AUGUST 2016 # 43

the Analytical Scientist

Upfront
NASA's flying lab takes PTR-MS on a trip to Asia
13

Awe & Wonder
DNA origami replicates van Gogh's Starry Night
36 – 41

Health & Security
Dandelion clocks, timeless HPLC and... floating carrots
46 – 49

Sitting Down With
X-Ray visionary and art lover Koen Janssens
50 – 51

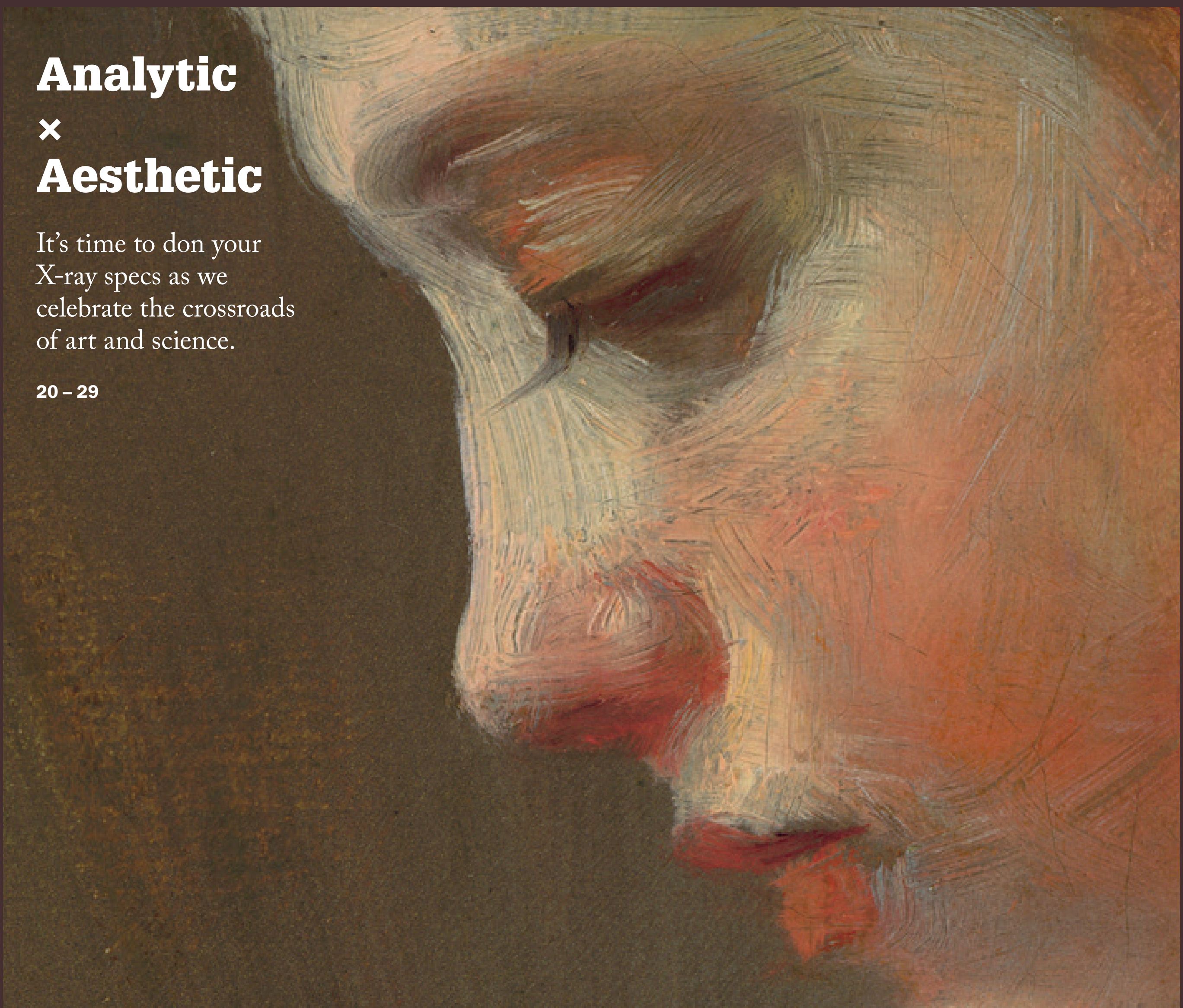


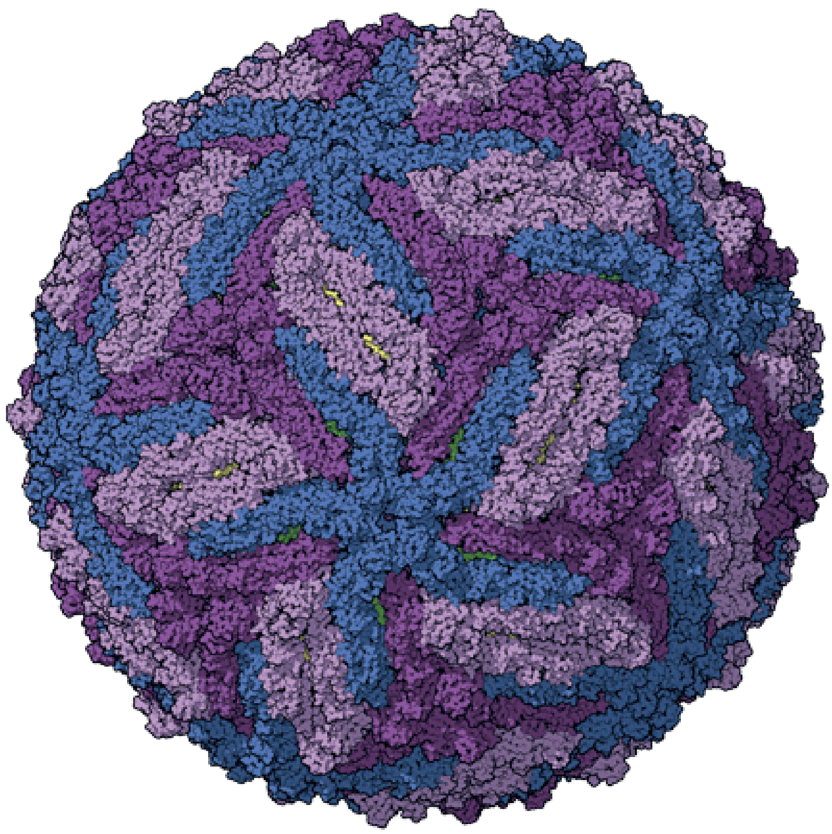
Image of the Month

Big Love

A point-of-care immunoassay device, developed by AGPlus Diagnostics and The Zoological Society of London, was used to keep track of Asian elephant Karishma's progesterone levels prior to the birth of her calf, Elizabeth, as part of a trial at Whipsnade Zoo, Bedfordshire, UK. If successful (and Elizabeth is partial proof of that) there's a chance it will be rolled out as a handheld diagnostic system to help develop on-site animal care. Handy if there's an elephant in the room…

Would you like your photo featured in Image of the Month?
Send it to rich.whitworth@texerepublishing.com

Contents

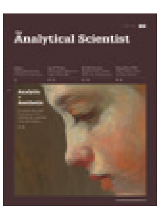


10

03 **Image of the Month**

09 **Editorial**
The Selfless Scientist,
by Rich Whitworth

On The Cover



Close up of Jean-Honoré Fragonard's Young Girl Reading.

