman spectroscopy offers great chances to fulfill currently unmet medical needs. One is in infectious diseases where it can be used to determine the host response (to define viral, fungal, or bacterial infection) and in case of bacterial infection enable the rapid identification of the causing bacteria and its antibiotic resistance profile. The second big field of application is intraoperative spectral histopathology in terms of tumor boundary detection, staging, and grading. To translate Raman spectroscopy into clinics, surgical microscopic or endoscopic Raman spectroscopy and compact point-of-care Raman setups have been developed in conjunction with clinicians.

However, despite these great advances, Raman spectroscopy has not yet established itself in the clinic – and there are several reasons as to why. One is a lack of reliable tools for the automated analysis of Raman spectra. After all, the success of Raman spectroscopy in biomedical diagnostics is inextricably linked to the development of tailored algorithms for evaluating Raman measurement data (for example, spectral data sets and image data) into qualitatively and quantitatively usable information for end users.

Until recently, the main methods used were based on classical machine learning, but now as the number of Raman datasets and biomedical Raman studies increases, the application of deep learning approaches using neural networks is rapidly entering Raman spectroscopy and becoming increasingly important. And with the growth of AI, we could be on the cusp of a powerful synergy that incorporates both AI and deep learning in Raman spectroscopy. This combination could be the missing link necessary to ensure Raman is routinely used for clinical applications.

Some hurdles remain. As a community, we are not entirely ready to embrace this technology – far from it, in truth. But I am hopeful that we are open to studying the performance of AI in biophotonics and spectroscopic diagnostics. Recently, I have been reading more manuscripts reporting on automated analysis of biophotonics data – for example, ophthalmic OCT datasets using deep learning – which looks promising.

Undoubtedly, AI will be a game changer. In a few years, it will be indispensable in many fields – and certainly digital pathology. Whether this is good or bad remains to be seen, because, as with many things, AI offers not only benefits but also dangers, which justifies the hesitation of the community.

One concern in using AI in general and deep learning approaches for image analysis and Raman spectral analysis is the foundation on which



the analysis is based – something that can be elusive. It is often the case that one does not know the origin of an AI algorithms' decision. Therefore, it is important to approximate and understand AI tools in order to make them interpretable and understandable for humans.

Of course, the application of AI – not only in medicine – always raises the question of liability. The legal foundations must be laid here in the near future, because I am certain that AI will play a major role in our daily lives in the future.

This spectroscopic-AI synergy is undeniable and could set the foundation to integrate this fruitful combination of Raman spectroscopy and AI into clinical settings. From a technological point of view, the stage is set and clinically applicable – and medical approved Raman equipment is available. There may be hurdles to overcome before AI's full potential in clinical research can be reached. But the time is ripe to finally start clinical trials with large patient cohorts showing the great possibility of deep learning in terms of automatically interpreting Raman spectra. However, there are still regulatory hurdles to overcome such as compliance with the EU Medical Device Regulation (MDR) 2017/745 in Europe.

Juergen Popp is Scientific Director of the Leibniz Institute of Photonic Technology, and holds a chair for Physical Chemistry at the Friedrich-Schiller University Jena, Germany

APPLICATION NOTE

Tackling Water Quality Challenges with Compact UV Spectroscopy

Navigating the future of water quality with UV technology

Water quality management is a growing concern globally due to factors like population increase, intensified farming, and industrial waste, which compromise water purity. Hamamatsu Photonics introduced an advanced UV spectrometer designed to address these challenges for environmental and water quality monitoring.

Environmental monitoring

Human activities often lead to nutrient-rich bodies of water, causing oxygen levels to drop and aquatic life to perish. Monitoring wastewater quality is essential for detecting pollution and ensuring compliance at treatment facilities. Specific sources, such as hospitals and pharmaceutical plants, produce concentrated antibiotic wastewater needing thorough treatment and analysis before environmental release.

Water quality monitoring

Water utilities strive to meet World Health Organization standards for drinking water. Through rigorous monitoring and treatment systems, these utilities aim to detect and mitigate potential hazards, ensuring the provision of safe, reliable drinking water.

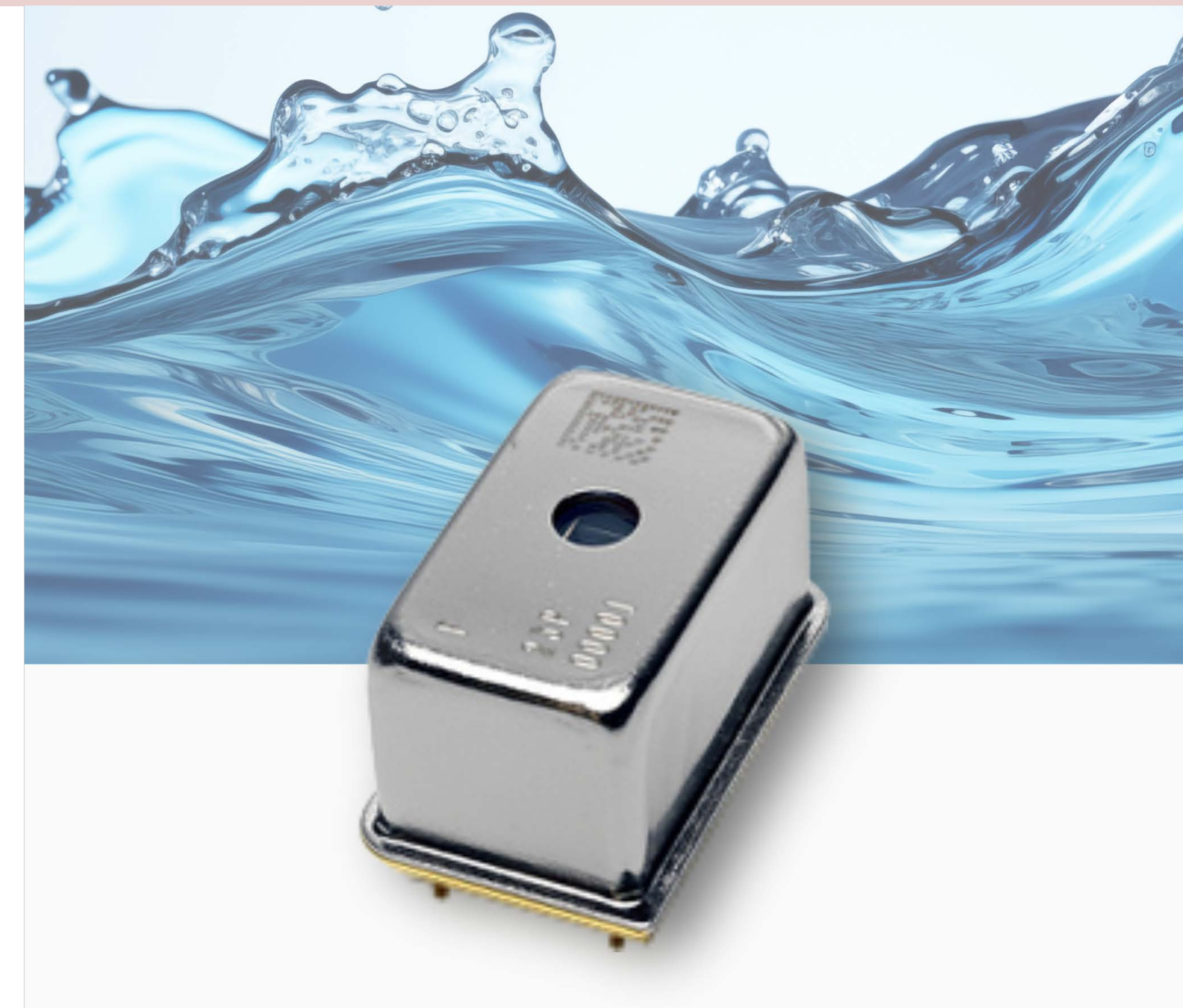
UV-Vis spectroscopy for online water monitoring

UV-Vis spectroscopy, employing spectral remote sensing in the UV and visible wavelengths, offers a physical method for water quality assessment. This technique correlates a substance's absorption of specific light wavelengths to its concentration, allowing for reagent-free, real-time water quality measurements without the need for sample filtration. Parameters measurable by UV-Vis spectrophotometers include color, nitrate, Depleted Oxygen Content (DOC), Total Oxygen Content (TOC), and the spectral absorption coefficient. Recent advancements have expanded parameter monitoring to include dissolved organic matter, chemical oxygen demand (COD), and disinfectants in drinking water.

Compact UV spectrometers

Hamamatsu's UV-VIS spectrometer combines advanced technology and practicality for accurate, efficient, real-time analysis. Features include:

- **Precise measurement:** Exceptional sensitivity across 190 to 400 nm wavelength range, enabling precise measurement of critical water quality parameters for comprehensive water composition insight.
- **Compact design:** The spectrometer's compact form allows seamless integration into miniature and handheld instruments, facilitating easy incorporation directly within water pipelines.
- **Reliability outdoors:** With an unparalleled dynamic range, these spectrometers ensure dependable measurements under varying environmental conditions, ideal for outdoor operation.
- **Early detection:** A high Signal-to-Noise Ratio (SNR) enables the early detection of subtle water quality fluctuations, allowing for preemptive actions.



- **Enhanced accuracy:** Design optimizations reduce crosstalk among wavelength readings, enhancing measurement accuracy and reliability.

Hamamatsu's UV spectrometer is a pivotal solution to global water quality challenges, from addressing nutrient imbalances affecting ecosystems and food supplies to meeting strict drinking water standards. This technology underscores Hamamatsu's commitment to improving water quality management and securing the purity of essential water resources.

READ THE APPLICATION NOTE

FEATURE

Ten Year Views: With George Chan

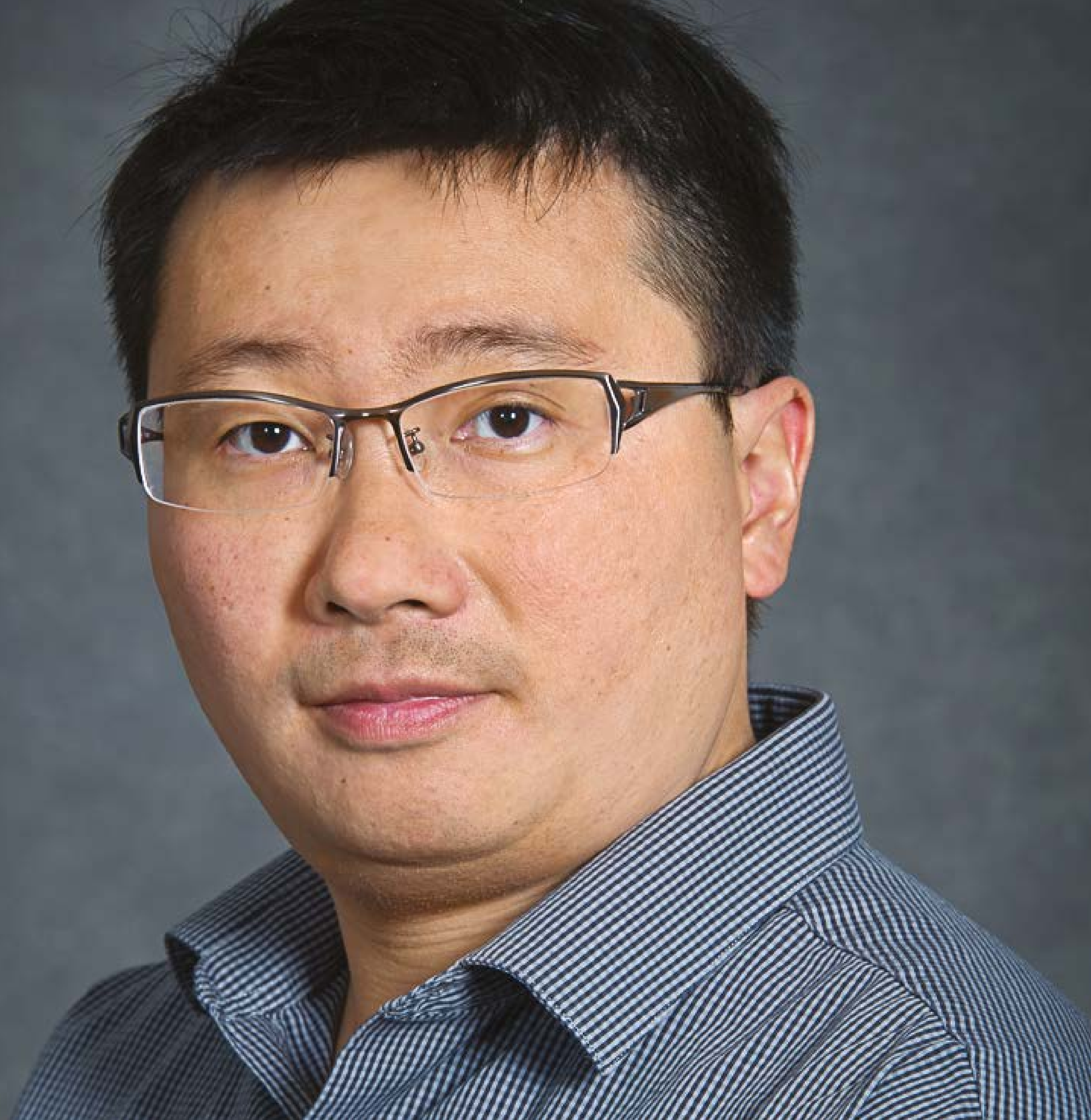
George Chan discusses the decade's developments in analytical atomic spectrometry, concerns for the field, and future predictions

Could you give us a brief introduction to analytical atomic spectrometry? What falls within its scope?

It is logical to refer to analytical atomic spectrometry as analysis for elemental (atomic) information based on the principle of either electromagnetic radiation (optical spectrometry), or charged particles (mass spectrometry).