Upfront

10 Putting Zika to the Test

12 Adze Marks the Spot

13 Blue Sky Science

14 A Sense of Security

15 Great SciX-pectations Part II

16 Sample Prep, Screening and Software in the Cloud

the Analytical Scientist

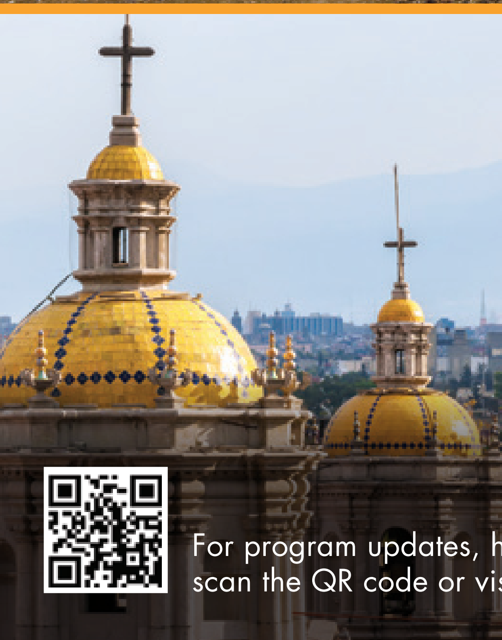
ISSUE 43 - AUGUST 2016

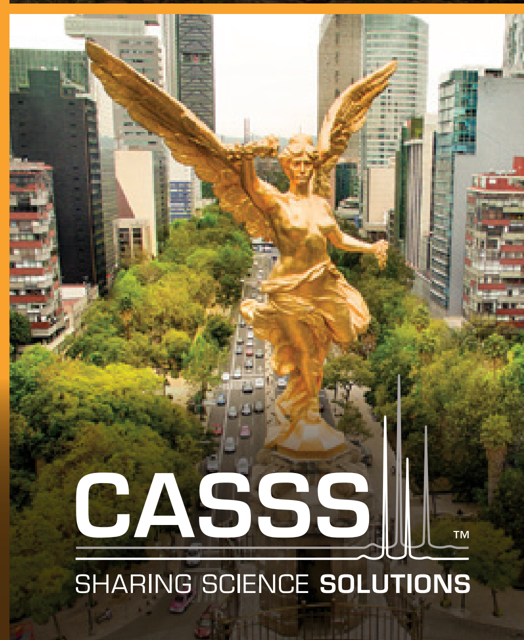
Editor - Rich Whitworth
rich.whitworth@texerepublishing.com
Associate Editor - Joanna Cummings
joanna.cummings@texerepublishing.com
Scientific Director - Frank van Geel
frank.vangeel@texerepublishing.com
Editorial Director - Fedra Pavlou
fedra.pavlou@texerepublishing.com
Publishing Director - Lee Noyes
lee.noyes@texerepublishing.com
Sales Manager - Chris Joinson
chris.joinson@texerepublishing.com
Head of Design - Marc Bird
marc.bird@texerepublishing.com
Designer - Emily Strefford-Johnson
emily.johnson@texerepublishing.com
Junior Designer - Michael McCue
mike.mccue@texerepublishing.com
Digital Team Lead - David Roberts
david.roberts@texerepublishing.com
Digital Producer Web/Email - Peter Bartley
peter.bartley@texerepublishing.com
Digital Producer Web/App - Abygail Bradley
abygail.bradley@texerepublishing.com
Digital Content Assistant - Lauren Torr
lauren.torr@texerepublishing.com
Audience Insight Manager - Tracey Nicholls
tracey.nicholls@texerepublishing.com
Traffic and Audience Associate - Lindsey Vickers
lindsey.vickers@texerepublishing.com
Traffic and Audience Associate - Jody Fryett
jody.fryett@texerepublishing.com
Apprentice, Social Media / Analytics - Ben Holah
ben.holah@texerepublishing.com
Events and Office Administrator - Alice Daniels-Wright
alice.danielswright@texerepublishing.com
Financial Controller - Phil Dale
phil.dale@texerepublishing.com
Chief Executive Officer - Andy Davies
andy.davies@texerepublishing.com
Chief Operating Officer - Tracey Peers
tracey.peers@texerepublishing.com

Change of address:
tracey.nicholls@texerepublishing.com
Tracey Nicholls, The Analytical Scientist,
Texere Publishing Ltd, Haig House, Haig Road,
Knutsford, Cheshire, WA16 8DX, UK

General enquiries:
www.texerepublishing.com
info@texerepublishing.com
+44 (0) 1565 745200
sales@texerepublishing.com

Distribution:
The Analytical Scientist (ISSN 2051-4077), is published monthly by Texere Publishing Ltd and is distributed in the USA by UKP Worldwide, 1637 Stelton Road B2, Piscataway, NJ 08854.
Periodicals Postage Paid at Piscataway, NJ and additional mailing offices
POSTMASTER: Send US address changes to The Analytical Scientist, Texere Publishing Ltd, C/o 1637 Stelton Road B2, Piscataway NJ 08854
Single copy sales £15 (plus postage, cost available on request tracey.nicholls@texerepublishing.com)
Annual subscription for non-qualified recipients £110
Reprints & Permissions – tracey.nicholls@texerepublishing.com





Analytic x Aesthetic

22 **What Lies Beneath**
What secrets lurk under the uppermost paint layers of famous masterpieces? Five experts reveal all...

30 **Air & Water**
From galactic dark matter detectors to seaside spectroscopy, analytical scientists know no bounds.

36 **Awe & Wonder**
Marvel at multi-colored lasers, super-cold condensates and DNA origami.

43 **Food & Drink**
Whether testing tomatoes or assessing wine spoilage, analytical science is key to satisfied – and safe – consumers.

46 **Health & Security**
From astronaut metabolomics to protein purification, separation science is everywhere.

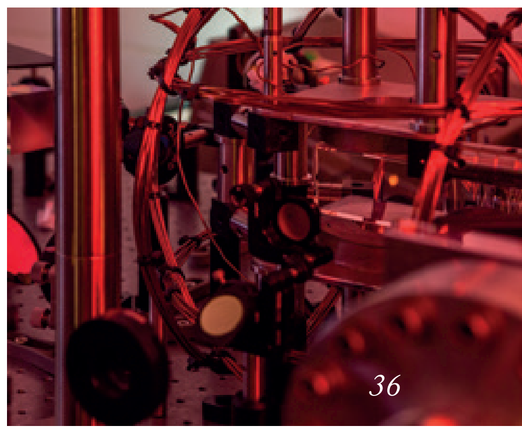
Reports

17 Cheers to UHPLC, by Rainer Bauder

18 VUV En Vogue, with Kevin Schug, Nicholas Snow, and Luigi Mondello

Sitting Down With

50 **Koen Janssens**, Full Professor of General and Analytical Chemistry, University of Antwerp, Belgium.



The Selfless Scientist

How do you feel in a 'supporting role'? If you're an analytical specialist – whether chromatographer, spectrometrist or chemometrician – I salute you!

Koen Janssens' closing remark on page 51 – "...working hard to achieve other people's goals" – struck a chord with me; it's a sentiment that succinctly defines the role of the analytical sciences. In isolation, it could be read in two ways. Koen is either disillusioned by being in the backseat – the glass is half empty – or he is happy to be an integral part of something bigger. When you read the whole interview, I am sure you will agree that Koen's glass is half full – if not brimming. After all, he clearly loves what he does.

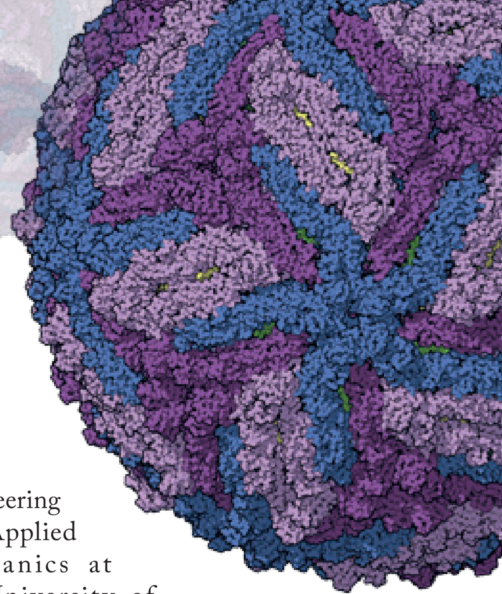
And yet, playing a 'supporting role,' however vital, can sometimes have its disadvantages. When it comes to receiving funding or hitting the headlines, analytical science is not always in pole position – which is why I am always thrilled to learn of analytical chemists winning large research grants. We covered Peter Schoenmakers' €2.5 million from the European Research Council (ERC) back in May – but we must also offer a belated congratulations to VUB's Gert Desmet, who received a similarly big slice of funding. Both Peter and Gert are using the funds to tackle intractable challenges in separation sciences – in particular, addressing the dizzying complexity of biological samples. Having spoken to both Gert and Peter at Riva 2016, it's clear that such funding not only recognizes the individuals and groups receiving them, but also highlights the increasing importance of analytical chemistry – even if it is 'just' a supporting role. Look out for a feature on this topic in the near future.

The reality is, without analytical support, science is blind – much like art-historians, who could never know the secrets that "lie beneath" the surface, if it were not for dedicated analytical scientists both developing advanced techniques and operating them with great skill and care (see pages 20–29).

The best thing about being an analytical scientist? New challenges – or rather opportunities – are constantly coming to light either because innovative instrumentation allows you to do something novel or because a new industry demands your attention.

To this latter point, The Analytical Scientist is partnering with the Cannabis Science Conference (www.cannabisscienceconference.com) to produce a special supplement – The Cannabis Scientist – as well as its official guide. Why? Because the nascent medicinal cannabis industry is in serious need of analytical support. Canncon, the NPO behind the October 2016 conference, was founded principally to unite the two communities – and we want to help. Many of you (especially those in the established food and pharma fields) have a great deal of relevant experience to share. Chromatographers, spectrometrists, chemometricians, lend me your ears (and expertise)!

Rich Whitworth
Editor



Upfront

Reporting on research, personalities, policies and partnerships that are shaping analytical science.

We welcome information on interesting collaborations or research that has really caught your eye, in a good or bad way. Email: rich.whitworth@texerepublishing.com

Putting Zika to the Test

Promising low-cost point-of-care ZIKV diagnostic works without electricity

A research group from the University of Pennsylvania have developed a portable, low-cost and easy-to-use test that could help with diagnosis of the Zika virus (ZIKV). The Micro and Nano Fluidics laboratory (http://bau.seas.upenn.edu/) has made significant advances in point-of-care (POC) diagnostics, but it was the recent outbreak of ZIKV in the Americas that kickstarted the current research.

"When we learned about the virus and its devastating consequences for pregnant women and their fetuses, as well as the lack of appropriate diagnostic tools, we recognized that we were in a position to provide an appropriate solution," says Changchun Liu, Research Assistant Professor (Department of Mechanical Engineering and Applied Mechanics at the University of Pennsylvania's School of Engineering and Applied Science).

RT-PCR (reverse transcription polymerase chain reaction) assays – the only laboratory-based molecular tests approved by the Centers for Disease Control and Prevention (CDC) for use on an emergency basis – require a well-trained technician and expensive instrumentation, conditions that are not optimal for POC diagnostic applications. Therefore, there is a strong need for a new diagnostic technique.

"Generally, lateral flow tests suffer from low sensitivity. They also suffer from low specificity, since antibodies to ZIKV cross-react with other flaviviruses prevalent in Zika-endemic

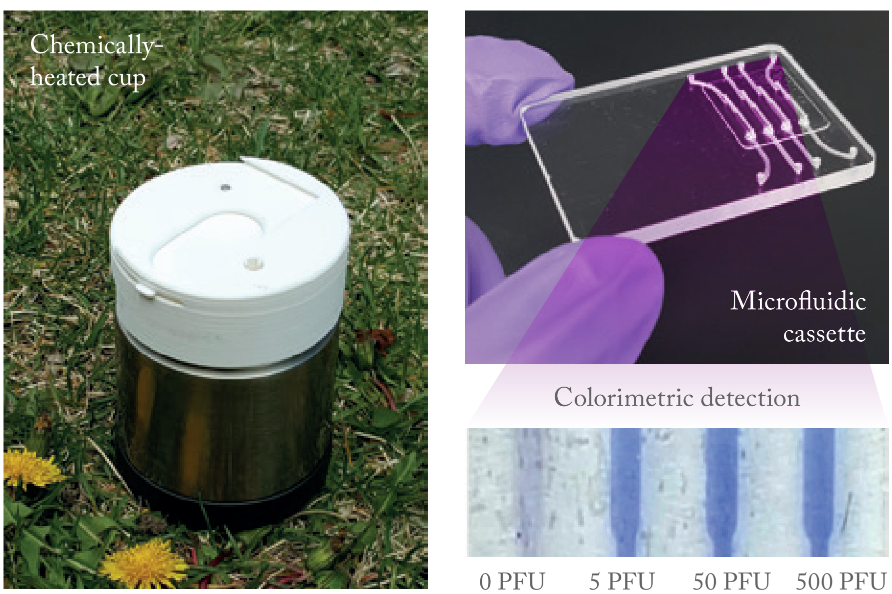
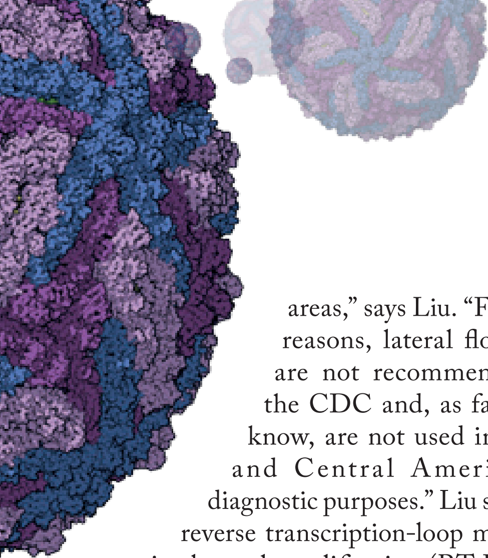


Figure 1. Zika virus POC diagnostic.



areas," says Liu. "For these reasons, lateral flow tests are not recommended by the CDC and, as far as we know, are not used in South and Central America for diagnostic purposes." Liu says that reverse transcription-loop mediated isothermal amplification (RT-LAMP) could be a highly sensitive (detecting the presence of the ZIKV before antibodies appear) and specific alternative to RT-PCR. "We developed a simple, sensitive RT-LAMP assay. RT-LAMP is also more suitable for POC applications because it is isothermal, can be carried out with minimal or no instruments, consumes less energy, and is more inhibitor-tolerant than PCR."

The group chiefly focused on two distinct facets: i) the design of new RT-LAMP primers for ZIKV detection, and ii) the implementation of the assay in a microfluidic format suitable for POC applications with minimal instrumentation. Using data mining, they identified highly conserved regions of the ZIKV genome that are divergent from other known pathogens. They then designed appropriate primers to recognize this sequence. The result? An assay suitable for applications in the laboratory and in the field, as well as a low-cost POC system that consists of a diagnostic cassette and a processor composed of a chemically-heated cup (see Figure 1) that can be operated by minimally trained personnel – without the need for electricity.

"The cassette isolates, concentrates and purifies nucleic acids, and carries out enzymatic amplification," explains Liu. "The results are quantified with a leucocrystal violet (LCV) dye that changes from colorless to violet in the presence of double-stranded DNA." The processor is also able to interface with a smartphone for signal excitation, acquisition, processing, archiving, and transmission (including GPS coordinates and a time stamp).

To test the assay's efficacy, the researchers collected saliva samples from healthy adult volunteers and spiked them with known amounts of ZIKV. After inactivation, the virus was filtered through an isolation membrane. The RNAs bound to the membrane then served as templates in the RT-LAMP amplification process without the need for an elution step, reducing the number of operations and simplifying flow control. The flow-through design of the reactor decoupled the sample volume from the reaction volume, enabling the group to use relatively high sample volumes and achieve high sensitivity.

At the moment, the work is at the "proof of concept" stage and needs to be tested more extensively before the assay can be adapted for medical use. Says Liu, "We must experiment with patients' samples and ensure that our assay and system match the performance of the gold standard (laboratory-based RT-PCR) and operate reproducibly and reliably." *JC*

Reference

1. *J Song et al., "Instrument-free point-of-care molecular detection of Zika virus", Anal Chem, [Epub ahead of print] (2016). DOI: 10.1021/acs.analchem.6b01632.*

Adze Marks the Spot

Polynesian artifacts matched to their source with ICP-MS-driven 'geochemical fingerprints'

Top: Excavations in progress during 1991 at the Tangatatau rockshelter, Mangaia Island, Southern Cook Islands. (Photo, Patrick Kirch, University of California, Berkeley. Kirch directed the excavations of the Tangatatau rockshelter on Mangaia, southern Cook Islands.).
Bottom: Adzing hull: a steel adze used like the ancient stone adzes. (Photo, Marshall Weisler, University of Queensland).

The prehistoric settlement of the Pacific Islands is thought to have involved one of the great marine migrations in human history, with modern research suggesting that colonization and subsequent trade extended across vast portions of the South Pacific. Marshall Weisler from the University of Queensland has been "sourcing" stone artifacts to try and determine whether trade continued far longer than previously thought.

After his long-term study on the island of Molokai in the Hawaiian Islands, Weisler was interested to find out if the material from stone adzes (tools made form volcanic rock) he had found at numerous habitation sites on the leeward side of the island were "petrographically unique."

Weisler describes inductively-coupled plasma mass spectrometry (ICP-MS) as the "gold standard" for analyzing fine-grained basalt artifacts, such as Polynesian adze materials. "MS offers tremendous benefits compared to older, less robust geochemical techniques. We analyze about 50 trace elements and three isotope suites (Pb, Nd, Sr) that allow us to understand the geochemical variability of the sources or quarries, then analyze the artifacts using the same range of elements and isotopes and look for quarry matches," he says. "Over the past few decades, I have become more involved with geochemical techniques, as the results are precise, accurate and fully quantitative."

Focussing on adze materials from a habitation rockshelter on the island of Mangaia, southern Cook Islands, East Polynesia, the geochemical data, when coupled with the associated dates from the excavated archaeological site, allowed Weisler's research team to reconstruct the ancient routes of contact. They discovered that over a third of the adzes had come from other island groups, demonstrating that the Polynesian voyaging network extended beyond the Cook Islands to include the Austral, Samoa, and Marquesas archipelagos – a distance of up to 2400 km. Based on the dating of particular adzes (400 to 500 years old) originating from the Tatangamatau quarry, Tutuila Island (Samoa), the team postulate that Polynesian inter-archipelago voyaging lasted up to the 1600s, suggesting that long-distance interaction continued to influence the development of social structures in East Polynesia well after initial colonization. *JC*

Reference

1. *MI Weisler et al, "Cook Island artifact geochemistry demonstrates spatial and temporal extent of pre-European interarchipelago voyaging in East Polynesia", Proc. Natl. Acad. Sci. USA, 29, 8150–8155 (2016)*

Blue Sky Science

PTR-TOF-MS takes a trip on NASA Flying Lab to analyse South Korea's atmosphere

South Korea is a heavily industrialized and densely populated country – and the combination of local pollutant emissions and transported pollution from China means the country suffers from increasingly poor air quality. The Koreans are making efforts to clean up the air – yet to be successful, scientists first need to understand exactly how different sources, transport and transformation of air pollution contribute to the problem.

Enter: NASA's DC-8 Flying Laboratory.

NASA monitors the atmosphere of Earth using satellites, research aircraft and ground-based observatories. The research planes move at a speed of 100-200 m/s, requiring them to carry very fast chemical sensors. This latest campaign involved 20 research flights over the Korean peninsula and the Yellow Sea. Twenty-four teams from renowned universities and research institutes contributed their instruments to create "the most advanced chemical laboratory in atmospheric science", including a group of physicists and chemists from the Universities of Innsbruck and Oslo, and company Ionicon.

"South Korea is one of the countries that will, in the near future, monitor its air quality from space using satellite-based spectrometry," says Armin Wisthaler, Instrument Principal Investigator and Adjunct Professor, Institute for Ion Physics & Applied Physics, University of Innsbruck. "However, satellite remote sensing data are difficult to interpret – which is why in situ data from the atmosphere need to be collected beforehand."

The Innsbruck/Oslo/Ionicon team flew a prototype of an improved proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) – described by Wisthaler as "the world's fastest and most sensitive sensor for volatile organic compounds in the Earth's atmosphere." The instrument drew air from outside the aircraft into an ion drift tube, where organic analytes were protonated by gaseous hydronium ions. "The resulting analyte ions are then analyzed in a medium mass resolution orthogonal acceleration TOF-MS, which collects data at a frequency of 10 Hz," says Wisthaler. The prototype includes an RF ion funnel and an RF ion guide, both developed by Ionicon, which boost the instrument's sensitivity by almost one order of magnitude. "If we integrate the mass spectra for 1 second, we reach detection limits on the order of 10 ppt (pmol/mol)."