On the optical spectrometry side, techniques are typically classified according to their working principles – absorption, emission and fluorescence – with a wide variety of atom reservoirs and excitation sources. The wavelength range is vast, spanning from x-ray to near-infrared, although only a subset is used in almost all cases.

On the mass spectrometry side, there is also a wide range of ionization sources coupled to different types of mass spectrometers, and often, the same atom reservoir can be used as an excitation source in optical, and mass spectrometry. There are also some “hybrid” techniques that use optical transitions to achieve selective ionization – followed by detection of the charged particles. In addition, sample introduction techniques, instrument hardware, data handling, processing and reduction techniques – specific for use with the spectrometric methods – all fall within the scope of analytical atomic spectrometry.



What has been the most significant development in atomic spectrometry over the past 10 years?

There have been several significant developments. I think that the ChemCam instrument – which was installed on the Mars Curiosity Rover and landed on Mars in 2012 – is the most significant.

ChemCam combines a high-resolution remote imaging camera and a laser induced breakdown spectroscopy (LIBS) system to characterize the elemental composition of rock and soil samples on Mars. Although the development of LIBS is not new (it can be traced back to the 1960s shortly after the laser was invented), LIBS was still more like a laboratory research tool at the start of the 21st century. Sending a LIBS-based instrument to Mars shows the analytical community how advanced, capable, and reliable the LIBS technique and hardware is. The success of ChemCam, of course, is driven by the needs of a special mission, but advancement of the technology, and reliability of lasers and photodetectors are the keys to its success.

What have been the most important commercial developments over the past decade?

Array detectors are indispensable tools in optical spectrometric measurements – but they are not without their drawbacks. One limitation is that registered “detector counts” can not be readily reverted back to the number of photons or photoelectrons (for various reasons). Although some modern array detectors can be used in a photon-counting mode, the dynamic range is then greatly reduced as a pixel is temporarily “dead” after a single photon hits it – a phenomenon similar to detector dead-time in ion-counting mass spectrometry. An array detector with read noise significantly less than one electron only became available two years ago. In particular, the readout noise of the ORCA-Quest qCMOS camera from Hamamatsu is reported to be 0.27 electrons rms. This low level of read noise makes counting of multiple photoelectrons on a single detector-pixel possible. Although the global reset time of this camera is not yet fast enough to match the typical timescale of LIBS measurements, I consider it an important innovation in detector technology.

Do you have any concerns for the field?

My major concern involves the continuation and transfer of experience and knowledge to the next generation. There are several reasons for this concern. Firstly, without dispute, the academic community of analytical atomic spectrometry has been shrinking for the past 20 years. In almost all cases, retired faculty members specializing in analytical atomic spectrometry have been replaced by someone specializing in another area. As a result, there are now only a small number of active research groups that can transfer knowledge in atomic spectrometry to the next generation.

Secondly, the focus of many research programs has shifted from fundamental understanding and instrument development to method development and applications (for example, metallomics, speciation, forensics, environmental). A natural consequence of a heavy focus on applications is a de-emphasis on fundamental theory and mechanistic studies. Experience, knowledge, and expertise in the field of atomic spectrometry are often lost and not transferred to students or technicians.

Another concern is the potential harm that may arise from the ever-increasing computation power available for data mining, pattern recognition, and chemometrics. These are powerful tools, but there is also a danger of giving users a false impression that training in reading and understanding spectral data is old fashioned and no longer important.

A similar situation involving a lack of knowledge transfer to the next generation was noted about a decade ago in the field of nuclear science and engineering. To combat this problem, the US Department of Energy initiated several university consortia with generous support to ensure that a strong pipeline of new technical talent would be available in the future. I hope that someone with vision and power will see that a similar situation is developing in many other disciplines, including, but not limited to analytical atomic spectrometry, and take action before it's too late.

What are you most excited about?

In short, the joy of working with good people is what excites me most about the spectroscopy field. I also like the intellectual challenge

of solving difficult problems with my expertise. In particular, I like to conduct fundamental studies that explain new experimental observations and also explore novel applications with new tools. I am fortunate enough to continue conducting fundamental research even though my current position is not at a university. How? Well, some applications require fundamental characterization before methods can be formulated – one example is my project exploring the use of LIBS for optical isotopic analysis of uranium. We need fundamental details of the uranium LIBS plasma and an understanding of the behavior of the various uranium emission lines.

In some other situations, fundamental research is performed through collaborations with my friends at universities. For example, my collaborators and I submitted a manuscript in December 2022 on characterizing a plasma-based ambient desorption-ionization source using temporally resolved monochromatic imaging spectrometry. It was a fun project, and the idea of writing this work up for submission developed from a casual chat with Carsten Engelhard, University of Siegen, and Jacob Shelley, Rensselaer Polytechnic Institute, at a conference this past October. The data was not new, but we now have a different and better explanation compared with when we originally collected the results.

Overall, where do we go from here?

Development is highly funding-driven. I can see there will always be a need in analytical atomic spectroscopy for elemental and isotopic analysis. In addition, there will be a demand from users and stakeholders for techniques and instruments that, compared with current tools, are smaller, easier to use, while providing higher sensitivity and faster analysis times. The question is whether there will remain a sufficient supply of well-trained analytical spectroscopists for ongoing development.

George Chan is a Chemist Research Scientist/Engineer at Lawrence Berkeley National Lab, USA

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FEATURE

Ten Year Views: Duncan Graham


Duncan Graham discusses developments in SERS over the past decade, and where he thinks the field will take us next

Reflections on the past decade...

The surface-enhanced Raman scattering (SERS) field has certainly come a long way since PhD student Jim McQuillan reported an enhanced intensity Raman spectrum in 1973. The field really took off in 1977, when two papers attempted to understand the enhancement in the Raman scattering from the roughened metal surfaces, inspiring thousands of subsequent studies.

In 2012, there were approximately 1,250 papers published in the SERS field. Notably, among the total articles published in 2012, only 1.9 percent and 5.5 percent covered medicinal applications and biochemistry, respectively. Fast forward to 2022 and we find that over 2,350 papers were published. We still see that chemistry dominates, but the materials aspect of SERS has dropped to 19 percent. Interestingly, medicinal applications jumped to 2.3 percent and biochemical use of SERS went up to 9 percent. And so I would say the most significant development in the last 10 years is the realization that SERS is useful for biological, biochemical, and medical applications – linking to an increase in portable Raman spectrometers.





“I am most excited about the integration of AI with SERS data. SERS data has got a reputation for being variable – although this can be controlled and minimized. The integration of AI with data processing will advance the presentation and interpretation of data beyond what is currently possible.”

In 2012, there were 50 articles published containing the words “SERS” or “assay,” but, in 2022, there were 108. This increase is driven by the combination of SERS with lateral flow assays. In light of the COVID-19 pandemic, colorimetric lateral flow assays became incredibly important. These assays are simple to convert by adding a Raman reporter and interrogating the lateral flow device with a portable Raman spectrometer. Benchtop Raman spectrometers can also be used to analyze lateral flow strips – although this may not be in the spirit of lateral flow assays, which are designed for point-of-use and rapid response.