They have come back from the field with 250 GB of data in the form of raw mass spectra, but, says Wisthaler, it is too early to make any qualified statements. "During the forthcoming months, we will analyze and quality assure our data – which will then become publicly available on a NASA data archive along with the data from the other instruments," he says. "Only then can a comprehensive analysis begin." The team's collaborators will use this data to feed their air quality models and to improve the interpretation of satellite data. And in the meantime? Wisthaler and crew are getting ready for NASA's next aircraft mission over the North Atlantic.

Wisthaler was "very proud" to be part of the project, despite having to work under demanding conditions. "It was a unique experience to fly over the Yellow Sea in this highly instrumented aircraft, tracing the pollution outflow from China. However, 150 hours in the air, most of the time spent in the turbulent boundary layer at a cabin temperature of 35°C, is definitely a challenge for both the instrument and the operators ..." *JC*

More information: http://blog.ionicon.com/2016/06/nasa-campaign-korus-aq-ionicon-ptr-tof-monitor-vocs-smog-korea

A Sense of Security

Dual-comb spec offers "elegant" way to screen for explosives

A research team from MIT have developed a form of terahertz spectroscopy that could be key to non-invasive security screening. The group has been working in the terahertz region for more than 20 years, and after demonstrating THz quantum cascade laser (QCL) frequency combs in 2014 (1), the main research goal became to improve the laser frequency comb performance. "The main focus of our research is to develop better THz QCLs as well as related applications," says Yang Yang, graduate researcher. "The fascinating frequency comb-based spectroscopy results coming from the mode-lock laser community made us want to try comb-based spectroscopy using our own lasers. As soon as we got decent lasers, exploring laser based spectroscopy systems became the natural choice!"

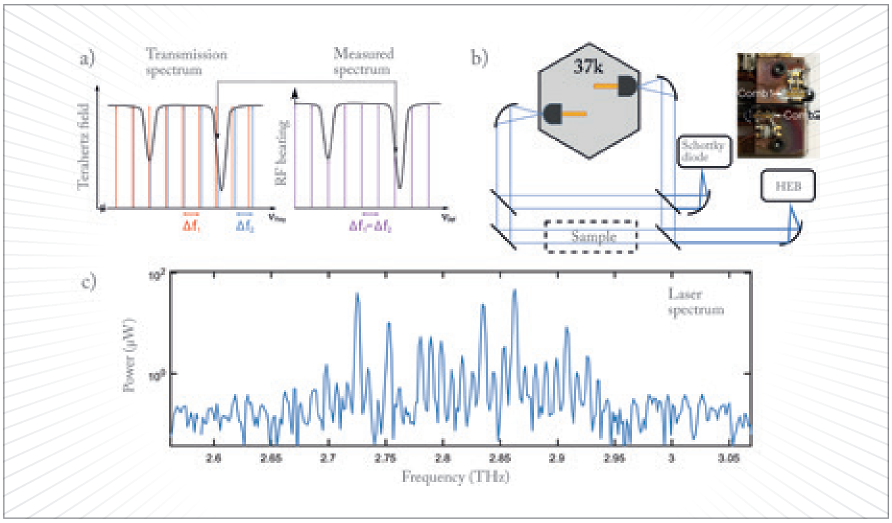


Figure 1. (a) Multiheterodyne spectroscopy (two frequency combs with somewhat different repetition rates). (b) Experimental setup (inset photo: laser frequency combs on copper mount – both silicon lens-coupled). (c) Spectrum of one device under comb operation.

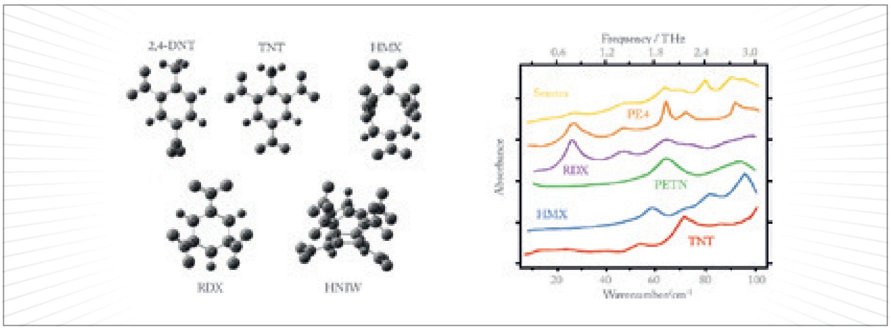


Figure 2. Broadband THz spectroscopy facilitates detection of different explosives, which absorb strongly in the THz range, providing a THz fingerprint.

Yang says that terahertz is a unique field of great importance for spectroscopy, as it is a range where lots of molecules have fingerprints. "By conducting broadband spectroscopy at terahertz, one can not only elucidate those molecules but also identify their concentrations," he says. "Frequency combs based on terahertz QCLs feature broadband coverage and high output powers in a compact package, making them an attractive option for broadband spectroscopy."

According to Yang, multiheterodyne spectroscopy based on two frequency combs (2,3) – also known as dual-comb spectroscopy – offers an "elegant" way of conducting broadband spectroscopy, as it features broad spectral coverage, high frequency resolution, and high signal-to-noise ratios obtained over short acquisition times – all without mechanical moving parts. "The significance is that it demonstrates the feasibility of THz QCL combs for spectroscopy applications given their chip-size volume – THz QCLs are the only chip-size coherent light source at THz. Their performance is compatible to traditional coherent THz sources, such as gas lasers, which are much larger," says Yang. "We have spent a long time developing an algorithm to retrieve data given strong environment feedback, and we can use that same algorithm to analyze data when our combs are under pulsed-mode biasing – something we previously believed to be impossible. That was quite surprising."

With its potential for detecting explosives and noxious gases (as well as screening mail and personnel), the new technique could play an important role in homeland security. "Explosive materials absorb THz light strongly at certain terahertz frequencies but not at others, and this 'terahertz fingerprint' can be used to identify an explosive, distinguishing it from clothing or other inert materials," Yang says. "Because clothing is transparent at terahertz frequencies, the THz light can pass through several layers, including common garments and shoes, providing a less invasive screening method." Manufacturer TeraView claims the technology is capable of detecting different types of plastic explosives, including PETN (pentaerythritol tetranitrate) – a material used in several terrorist bombings but notoriously difficult to detect. *JC*

References

1. *Y Yang et al., "Terahertz multiheterodyne spectroscopy using laser frequency combs", Optica, 3, 499–502 (2016).*
2. *S Schiller, "Spectrometry with frequency combs", Optics Letters, 27, 766–158 (2002).*
3. *F Keilmann et al, "Time-domain mid-infrared frequency-comb spectrometer", Optics Letters, 29, 1542–1544 (2004).*

Great SciX-pectations Part II

As 2016's "Great Scientific Exchange" draws closer, we ask five SciX fans why you should attend

"The SciX convention this year will offer me the opportunity to see the breadth of spectroscopy work across a number of wavelengths, techniques, and disciplines. This will be a rare opportunity to meet researchers both in fields related to mine and those that I have little insight into at present. Often, the most exciting ideas and discoveries come from connecting with researchers with knowledge and capabilities beyond your current boundaries. I very much looking forward to some exciting presentations and discussions and hope to leave the conference full of new ideas for exploring the planets using spectroscopy as a tool." – *Ray Arvidson, James S. McDonnell Distinguished University Professor, Washington University in Saint Louis*

"I think it's very exciting to welcome the International Symposium on Electro- and Liquid-phase Separation Techniques (ITP 2016) as a co-meeting partner for the first time. One of the benefits of the SciX meeting is for attendees to be exposed to cutting edge developments in disciplines outside of their own, and the addition of ITP2016 to the program continues and strengthens this goal. I always appreciate the award plenaries because my students have the opportunity to see and hear from luminaries in a wide range of analytical disciplines. My favorite session is always the FACSS Innovation Award session on Thursday afternoon, especially because of the rigorous Q&A session following each talk." – *Glen Jackson, Ming Hsieh Distinguished Professor, Forensic and Investigative Science & C. Eugene Bennett Department of Chemistry, West Virginia University*

"I'm looking forward to seeing the new breakthroughs in vibrational spectroscopy, especially in Raman spectroscopy. New applications in bioanalytical chemistry and aqueous solutions look extremely promising!" – *Paul S Cremer, J. Lloyd Huck Chair in Natural Sciences, Penn State University*

"I am interested in discovering how the NanoIR and discrete frequency IR communities have moved forward. In particular, I am interested in learning about any killer applications of NanoIR, especially in the biomedical / clinical domain for the excellent hardware that has been developed over the past few years. It will also be great to have the opportunity to see the breadth of research available at SciX – it is good to be able to mix Raman and IR analysis with novel hardware development, data analysis and some mass spectrometry." – *Matthew Baker, Senior Lecturer in Chemistry, Department of Pure and Applied Chemistry University of Strathclyde*

"I always enjoy attending SciX to experience the newest developments in applied and process Raman spectroscopy. This year, I am excited to see what new Raman developments will be presented both in the technical sessions and at the exhibits. I am looking forward to attending some of the LIBS talks as well." – *Brian Marquardt, Applied Physics Lab, University of Washington*

For more information and to register for SciX 2016, visit www.scixconference.org

Sample Prep, Screening and Software in the Cloud

What's new in business this month?

In our regular column, we partner with www.mass-spec-capital.com to let you know what's going on in the business world of analytical science. The past month has seen a flood of exciting new products entering the market, from GC-MS systems to innovative lab software.

Products

Merck expanded its portfolio of Cerilliant certified reference materials (CRMs).

Thermo Fisher Scientific presented its new cloud-based LabLink xL 2.0 Software and announced its new Thermo Scientific Exactive GC Orbitrap GC-MS system.

Pressure BioSciences announced initial shipments of its new Barocycler 2320EXTREME.

Agilent Technologies introduced two new 7000 Series Triple Quad GC/MS systems.

Shimadzu introduced its LIGHTNIRS Portable fNIRS System and released its LabSolutions IR thermal-damaged plastics library, a unique library of infrared (IR) spectra data.

Phenomenex launched the new Presston 100 Positive Pressure Manifold for sample preparation.

bioMérieux has broadened pathogen identification with its MALDI-TOF VITEK MS system and database.

Bruker introduced a new NMR profiling module for lipoprotein subclasses.

Collaborations

Labor Limbach in Germany is now using the NMR-based IVD Test LipoComplete from Numares.

Evotec has selected Genedata Screener as a screening platform.

Investments and acquisitions

Agilent Technologies completed the asset acquisition of iLab Solutions, a provider of cloud-based laboratory management software.

Biodesix raised a $7m follow-on Series F financing.

NMR firm Numares AG completed its financing round.

Eurofins has acquired food-testing firm AgFirst Bay of Plenty in New Zealand.

Stratec Biomedical has completed the acquisition of Sony DADC BioSciences.

Danaher has completed the spin-off of Fortive Corporation.

Peak Scientific has opened a new office in Singapore.

People

PerkinElmer has elected former Affymetrix CEO Frank Witney to its Board of Directors.

German Merck has appointed Dietmar Eidens as Chief Human Resources Officer.

Danaher has appointed Robert J. Hugin, former Celgene CEO, to its Board of Directors.

Agena Bioscience has appointed David Coorey as Head of the EMEA Region.

Further information on all announcements (plus quarter/half-year results for bioMérieux, Bruker, Danaher, Eurofins, Proteome Sciences, Thermo Fisher Scientific and Waters) is available on the online version of this article: tas.txp.to/0816/BUSINESS

Cheers to UHPLC!

Rainer Bauder raises a glass to more reproducible, more efficient, and more productive analytical workflows in the beverage industry.

I started working with (high performance) liquid chromatography in the early 1990s, and there have been some serious changes since then. For me, the emergence of better software has been key – both in terms of instrument control and the acquisition and processing of data. It's really changed the way people work. The focus has shifted from simply acquiring the data to doing more sophisticated data analyses and archiving. Notably, the advances in software coincided with regulatory changes, with good laboratory practice (GLP) and good manufacturing practice (GMP) filtering down from the pharmaceutical industry into the food and beverage markets.

Today, there are more regulations and accreditation requirements than ever before in the food and beverage market. To me, this is an acknowledgement of the fact that, in an increasingly global market, authenticity and correct label claims are paramount. Indeed, correct and compliant label information has become a key aspect in satisfying a more educated and interested consumer community.

Smart software also brought with it the opportunity to do more automation. In the 1980s and 1990s, manual injection systems were commonplace. Nowadays, almost all industrial HPLC setups use autosamplers and automated injection devices – that not only means reduced operator time and higher throughput, but also an increase in reproducibility.

If we look at the beverage industry specifically, there have been a couple of shifts that have altered the focus of analysis. First, there was a move from traditional products to more 'designed' products – and the subsequent introduction of additional coloring, flavoring and preservatives. More recently, I sense a shift towards more naturally sourced or even organic coloring and additives to meet the demands of more content-aware consumers. To that end, the analytical efforts on initial design of beverage products, as well as continued quality control, have been ramped up. After all, more complex products demand more complex analysis; raw material testing has become more challenging because of the increased diversity of compounds and more intense because of the need for authenticity testing.

With more components to monitor and the not-insignificant challenges of authentication, technological advances in HPLC – in particular, the birth of UHPLC – have been a boon to the beverage industry. Indeed, UHPLC offers gains in efficiency and productivity that cannot be ignored by routine labs in this space. Other advances have seen sample preparation or cleanup move away from the bench and into (U)HPLC instrumentation.

Bottoms up

In some ways, the beverage industry should be at the cutting edge of routine analytical workflows; with easier matrices to work with than its cousin, food analysis, and less hampered by regulation than the pharma industry, beverage analysis is well-positioned to take advantage of automation and efficiency advances. But as with many industries, cost is an issue – particularly in manufacturing, where internal quality control can eat into the bottom line.

Nevertheless, where safety is concerned, beverage producers (and the contract analytical labs that support them) have been very keen to embrace new technology that i) reduces cost of analysis (through increased throughput) and/or ii) increases confidence in the results, to avoid costly complications. Here, the very standard methods routinely employed for contaminant analysis (for example, pesticide analysis) can be made more efficient and reproducible through modern (U)HPLC systems. I don't think there is any doubt that general improvements in the quality of instrumentation (which is an inherent attribute of UHPLC) have clearly brought increased assay consistency – and, of course, such an advantage is not limited to the beverage industry.

In our latest Vanquish UHPLC platform, we have introduced a number of advances that have a real impact on assay reproducibility, by making retention times and elution profiles highly stable – which in turns simplifies data processing. How is the Vanquish platform able to lead the way in this regard? For one, by using smarter injection technology; the sample is pre-compressed before injection, which prevents pressure drop or pressure shock, making the flow more continuous. And we've also introduced more advanced technology to control the temperature of the column, which has a real influence on both elution time stability and peak shape.

In the past, striving for gains in instrument performance through an upgrade to UHPLC tended to result in a headache for method development teams – a blocker for many. And that's why we've also spent a great deal of time working on method transfer tools that ease the process dramatically.

Automation, much improved instrument quality, and more advanced software tools are all readily available nowadays – I could have only dreamt of such things back when I started in the 1990s. It's never been easier to benefit from better chromatography.

Rainer Bauder is HPLC Solution Manager at Thermo Fisher Scientific.

VUV En Vogue

In just a few short years, vacuum ultraviolet (VUV) detection for GC has risen from novel curiosity to serious contender. Here, Kevin Schug, Nicholas Snow and Luigi Mondello share GC-VUV thoughts and experiences.

First to See the Light

By Kevin Schug, Professor, University of Texas at Arlington, USA.

The team behind VUV Analytics originally approached me in 2009. They'd heard that I had a keen interest in all new separation science technologies – and my close proximity was also advantageous. I'll admit that I can be easily distracted by shiny objects, but that's often a good thing – as is open-mindedness. I remember sitting down with them in my office and looking through some data from a couple of direct injections on an 'alpha' system. I saw signatures for water in ethanol amongst other things and, over the course of an hour-long conversation, it hit me just how innovative the technology was.

In around 2012, we got one of the first beta systems in our lab. Those were exciting times; whenever we put a new compound onto the system, we were essentially seeing the very first VUV spectral signatures. And we've been pioneering GC-VUV ever since.

Riva two years on

I had the privilege of sharing some of the first public data at Riva (GC×GC and ISCC) in 2014 and, of course, analytical chemists start off by wanting to poke holes in novel technology before they embrace it. Just two years later at Riva 2016, I was heartened to see eight or so posters and presentations that included the use of GC-VUV – and GC×GC-VUV. I got the sense that there was a real buzz about the system. When I was in Messina with Luigi Mondello's group, I saw firsthand the potential of GC×GC-VUV, which we've not tried in our lab. The fact that the detector can keep up with GC×GC for complex samples is impressive and made me realize the power all that much more.

Where mass spectrometry has problems – isomeric species, low-molecular weight compounds or fragile/labile species – you can make a strong case for VUV detection and its ability to provide new information.

GC-MS killer?

I think we can all agree that, in reality, GC-VUV is complementary to MS – as noted in the examples above or in cases where a second piece of evidence to confirm the identification of a compound is important. That said, I consider it disruptive – mass spectrometry is no longer the only serious qualitative detector for GC. One area that we're currently looking into is environmental forensics, where the use of a simpler analytical technology helps make the explanation of scientific data to a layperson jury or judge easier and more defensible – I suspect other niche application areas will follow.

We are working on two exciting areas that will make VUV detection even more attractive. Firstly, pseudo-absolute (or calibration-free) determination is set to be a very powerful tool, and we'll be publishing something on that very soon. In short, because we can register the absorption cross section of a molecule in the library, it's possible to determine the number of molecules that cause a given absorption event in the flow cell. From an analytical workflow point of view, the ability to rapidly gain relative quantitative values for molecules in a mixture without calibration will be a big advantage going forward. Here, I can see further applications in more efficient diagnostics.

The second advance we're assessing is time-interval deconvolution, which allows you to rapidly speciate components in a mixture based on class- and species-specific absorption spectra. For example, you could quickly screen through a chromatogram if you wanted to classify a fuel and know how many aromatics, saturates or unsaturates are present.

VUV Newcomer

With Nicholas Snow, Professor, Seton Hall University, New Jersey, USA.

What does VUV detection mean for GC?

What I've been seeing over the past 10 years – and the VUV instrument is a very exciting part of this – is that people are developing new techniques and instruments that are specifically built to take full advantage of the capabilities of capillary GC. First, SPME and electronic pneumatic controls followed by a renaissance in specialty column chemistry. Now, attention has been turned to detection – better benchtop MS systems and most recently VUV detection – and I'm looking forward to watching them figure out their little competition with each other!

How is VUV detection being received in GC circles?

The technique is still relatively new – but, as a peer reviewer, I'm starting to see articles that feature GC-VUV with increasing frequency. Over the next few years, I suspect we'll see quite a lot more literature. Researchers are getting their hands on the system, and they're doing some legitimate research on what they clearly see as a good detector.

One thing that I really like about VUV is that it can be considered a universal detector but with the advantage of being familiar technology; we all used UV spectrometers in school. If you're interested in VUV, I would recommend taking a look at the methods that are challenging for your current detection system, and use that as a place to start your VUV exploration.