I’d also add that there have been significant industrial developments to Raman spectrometers. The high-end microscope systems are highly valuable for research but, in terms of translating this growth of SERS for non-experts, Raman spectrometers need to be made more accessible. Firstly, they need to be within laboratory budget parameters in terms of research; secondly, they must be easy to use with software that doesn’t require interpretation by an expert spectroscopist.

The decade(s) to come...

The SERS field continues to be buoyant and there are a number of ongoing research projects that are extremely interesting. My main concern is that those beyond the spectroscopic community are limited in their awareness of SERS as a technique that can be used when other methods fail to fulfill the required measurement criteria. There are many examples of this in literature, and the concern is whether the end user base is open enough to use SERS to its full potential. We are still without a large-scale SERS application that transforms the end user base.

I am most excited about the integration of AI with SERS data. SERS data has got a reputation for being variable – although this can be controlled and minimized. The integration of AI with data processing will advance the presentation and interpretation of data beyond what is currently possible. Of course, there needs to be caution in terms of overreliance on AI, but steps are being taken by researchers to integrate this capability into the SERS community. Advances in this

area would really help with the reliability and presentation of data for non-experts of SERS.

In the future, I hope we will see SERS applied in several new and unique ways – such as non-destructive, real-time analysis of multiple species simultaneously at ultra sensitive concentrations and in a quantitative manner. If this can be achieved, we’ll see greater advances in SERS from the research laboratories into the hands of the end user – ultimately benefiting society. SERS is finally being acknowledged as a promising technique – one that is going to deliver on several meaningful applications. But we need to continue with the strong research base and the integration of researchers working with industry partners to overcome the barriers that are in place for translating research into commercial reality. The pandemic has proved that working collaboratively, rather than competitively, provides results. Collaboration will benefit the whole spectroscopic SERS community – as well those beyond.

Duncan Graham is the Associate Principal and Executive Dean of the Faculty of Science, University of Strathclyde, UK

FEATURE

Ten Year Views: With Vassilia Zorba

Lasers, plasmas, Mars, and more lasers...



In your opinion, what has been the most significant development in spectroscopy over the past 10 years?

It's difficult to pin down just one, as there have been so many great developments during that time. There have been some interesting advancements in nonlinear optics and their integration in the field of analytical chemistry. Specifically, the use of nonlinear ultrafast laser-matter interactions in the laser plasma formation regime, which has been instrumental in addressing issues like improving spatial and depth resolution. We've also made advances in our ability to propagate pulsed laser beams and deliver energy at long distances. With this development, we're now able to suppress diffraction, which allows us to concentrate pulsed laser energy to a target at a remote location. This discovery has been a critical component in our ability to generate plasmas for remote spectroscopy applications.

Another pivotal moment has to be the ChemCam mission to Mars. This was a very challenging problem to tackle and ChemCam's success has been extremely beneficial for the field of laser-induced breakdown spectroscopy (LIBS). This tremendous milestone has demonstrated the amazing possibilities of LIBS as well as introducing its capabilities to a wider audience. We've seen the flexibility of the technique and what can be achieved – which has encouraged many researchers to use LIBS in their work. Seeing such advancement in technology is always an exciting moment.

What are some of the key applications for lasers?

Energy conversion and storage are significant application areas – laser spectroscopy allows us to understand variations of chemical composition in solar cells and Li-ion batteries. Researchers have

also been looking at biomedical imaging with laser spectroscopy, including LIBS.

Personally, I favor the recent direction towards all-optical isotopic techniques, which unlock completely different types of applications. The development of the laser ablation molecular isotopic spectrometry (LAMIS) technique in particular has opened up new horizons in terms of what is possible for many different areas in biomedical and environmental research. When it comes to nuclear security, the ability to detect isotopes optically is incredibly important for measuring the levels of enrichment in nuclear safeguards and forensics. Isotope ratio mass spectrometry has shown the tremendous information we can gather regarding when or where something was made – based on high precision measurements of isotopic ratios. Transitioning even a few of these isotopic ratio measurement capabilities from mass spectrometry

to laser spectroscopy can be a real game-changer for rapid analysis in the field. It all comes down to the level of precision; for some applications, laser spectroscopy can already do very well – for others requiring very high levels of precision we're not quite there yet, but we're getting closer!

What about your own work with next-gen laser tools?

In the past, I worked on the utilization of ultrafast LIBS to analyze lithium ion batteries with high resolution. This involved using three-dimensional imaging to look at the composition of minor elements in complex matrices. Additionally, by looking at interfacial layers as thin as 50 to 100 nanometers, we can understand how chemical reactions during battery charging can affect the macroscale battery performance after electrochemical cycling.

More recently, I've been looking into applications in nuclear security and nonproliferation. By using ultra-fast laser tools and advanced optics, we can propagate a pulsed laser beam over long distances for remote sensing from solids. There are multiple forms of interesting spectroscopic information we are only now able to unveil as some of the technology components are becoming more mature. A lot of work goes into manipulating beam propagation and phase wavefront – for example, using laser filaments or orbital angular momentum beams to deliver a high amount of energy across a remote distance. The pulsed laser energy must be high enough to form a plasma from a solid sample so we can extract elemental and isotopic information.

You mentioned lithium ion batteries – how can analytical science help us here?

In the semiconductor industry, we know that there is very tight control in standardization of the process – for example, fabrication is performed under clean room conditions. However, this is not the case for battery manufacturing – which means that batteries can often work successfully despite the presence of impurities or compositional variations.

But when it comes to large format applications, such as electric vehicles, we need to better understand the composition of raw materials to be able to control the macroscale battery performance. Once you start charging a battery, electrochemical reactions take place which adds a layer of complexities. Understanding composition and mapping variations of composition as a function of space and depth can give electrochemists clues to making better batteries. This includes battery components such as anodes, cathodes, solid state electrolytes, and interfacial layers formed on battery electrodes.

What is most exciting to you about the future of spectroscopy?

A new concept that has been introduced in the laser-metal interaction community, which is called cold ablation or ablation cooling. Thanks to tremendous developments in laser technology, we have the capability to produce gigahertz (GHz) bursts of femtosecond laser pulses – these are nanosecond-spaced series of pulses of femtosecond duration. Recent research looked into the mechanisms of GHz burst ablation with femtosecond pulses for the first time, and the results showed significant differences to traditional

femtosecond plasmas – both in terms of expansion of the ablation ejecta and what we do on the surface. I think this is a very exciting direction to go into – and it offers possibilities for improving our spatial and depth resolution even more as well as improving our analytical performance as a whole.

What would you personally like to achieve in the next 10 years?

I have two main goals. The first is to fuse advanced optics and nonlinear concepts with analytical spectroscopy to improve current capabilities in cross cutting applications. The second involves training the next generation of scientists to drive further progress in the spectroscopy field. Specifically, I want to make the field more appealing for students by giving them a taste of the possibilities within spectroscopy.

What advice do you have for someone who is new to the field of analytical science?