How about your own VUV exploration?

We only got our VUV instrument in June, when we interfaced it with a 25-year-old 5890 GC system (it's just what I had available). It took us about five minutes to set up the automatic GC start with the new software system, which was impressive. Connecting to the GC was also simple – we popped out a panel and slid the transfer line straight in. We were up and running (including training) very quickly. And though we're still working on some of the nuances, that early simplicity was a refreshing change.

Right now, we're focused on getting good data for our analysis of various isomers of polycyclic aromatic hydrocarbon (PAH) monohydroxy derivatives, which tend to have very similar mass spectra, but very different UV spectra. PAHs are some of the nastier components of oil spills that get metabolized by fish.

Just this week, we ran some samples that had been extracted in an ethanol–water mixture, which resulted in two big solvent peaks. Not only did it confirm that our injection technique was excellent(!), but it also got me thinking about the potential of revisiting water analysis in various contexts...

Any applications where VUV could supplant MS?

About 15 years ago, I predicted that GC-MS would kill off all the other selective detectors – that hasn't happened. So I'm not sure I dare make too many predictions. I will say that it really comes into its own with complex mixtures of isomers or very similar structures. I'll also note that it's non-destructive, and has an outlet that could be interfaced to other detectors. So while I've been burned before and won't name a "killer app", I will state that I'm very positive about the additional information it can provide in a wide range of application areas. While VUV may not kill off the mass specs, it's likely to do some damage to it and other selective detectors...

VUV Sails into Riva

With Luigi Mondello, Chair of Riva 2016, and Professor, University of Messina, Italy.

Did you expect VUV to have such a solid presence at Riva 2016?

It was a big surprise, considering that it is quite a new technology. I've also noticed an exponential increase in the number of papers published in this field over the last three years. I think that the success of VUV stems from it being perceived as a powerful universal detector, capable of providing both qualitative and quantitative information. In fact, all organic chemical compounds absorb UV radiation in the 115-240 nm range, and photons in this region are related to high-energy electronic transitions that offer a great deal of complementary information to MS and IR spectra. Moreover, spectra acquired in the gas phase do not suffer from the broadening effect seen in absorption spectra taken in solution.

Could you share your personal experiences with VUV?

My lab started working with the VUV detector earlier this year, when we coupled it to a Shimadzu GC system to fully exploit its rapid acquisition rates in fast-GC and comprehensive 2D approaches. In direct GC, the use of VUV is straightforward; in GC×GC with flow modulation (FM), we needed to do extensive method optimization – after all, it was the first time an FM GC×GC instrument had been coupled with a VUV detector! After optimization, the average peak width at the base was comparable with those obtained with other detectors.

What is your research focus with VUV detection?

My group in Messina is mainly focused on two projects. The first is the aforementioned hyphenation of VUV to FM GC×GC (in particular, in applications devoted to FAMEs and biodiesel), where the VUV detector acts as a third analytical dimension. The second project is to build a VUV spectral database for lipidomics. Gas phase VUV absorption spectra are strongly affected by chemical features, such as the degree of unsaturation and the presence of conjugation in the analyte. As a consequence, evaluation of the VUV spectra allows us to discriminate between different classes (for example, linear, hydroxylated, monounsaturated, polyunsaturated, and so on). And by combining VUV spectral similarity with a linear retention indices (LRI) filter, the number of candidates can be reduced, providing unique identification.

Where does VUV fit in the analytical toolbox?

I see VUV technology being a big help in understanding the nature of complex mixtures in different fields, especially where compounds cannot be reliably identified using traditional approaches (GC-MS); for example, isobaric, isomeric or labile components. Whatever the application field and the analytical goal, the demonstrated ability to use VUV data analysis software for deconvolution of multiple overlapping signals from post-column co-eluting compounds represents an additional means for analyte differentiation – much like the secondary dimension in comprehensive GC.

Can you predict the future of VUV detection?

VUV detection is likely to follow two different trends. First, I see an integrated platform that merges the complementary information afforded by MS, IR and VUV spectra for unambiguous identification of GC-separated compounds, together with LRI. Second, the VUV detector will be used as a universal, calibration-free tool that provides the relative quantitative values of distinct molecules in mixtures in a rapid manner.

The full version of this article is available online: tas.txp.to/0816/VUV

ANALYTIC × AESTHETIC

For the third year running, we bring together two very different but complementary worlds to prove that scientists have a real eye for beauty.

22-29
What Lies Beneath
We speak with the scientists using advanced analytical techniques to solve some of the biggest mysteries in the art world.

30-35
Air & Water
Analyzing deep-sea sulfides and monitoring London's pollution.

36-41
Awe & Wonder
Finding beauty in science and science in beauty.

43-45
Food & Drink
Measuring maple syrup quality and making rapid rum.

46-49
Health & Security
Diagnosing disease and securing our future.

What Lies Beneath

Ever wanted to understand the thought process of Rubens or the creative process of van Gogh? Modern analytical techniques and passionate analytical scientists are digging up the answers to such questions – and discovering a new world of art that has been lost for centuries.

Young Girl Reading

By John K. Delaney, Yuriko Jackall, and Michael Swicklik

The paintings of Jean-Honoré Fragonard (1732–1806) are known for their brilliant coloring and alla prima brushwork. The National Gallery of Art's Young Girl Reading is one of the most beloved examples of his virtuoso painterly style.

In 2012, the surprise rediscovery of a drawing by Fragonard, further confirmed the rarity of Young Girl Reading. This remarkable sheet is covered with "thumbnail-sized" sketches, each showing a single figure. These sketches clearly relate to Fragonard's so-called "fantasy figures," a series of boldly-colored paintings of individual models in extravagant fancy dress. Today, the "fantasy figures" are distributed amongst the most distinguished public and private art collections in the world, including the Musée du Louvre and the Metropolitan Museum of Art.

At the Gallery, the revelations of the drawing prompted a two-year investigation of Young Girl Reading, conducted as a collaborative effort by the authors. Our findings indicated that underneath the profile of Young Girl Reading lay another face entirely, that of a woman turned outwards, looking directly at the viewer. This now-hidden woman once had a large plumed and beaded headdress, similar to those of the "fantasy figures." Scientific standoff chemical imaging (RIS, XRF and RTI) and study of a cross-section taken in an area of change indicated that the artist first intended to depict a woman looking outwards, holding a book. He completed this composition, then left it alone, perhaps for as long as a year before returning to adjust the orientation of the head of his model, repurposing it as the Young Girl Reading known today. In her original pose, Fragonard's woman holding a book corresponds to one of the sketches on the newly-discovered drawing, thereby confirming that the painting underlying Young Girl Reading was conceived as a "fantasy figure."

Using similar multidisciplinary methods (art-historical research, conservation science, imaging techniques), the authors are currently researching other "fantasy figures" in the hopes of shedding further light upon Fragonard's conception of and approach to the ensemble as a whole. Our findings will be presented with the forthcoming exhibition, Fragonard's Fantasy Figures, at the National Gallery of Art, Washington, from October 8 through December 3, 2017.

The Toolbox

Multi-modal imaging – diffuse reflectance imaging spectroscopy (RIS), x-ray fluorescence (XRF) imaging, reflectance transformation imaging (RTI) and high-resolution color photography – were used to reveal as much as possible about the underlying painting beneath Young Girl Reading. Diffuse reflectance imaging from 1000 to 2500 nm

Top left: Color detail of Jean-Honoré Fragonard's Young Girl Reading. Top right: False color diffuse-reflectance near-infrared image (1000, 1300, 2100 nm) (J. Delaney and K. Dooley). Bottom right: XRF image obtained from mercury-alpha line, likely associated with vermilion. Bottom left: Hypothetical simulation of figure underlying Young Girl Reading extrapolated from technical images (image by B. Goodman and D. Doorly).

was performed with a recently designed and constructed hyperspectral near-infrared imaging camera with 2.7 nm spectral sampling. Narrow spectral band NIR reflectance imaging has been found to give some of the clearest images of underlying paint compositions or underdrawing, as well as aiding in the mapping of artist materials (pigments & paint binders). XRF imaging spectroscopy, using a home-built scanning sensor, provided elemental maps to help complete the 'picture' of the underlying figure (particularly useful were maps for lead, mercury and iron).

John K. Delaney is senior imaging scientist, Yuriko Jackall is specialist in eighteenth-century French paintings, and Michael Swicklik is senior conservator of paintings, all at the National Gallery of Art, Washington, USA.

Reference

1. *Yuriko Jackall, John K. Delaney, and Michael Swicklik, "'Portrait of a woman with a book': a 'newly discovered fantasy figure' by Fragonard at the National Gallery of Art, Washington." The Burlington Magazine, CLVII (April 2015): 248-254.*

X-ray Master Class

Why are Rubens' reds not red? What was van Gogh thinking? And is that really a van Eyck?

Koen Janssens and his team at the University of Antwerp in Belgium spend much of their time digging into the backstory of masterpieces. Here (and on page 50), Janssens lets us into the secrets of advanced art analysis.

Analytical palette

It's fair to say we rely pretty heavily on X-rays! X-ray fluorescence (XRF), for example, allows us to discover the elemental content of materials. Handheld XRF systems are now used throughout the world by anyone who has access to basic funding, which has really opened up this kind of research. Nowadays, they have essentially become black box instruments. Basically, you irradiate a square centimeter of a painting and figure out – indirectly – which pigments were used to paint the different colored areas.