Perseverance is the number one thing to learn. It's also useful to keep an open mind about learning and fusing different concepts – even those from other disciplines. Research is becoming more interdisciplinary, and by incorporating a diversity of ideas and principles from chemistry, physics, and engineering, you could unlock a multitude of possibilities. Overall, being prepared to work hard and not being afraid to expand your scientific horizons will help you advance in your career and contribute to the field.

Vassilia Zorba is Group Leader, Lawrence Berkeley National Laboratory, Berkeley, California, USA.

FEATURE

Lighting Up Archaeological Science

Rachel Popelka-Filcoff explains how she's developing novel methods and incorporating spectroscopic technology from various industries to analyze Indigenous Australian rock art and pigments

What sparked your interest in science and analytical chemistry in particular?

I've always been interested in natural materials, ancient cultures, and archaeology, and, as a high schooler, wondered how I could use analytical science to understand the past. Mr Tony Kardis, my chemistry teacher in high school, introduced me to the world of spectroscopy by demonstrating the changes in electronic state in gasses and how to use a diffraction grating to view the atomic spectra. He continued to be my mentor and advisor as I worked on independent research projects analyzing historic ceramics from the 1904 St Louis World's Fair. From this point, I attended several local and state science fairs, and the International Science and Engineering Fair, and the rest, as they say, is history.

How did you get into archaeological science?

The intersection of physical sciences and social sciences is highly interesting to me and archaeological science naturally expands the frontiers and benefits of both. In my undergraduate and graduate



degrees, I studied analytical chemistry and spectroscopy, as well as field archaeology in several locations around the world, which ultimately led to a career in analytical chemistry-based archaeological science. With both field and lab experience, I'm fortunate to work across both disciplines and I'm very grateful for all the opportunities, supervisors, and interdisciplinary projects that have supported my career thus far.

What are the main challenges for analytical scientists working in the archaeological space?

Objects and artifacts are often looked at in isolation – especially if they're based in a museum or collection site outside of the excavation. However, when we examine cultural heritage items, we analyze at a microscopic level while also looking at the entire object and where it fits in the cultural landscape. Our archaeological science lab group at the University of Melbourne also explores why each material might have been used and where they were sourced. Ultimately, these cultural artifacts are often composed of both inorganic and organic compounds where several different types may interact. Therefore, pigments are often layered systems that have different interactions with various parts of the electromagnetic spectrum.

Additionally, most communities, traditional owners, and curators generally prefer that analysis is non-destructive. Spectroscopic methods are often advantageous here due to the non-destructive properties of light. However, sometimes getting the object to fit in

a microscope or sample holder can be challenging, or impossible in some cases, due to its size or analysis permissions. We often spend a fair amount of time pondering if studying small samples accurately reflect the whole material, especially when dealing with complex mixtures. Our experimental focus is on sampling, data analysis, and subsequent statistical analysis. Another key challenge revolves around finding suitable reference materials that effectively model cultural or archaeological materials. Ultimately, the spectroscopic data obtained often needs to be integrated into a larger study and interpreted as part of a bigger cultural or archaeological question.

You have previously adapted techniques from other fields (such as mining) for archaeological science; what is your approach to finding innovative solutions to difficult problems?

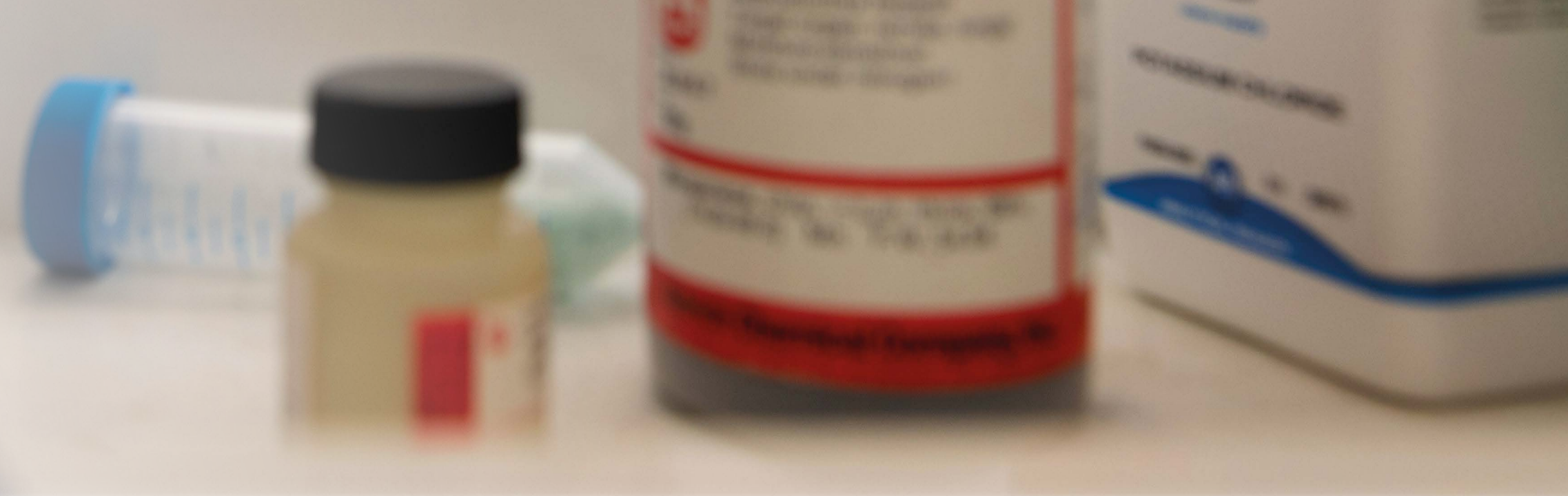
Our lab focuses on multidisciplinary approaches to analyze cultural materials, artifacts, and landscapes, which often provides extraordinary views into past cultures, current societal understanding, and future insights. Alongside analyzing ceramics and glass, for the past 20 years I've worked with cultural pigments from Australia and North and South America – primarily iron-based ochre pigments used by Indigenous people around the world. Natural mineral-based pigments are inherently complex mixtures with interesting colors and physical properties – and an ability to last for thousands of years, so they often demand innovative solutions. Over the years, our research has led to several novel methods in archaeological science.

For example, we were the first to apply synchrotron X-ray fluorescence microscopy analysis to pigments on Indigenous Australian objects – drawing on previous work on the XFM beamline at the Australian Synchrotron on canvas painting and work in art conservation. Our current research project on Australian ochre demonstrates that we can use soil bacteria metagenomics to distinguish ochre sources, which has evolved from studies in soil forensics.

In this way, we're not only expanding the use of current novel technology for archaeological research, but also pushing boundaries for methods and developments in their original application and in multidisciplinary areas. Innovation is key in driving these approaches – across the technology, data modeling, and spectroscopic instruments. It's also important to have a broader view of big research questions while exploring nuances of particular research projects.

Is there anything missing from the analytical toolbox that would help the archaeology field?