The high-end of the X-ray analysis spectrum relies on synchrotron radiation-based nano and microbeams (aka as synchrotron X-ray microprobes), which can be used to analyze tiny samples (a few 100 micrometers across) from famous paintings to investigate natural degradation processes. Depending on which pigments have been used and in what combinations, colors can change as they interact with physical or chemical agents in the environment. For instance, some of the reds that have been used by Rubens develop a degradative black or a white crust. Degradations such as these follow a sequence of chemical modifications and we can find traces of these sequences if we analyze paint samples at a very high spatial resolution. For example, vermilion red – mercury sulfide – transforms gradually to mercurous chloride (calomel) over three or four steps, involving exotic compounds called mercury sulfochlorides; our advanced imaging techniques allow us to see the difference between all these compounds and therefore to trace back the gradual transformation process from the sulfide to the chloride. And electrochemical methods help support our work in this area by assessing potential routes of degradation ahead of time (see page 50 for more details). Degradation information is important to conservators, who can investigate preventative conservation to shield or isolate the works of art from chemical agents that are likely to have a negative impact.

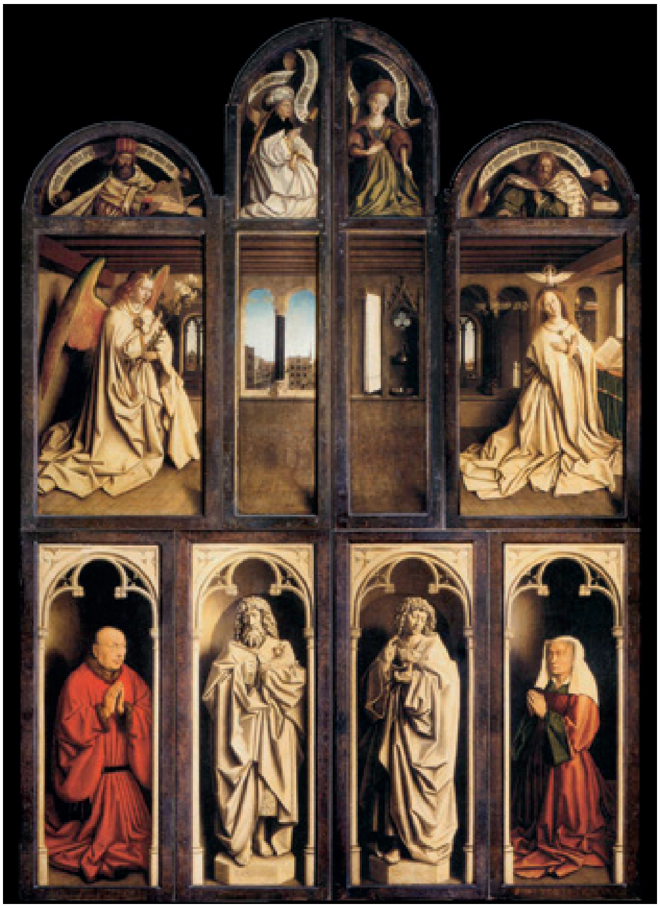
Another activity that is more directly aimed towards art historians and museum people moves away from the nano- or microscopic level, involves developing instruments that allow chemical imaging at the square meter scale. Such macro-scanning X-ray fluorescence (MA-XRF) instruments provide large-scale chemical maps that show both the painting and the distribution of chemical elements within it. We cannot only show what's on the surface, which allows art historians to learn about the materials the artist has used, but also what is present below the visual surface. If an artist has, during the creative process, changed his mind and overpainted part of the painting with something else (known as 'pentimento' in art circles), our X-ray "eyes" will see it. Such information can be highly relevant for art historians who seek to reconstruct the history of or understand the creative process behind a work of art.

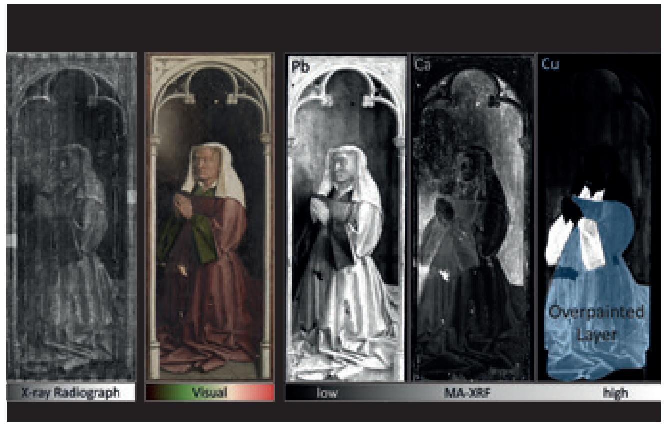
Chefs d'oeuvre

The 15th century Ghent Altarpiece (also called the Adoration of the Mystic Lamb or The Lamb of God) is currently housed in Saint Bavo Cathedral, Ghentand is considered one of the van Eyck brothers' masterworks. Using our MA-XRF scanner, we have been investigating a number of the panels over the last few years to help restorers, who suspected that the polyptych, as it is today, is not entirely original. Rather, the Ghent Altarpiece is actually an overpainted version of the original, which is still underneath; only the original was painted by the van Eycks. Despite their strong suspicions, the restorers could not produce compelling enough evidence to convince their colleagues that the upper layers should be removed to reveal again the van Eyck original – until we came along.

In such a major restoration, you not only have the restorers, who are the executive force, but also one or more international advisory committees. The restorers aimed to convince all stakeholders that such a painting should be restored to principles observed today, which means keeping original paint and removing all more recent overpaints. So we helped them by scanning the panels and finding visual ways of making the distinction between original van Eyck paint and the paint that was added ca 100 years later. Translating the very strong hunch of the conservation team into images meant that their international colleagues could be persuaded to remove all overpaint. The consequence? The removal of around 60 percent of the total paint! Clearly, this is invasive, but the original van Eyck paint will become visible again after being covered for around 400 years. I'm sure it will have a big impact and lasting consequences.

For another example, I'll skip from the 15th century to the 19th century. We have studied quite a few paintings by Vincent van Gogh over the last ten years (and, in fact, the first high-level painting we analyzed with our new imaging method was also by van Gogh). However, this example involves a specific piece associated with my hometown of Antwerp, which he painted while





Left: Van Eyck brothers, The Ghent Altarpiece (closed) – also known as Adoration of the Mystic Lamb or The Lamb of God (Dutch: Het Lam Gods), c. 1430–32. Top Right: One of the panels of The Ghent Altarpiece called "Elisabeth Borluut". The copper distribution shows that the robe of Elisabeth Borluut was completely overpainted at a later stage. Bottom Right: The hidden "wrestlers" uncovered by MA-XRF scanning found beneath Van Gogh's Still life with meadow flowers and roses c. 1886.

he was at the academy here. Van Gogh has a Dutch period, a short Antwerp period of only one month, and then he moved to Paris, where he met the Impressionists and continued on to Provence.

While in Paris, he encountered a completely new way of painting and came to dislike a number of his previous darker and less colorful works. He decided to paint over them, which is why there are a number of double-layered van Gogh paintings. We've examined a number of these, including Still Life with Meadow Flowers and Roses – a painting that is now in the Kröller-Müller Museum in the north of Holland. It was originally bought as a van Gogh but, at some point in the 1990s, was rejected as the real deal. Why? Because it was the wrong size, for one thing.

Indeed, the composition of the surface painting was not typically van Goghian, according to the art experts. It was removed from the catalogue of van Gogh paintings and was an orphan for about 20 years. In 2012, we reanalyzed the work with MA-XRF and showed, much more clearly – brushstrokes and all – the image of two wrestlers grasping each other by the arms beneath the surface. By combining that clearer image with what was understood of van Gogh's work in Antwerp, we could strengthen the link between the painting and van Gogh. As a result, the art historians of the van Gogh museum in Amsterdam and the Kröller-Müller museum reinstated the painting as a van Gogh the same year.

Koen Janssens is Full Professor, general and analytical chemistry, and Vice-Dean, Faculty of Sciences, at the University of Antwerp, Belgium.

The Syndics

By Petria Noble

The late paintings of Rembrandt van Rijn pose significant challenges because of their multi-layer build up, heterogeneous materials, compositional changes, degradation problems and complex histories. In The Sampling Officials of the Amsterdam Drapers' Guild from 1662, better known as The Syndics (Rijksmuseum Amsterdam), Rembrandt radically altered the position of several of the figures. Developments in analytical science are now making it possible to start answering some of the questions that arise. In 2013, the painting was investigated with portable macro-X-ray fluorescence scanning (MA-XRF) in the galleries of the Rijksmuseum using the Bruker M6 scanner. A series of 15 overlapping scans were captured over a period of a few days. The resulting elemental distribution map of lead associated with the pigment lead white, provides additional information regarding the repositioning, some four times, of the figure of the steward in the background, Frans Hendricksz Bel, which appears to have been fully painted in his former locations, at the far right and in between the two sampling officials – before being placed behind the two syndics in the centre of the composition. Elemental distribution maps for cobalt, nickel, arsenic and potassium associated with the pigment smalt also suggest that the hat of Jochem de Neve, the syndic to the right of Bel, was also reduced to accommodate the final position of Bel, although this change could also relate to the ranking of the officials. This offers new information on the much debated order, function and meaning of the changes. The X-radiograph and infrared reflectography (IRR) had already provided some information but were difficult to interpret. It is more often the case

that traditional imaging techniques, such as X-radiography and IRR, prove ineffective in the study of late Rembrandt paintings due to Rembrandt's choice of materials, particularly his use of radio-transparent quartz and earth-rich grounds, and pigments, such as organic lakes, smalt, earths and bone black.