I've often joked with colleagues that it would be terrific to have a magic gray box that we point at samples to give quickfire answers – similar to what is dramatized in forensic TV shows. However, we could be closer to this vision than we thought possible a few years ago. With further developments in sensor and nano technologies, we could see some exciting new applications in archaeological science.



“The most exciting part of my work falls in the discovery of connections between cultural and analytical aspects of these pigments.”

What other big trends in spectroscopy have you got your eye on?

Technological advances are continuously making smaller, portable, low-power, and high-resolution instruments for successful use in remote environments – this is key to our discoveries! For instance, we’ve analyzed rock art in remote locations that are often only accessible with four-wheel drive vehicles or by helicopter. Many lab-based technologies require stability, but with adaptations from the mining industry, for instance, we have more rugged instruments to withstand transport in pelican cases to sites.

What are you currently working on? And what gets you out of bed in the morning?

I’m involved in several major research projects surrounding the analysis of ochre and related pigments and larger archaeological science questions. One of which is funded by the Australian Research Council entitled “Ochre Archaeomicrobiology: A New Tool for Understanding Aboriginal Exchange,” which involves working with four Aboriginal Australian community research partners to understand if the ochre characterisation “fingerprint”

can change due to mixing, cultural use and environmental site changes.

Several spectroscopic methods are in use here, including XANES, XRD, and reflectance light spectroscopy, as well as metagenomic characterization of the ochre microbes. We’re in the final year of this project and expect several exciting manuscripts to be released shortly by students and project collaborators.

Another aspect of my work revolves around the analysis of Indigenous rock art – again, with traditional owner partnerships, mainly in Western Australia. These collaborations have led to portable analysis of rock art in various remote locations – applying spectroscopic technologies to probe complex and long standing pigments.

The most exciting part of my work falls in the discovery of connections between cultural and analytical aspects of these pigments. I am expanding on this research while working on a larger program in research and education for Archaeological Science at the University of Melbourne. The vision is to expand laboratories for Australian research studies, as well as those with international reach.

What advice can you offer those who wish to follow in your footsteps?

Archaeological science as a field continues to grow, especially from an analytical chemist’s perspective. Students and researchers with an analytical background are well placed to work within the field. Our archaeological history is an important aspect to understanding human past, present, and future – not to mention all the exciting projects that are currently underway to keep you interested!

There are several pathways into the field that might not follow the “traditional” academic approach, allowing students to direct their own way into the field based on their interests and career goals. With several academic programs across the world, including the University of Melbourne, offering research in archaeological science, there’s certainly something for everyone to start their analytical archaeological career.

Professor Rachel Popelka-Filcoff is Rock Art Australia Minderoo Chair in Archaeological Science, in the School of Geography, Earth and Atmospheric Sciences at The University of Melbourne, Australia

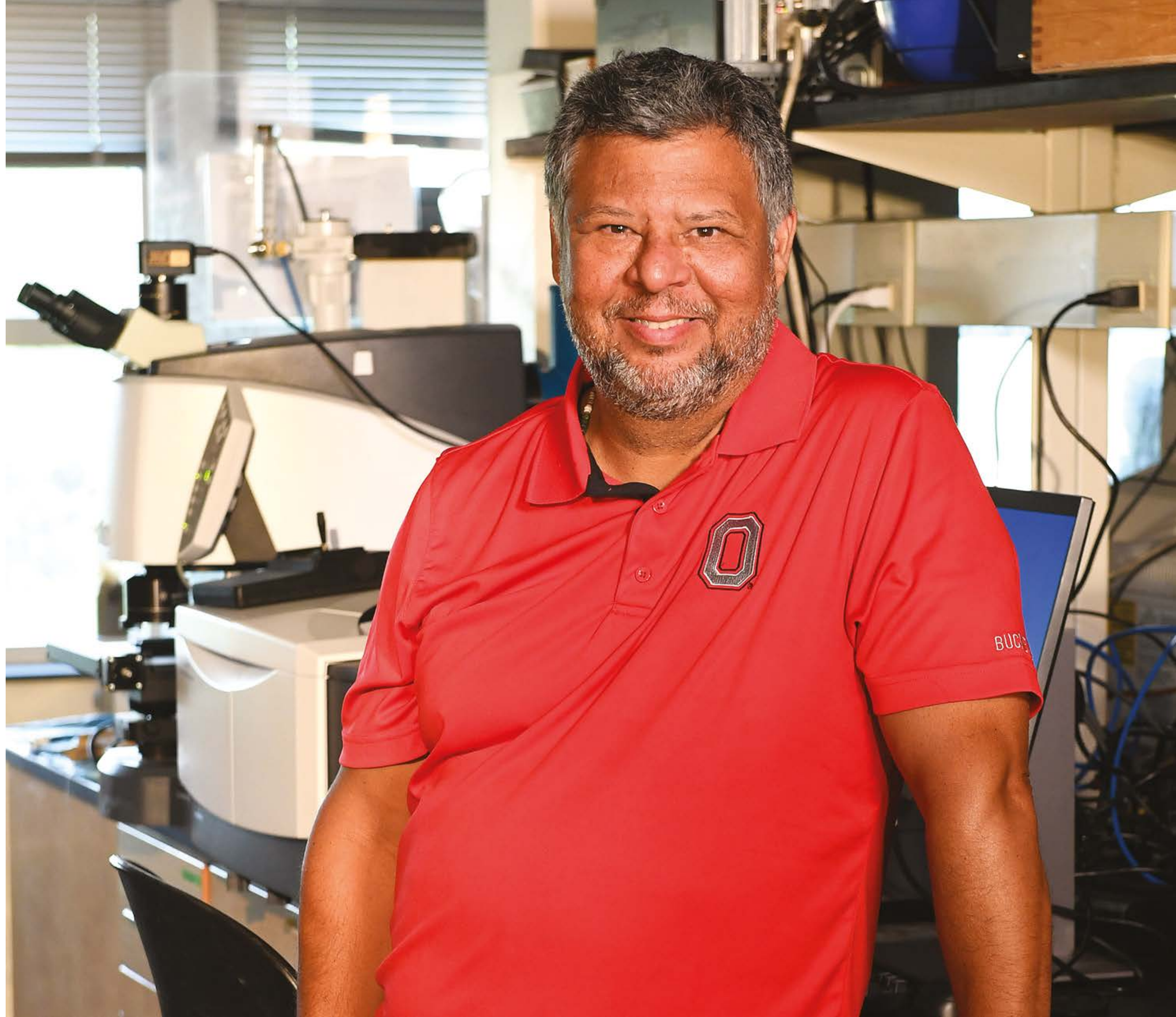
FEATURE

Picking Out the Bad Apples

Luis Rodriguez-Saona of Ohio State University discusses the spectroscopic techniques at the forefront of food analysis – and the hurdles involved in translating new technology from initial development through to application

What are your main spectroscopy research interests?

I apply novel analytical technologies to agricultural product testing, with a focus on developing portable and handheld sensors based on vibrational (infrared and Raman) spectroscopy to support quality, safety, and nutritional monitoring of food and agricultural products. In collaboration with leading optical sensing companies, my molecular vibrational lab has combined spectroscopy with chemometrics for food safety and quality assurance. We have also developed predictive models for the rapid detection, identification, and classification of chemical and microbial contaminants as well as food components with biological activity.



“The miniaturization of spectrometers – particularly using NIR spectroscopy – has opened doors for field analysis and allowed us to make measurements in-situ without transporting samples to the lab.”

What are the main applications – and specific advantages – of vibrational spectroscopy in food analysis?

FT-NIR and mid-IR spectroscopy are mainly used for the rapid and non-destructive detection of major components in food – including moisture, protein, fat, and carbohydrates. Dairy, grains, beverage, and meat sectors have all embraced the technology. Vibrational spectroscopy provides spectral information from diverse functional groups present in different samples, allowing us to obtain unique profiles from food analytes that can be used to quantitate target molecules or identify any potential tampering contaminants. NIR has been a benchmark for developing predictive models that estimate major component levels. While mid-IR provides higher fingerprinting capabilities and detection levels to screen for contaminants and adulteration, NIR can deeply penetrate materials – allowing the analysis of intact and non-homogeneous material. Mid-IR attenuated total reflectance (ATR) can only penetrate a few microns deep and requires homogenization of the sample.

Could you tell us a little about the use of optical sensor technology for food analysis?

The miniaturization of spectrometers – particularly using NIR spectroscopy – has opened doors for field analysis and allowed us to make measurements in-situ without transporting samples to the lab. There is now a broader range of wavelength selection technology

employed to disperse polychromatic light, such as MEMS, diffraction grating, volume phase holographic grating, LVF, the Fabry-Pérot interferometer and detectors, such as CCDs or InGaAs. Our work uses the technology to collect spectral information in the 1100 to 2500 nm range so we can access unique information from combination modes that appear in polyatomic molecules. We have explored the use of ATR systems operating in the mid-IR region for quality assurance, phenotyping of breeding materials, and identifying food contaminants.

Raman spectroscopy has revolutionized handheld systems and given access to unique fingerprinting capabilities for remote sensing. We have been working on applications of different systems equipped with excitation lasers in the NIR and visible regions. Raman equipped with a 1064 nm excitation laser effectively limits background fluorescence but weakens the energy for molecular vibrations of biological samples. Our research on SERS has shown limited signal by employing a 1064 nm excitation laser as opposed to a laser in the visible region.

What are the main analytical challenges that manufacturers face in the food and beverage industry?

The complex nature of foods often makes it difficult for the technology to be implemented in some application areas. In the fruit and beverage sector, the high content of water is a challenge because of its strong dipole nature. The water signal masks important features

in the spectrum – making it difficult to develop quantitative and classification algorithms.

The development of robust predictive models using chemometrics is another challenge. Models need to capture the variance of the samples and often require a large data set to provide robustness. Further, models need to be independently validated to determine their predictive ability. The field of chemometrics and machine learning is advancing at a fast pace, which will help us extract information from convoluted spectral data and create powerful algorithms that obtain maximum information from the raw data.

What are the most cutting-edge techniques in food analysis?

I’ve already name dropped several exciting technologies in this space! NIR handheld technology is advancing at a fast pace – and using micro-electromechanical systems – spectra collection can be widened to the short wave IR and help develop predictive models. Surface enhanced Raman spectroscopy (SERS) can improve detection limits into the ppb level; the Raman signal of a target analyte can be enhanced when it is in proximity to the SERS substrate – depending on the shape, size, and orientation of the nanoparticles. And there is exciting research on functionalized SERS substrates with unique recognition ligands and encapsulation. Nevertheless, improvements in SERS substrates are still required for consistent detection of analytes in complex environments. XRF is also an interesting technology for in-field elemental analysis – and detection limits are improving.

APPLICATION NOTE

The Role of NIR Spectroscopy for Food Analysis

Exciting developments in food analysis! Portable NIR spectroscopy offers non-destructive, rapid analysis of food composition and functionality.

The potential applications of NIR infrared spectroscopy in the food industry have been widely documented by numerous scientific publications for several years. The advent of portable instruments such as Hamamatsu Photonics' compact MEMS-FTIR Engine is now moving the analysis from lab to field, thus drastically reducing the wait for results. Most notably, this hardware miniaturization driven by Hamamatsu's MEMS technology happens without compromising sensitivity or resolution.

New computational techniques are continuously being developed to analyze and compare the absorption spectra and estimate the content of specific chemical compounds in food. These methods are making the technology increasingly accessible to non-technical users across the industry.

FTIR spectroscopy provides higher throughput and better sensitivity

There are two main methods for analyzing the absorption spectrum of organic materials in the NIR spectrum. The first method is diode-array-based spectroscopy. This technique uses dispersive grating to separate the light reflected or transmitted from the sample into its wavelength

components. Each component is then focused on a different pixel of a linear detector array. This method is considerably fast and can be used for real-time measurements. However, the light throughput of the diode-array spectrometer is inversely proportional to its spectral resolution, which limits its effectiveness. Additionally, the high cost of linear arrays sensitive in the near-infrared region may limit their adoption for certain applications, especially in agriculture and food.

The second method for obtaining an absorption spectrum is Fourier transform interferometry. In this method, the incoming light is split into two paths, with one directed toward a fixed mirror and the other toward a movable mirror. When these paths are recombined, an interferogram is obtained. By performing a Fourier transform of this interferogram, the spectrum of the incoming light can be obtained, and with proper calibration, the absorption spectrum of the sample can be determined. This technique measures all wavelengths simultaneously, providing better throughput and higher sensitivity without compromising spectral resolution (usually referred to as " Fellgett's advantage"). This technique uses only a single NIR photodetector instead of an array, keeping the cost low.

Portable FTIR analyzers can be a valuable tool to address many vital challenges in the food industry. For example, they can help improving crop yield thus providing an alternative to deforestation when facing an increased food demand. Integrating these technologies into farming can limit water waste when optimizing irrigation and limiting food waste across the supply chain. Finally, FTIR analyzers can contribute to the improvement of our food quality making it safer and healthier for us and for all the animals depending on us.

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SITTING DOWN WITH

Six Decades of Illumination

Sitting Down With... Richard N. Zare, Professor of Natural Science, Department of Chemistry, Stanford University, USA

How did your fascination with chemistry begin?

As a child, I was full of questions – asking why things were the way they were. In kindergarten, I remember asking my teacher what holds up the stars, and I was frustrated because she didn't give me a satisfactory explanation. I knew that light bulbs were in the ceiling, but I didn't understand how the lights from the stars were held in the sky.

My father failed chemistry in graduate school and I think that may be one reason why I gravitated towards it, despite his protests. In fact, my parents said that it would only lead to unhappiness, but I was enamored by the chemistry books lying around the house – sneaking them into my bedroom at night and reading under the covers with a flashlight.

They wouldn't let me have a chemistry set, so I went to the pharmacy (which these days would be similar to a drugstore) and asked for powdered charcoal, potassium nitrate, and sulfur. The pharmacist asked if I knew what I was doing, to which I said yes – despite setting the basement of my house on fire while meddling with magnesium in the upcoming months and years. But I loved playing around with chemistry and learning how and why reactions occurred.

What was it about light in particular that excited you?

When I was studying chemistry and physics at Harvard as an undergrad, I was frustrated because I couldn't understand light. Seeing is believing and I didn't understand because I couldn't see what was happening. As time went on, people would argue about whether light was a particle or a wave – now we know it's both (sort of), but this wasn't fundamental knowledge when I was starting out.

I still don't fully understand how light works, but I have had an increased appreciation and understanding since I was a boy. I think my drive to find an answer has continued throughout my career, and this has pushed me towards optics; in one sense, I wanted to solve the crux of the problem.

You received your PhD in 1964 and are still full time faculty. Have you seen much change as a researcher and professor over the past 60 years?

I think students are just as smart and creative today as they've always been. However, distractions – television, social media, and so on – have negatively impacted people's attention span. Everyone's looking for sound bites of information, as opposed to spending a reasonable amount of time researching a topic. There also isn't a lot of interest in math anymore.



“With LIF, we became the first people to see a single molecule in a solution at room temperature. This was a great achievement that I don’t believe got enough promotion at the time – but it was a breakthrough for the field nonetheless. I knew the future possibilities from LIF were going to be great.”

As a whole, I’d say I have seen surprisingly little change. That being said, I’ve been very lucky during my career to work with some wonderful people – both advisors and students.

You’ve collaborated on various projects over the years – can you explore a few of the outcomes?

I’m a big advocate for multidisciplinary work – bringing people together with different expertise from different fields is where the biggest breakthroughs occur. In these situations, you’re able to do things together that would be impossible separately – and everybody wins.

For example, I’ve worked with a medical doctor in China on a health related research project. The regulations for collecting data samples are much more relaxed in China than they are here in the US, so this collaboration granted me access to many different types of medical samples that I wouldn’t have had in solo projects.

I’ve also recently been in collaboration with Basheer Chanbasha, a professor of chemistry at King Fahd University of Petroleum and Minerals in Saudi Arabia, to explore nitrogen fixation. We’re actually able to take nitrogen from the air and turn it into ammonia or urea using water microdroplets striking a catalyst. The outcomes

of this are very exciting. There is a long way to go before this might be commercialized, but if we could push this process, we could be looking at something very different to the Haber-Bosch process for producing ammonia.

Please tell us about laser induced fluorescence – and what you accomplished...

When I was a graduate student, I worked with Dudley Herschbach while he was pioneering crossed molecular beams. The experiments looked particularly hard, so I got involved with the theory of molecules – using a mercury lamp to excite vapors of the iodine molecule and make I₂ fluoresce.

The laser was discovered in my lifetime and people didn’t know what to do with it. I decided to use it as a source to excite fluorescence of molecules. Some rather influential people at the time told me to forget it, but I continued to push further because I knew there was potential.

With more work I discovered that you can capture fluorescence with a photodetector by exciting a sample with a laser. This optical spectroscopic technique is now known as laser induced fluorescence

(LIF), and is regularly used to analyze gasses, liquids, and solids.

With LIF, we became the first people to see a single molecule in a solution at room temperature. This was a great achievement that I don’t believe got enough promotion at the time – but it was a breakthrough for the field nonetheless. I knew the future possibilities from LIF were going to be great.

What motivates you – and what keeps you on track?

I think what initially drove me was an attempt to please my father and show my worth as a scientist. Though as I’ve worked my way through the field, I think it is a combination of curiosity and the pleasure I receive in sharing new knowledge with others – I believe a lot of others in this line of work will share this sentiment.

Communicating this excitement with others and learning to look at the world differently is an extraordinary thing. In a sense, I think science and art are much more related than people often give credit. As a painter, you’d be frustrated if no one else saw your work, regardless of how much you enjoy creating art. Similarly, when I discover something about nature, I want to share this information with others. For me, it’s about being curious and interacting with others to share exciting knowledge.

SPOTLIGHT ON . . .

Technology



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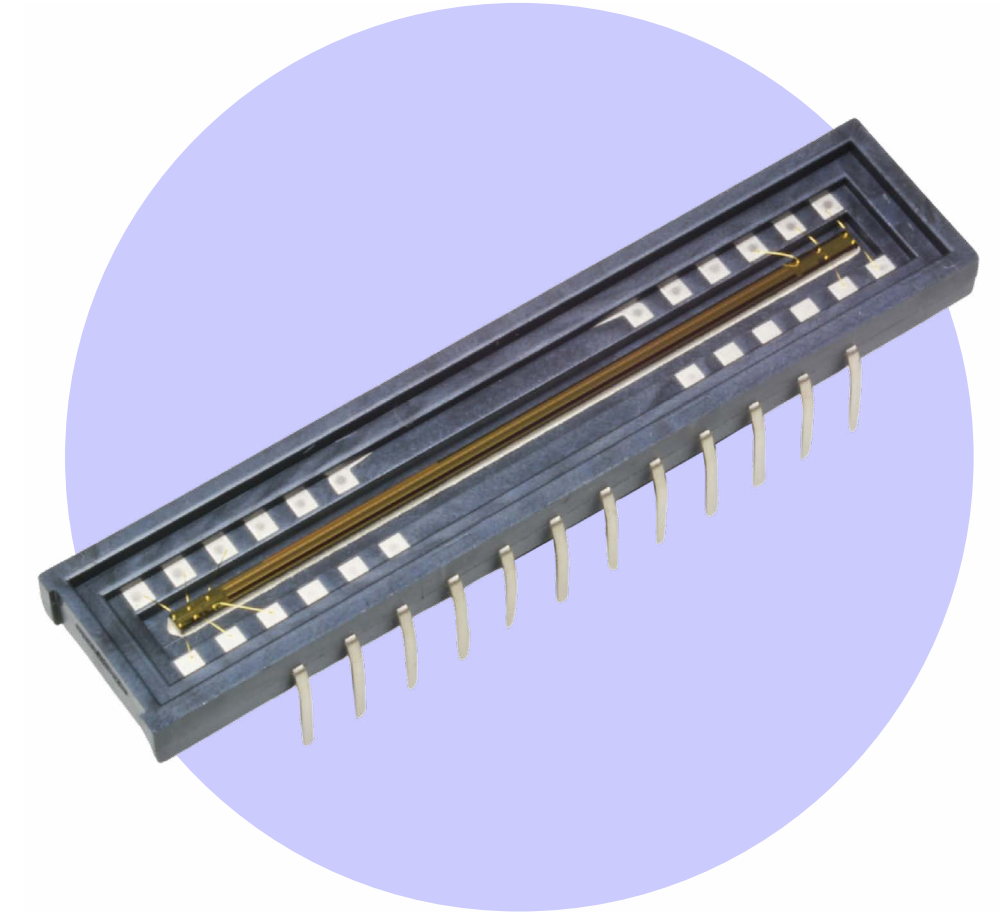
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