In this project, scientists, conservators and art historians are working together to develop and apply new imaging techniques to the study of (late) Rembrandt paintings. Partners include: Joris Dik (Delft University of Technology), Koen Janssens (University of Antwerp) and John Delaney (The National Gallery of Art, Washington) as well as: Mauritshuis, The Hague, Netherlands Institute for Art History (RKD), Cultural Heritage Agency of Netherlands (RCE), the Wallraf-Richartz Museum, Cologne and Synchrotron Soleil France. The MA-XRF scanning of the painting was carried out by Geert van der Snickt (University of Antwerp), Anna Krekeler and Lisette Vos. Results of this particular painting were presented at the Painting Techniques, History, Materials and Studio Practice, 5th International Symposium, (Rijksmuseum, 18-19-20 September 2013) and are illustrated in J. Bikker and A. Krekeler, "Experimental technique: The Paintings", in J. Bikker et al., [exh. cat], Rembrandt: The Late Works, 2014.

Revealing complex compositional changes in Rembrandt van Rijn, The Syndics, 1662. Oil on canvas, 191.5 x 279 cm, Rijksmuseum SK-C-6. a) visible light, b) X-radiograph, c) IRR, d) Pb-L and e) Co-K distribution maps. The macro-XRF elemental maps offer new information on the much debated, order, function and meaning of the changes.

Petria Noble is Head of Paintings Conservation at the Rijksmuseum and is researcher in the Science4Arts- ReVisualising late Rembrandt project (2012-2018) sponsored by the Netherlands Organization for Scientific Research (NWO) and the National Science Foundation.

The Enchanted Pose

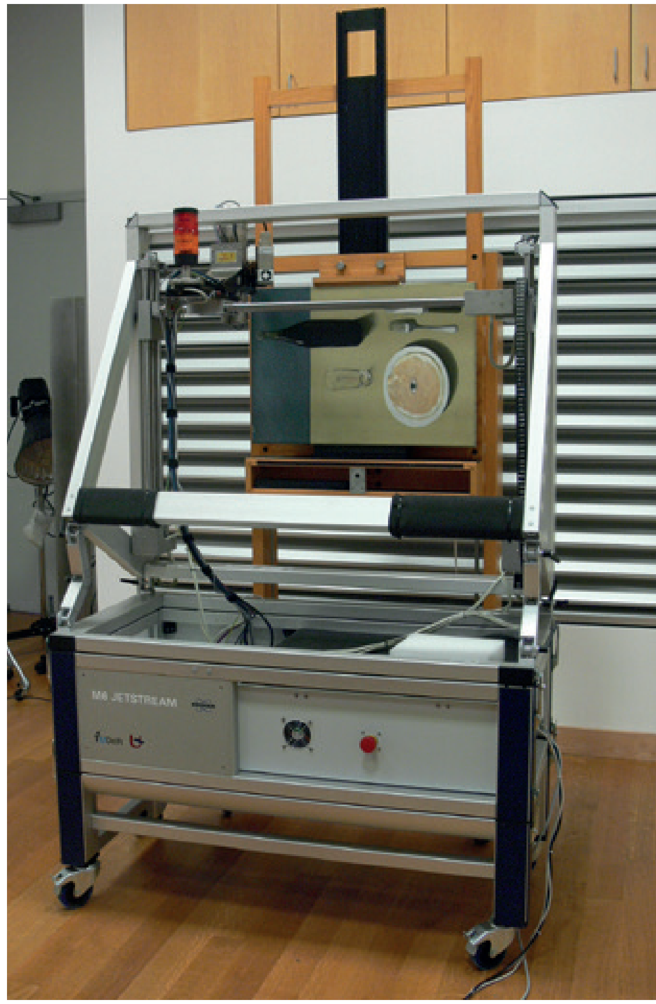
By Ana Martins

There is more than meets the eye in The Portrait (1935), a painting by renowned Belgian artist René Magritte. In the course of examining and treating the painting for an upcoming exhibit at MoMA in 2014 entitled Magritte: The Mystery of the Ordinary, 1926-1938, the museum conservators took an X-ray image of the painting and discovered an underlying composition representing the head and torso of a female nude (1; see Image 2). In fact, the hidden image corresponds to the upper left section of The Enchanted Pose, also painted by Magritte in 1927, and presumed lost since the early 1930s. The lower half of the nude was discovered shortly after under The Red Model (1935) and the quest continues for the remaining missing half of the original painting. Magritte painted right over the section of the painting, but the underlying paint in still visible around the edges of the painting and around the edges of the bottle. He also incorporated passages of the underlying composition in the new one, for example, in the brown reflection in the glass.

Why Magritte chose to sacrifice this composition and reuse the canvas remains a mystery. Maybe it was out of resentment after The Enchanted Pose was rejected for a 1932 group show in Paris, or he may have simply run out of canvas, or perhaps the work got damaged and could no longer be exhibited. Even if Magritte did not intend for us to see this painting, this study has allowed us to virtually reconstruct an approximate visual record of it and, in the process, help us understand his artistic development by studying what he created – but also what he chose to obliterate.

The toolbox

To learn more about the materials Magritte used for both top and underlying compositions, the painting was imaged using macroscopic X-ray fluorescence analysis (MA-XRF; Bruker), which maps the distribution of chemical elements that are representative of the pigments in the paints. The face of the hidden figure is revealed in both the lead and iron maps, suggesting it was executed with earth pigments and lead white-based paints. The mercury map, on the other hand, shows the lips were retouched with a paint containing vermillion. The sky around the figure is visible in the chromium map indicating the paint contains chromium oxide green, a bluish green pigment. The same paint appears in other late 1920s paintings by Magritte and has a similar composition as a blue household paint manufactured by Ripolin (2). The bottle in the upper composition is visible in the calcium and cadmium map, suggesting Mondrian modified the tonality of the bone black-



The Portrait is placed on an easel in front of the Bruker M6 Jetstream XRF scanner. The scanning took approximately 48 hours for a final resolution of a 0.5 mm. The instrument was on generous loan from the Delft University of Technology.

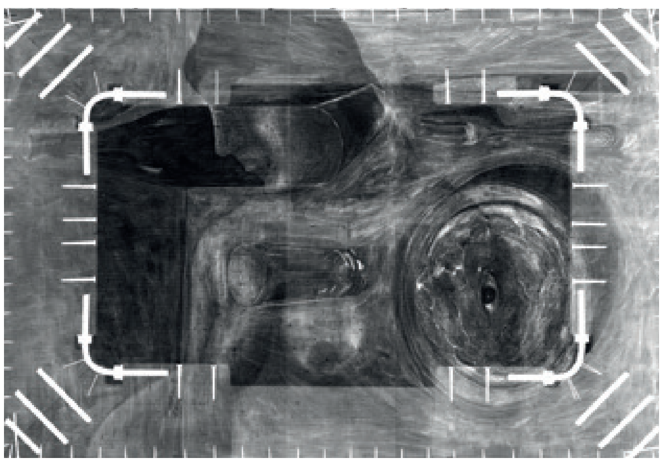


Image 2. 90° rotated X-ray image of René Magritte's Le Portrait (The Portrait), 1935. Oil on canvas, 28 7/8 x 19 7/8″(73.3 x 50.2 cm); part of Magritte's La Pose enchantée (The Enchanted Pose), 1927, can be seen. Department of Conservation, The Museum of Modern Art, New York. © Charly Herscovici – ADAGP – ARS, 2013.

based paint by mixing with cadmium yellow paint.

In total, twelve chemical elements were identified by MA-XRF and the stratigraphy of the painting (see Figure 2) can be inferred from the corresponding distribution maps and some complimentary analysis (3). This technique provided valuable insight into both the creative process and choice of materials of this artist in a noninvasive way, without the need of taking cross sections.

Ana Martins is a research scientist in the conservation department of the Museum of Modern Art (MoMA), New York, USA.

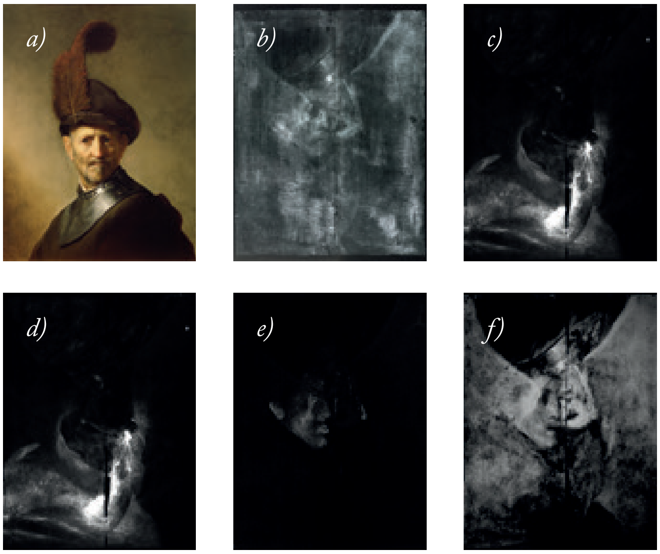
References

1. *M Duffy and A Albertson, "The Discovery of Magritte's 'The Enchanted Pose', Inside/Out, a MoMA-PS1 Blog, The Museum of Modern Art, New York, NY. http://www.moma.org/explore/inside_out/2013/10/31/the-discovery-of-magrittes-the-enchanted-pose.*
2. *G Gautier et al, "Chemical Fingerprinting of Ready-Mixed House Paints of Relevance to Artistic Production in the First Half of the Twentieth Century. Part I: Inorganic and Organic Pigments", Appl Spectrosc 63, 597-603 (2009).*
3. *G Van der Snickt G et al. "Exploring a hidden painting below the surface of René Magritte's 'Le portrait'." Le Portrait. Appl Spectrosc, 70, 57–67 (2016).*

An Old Man in Military Costume

By Karen Trentelman

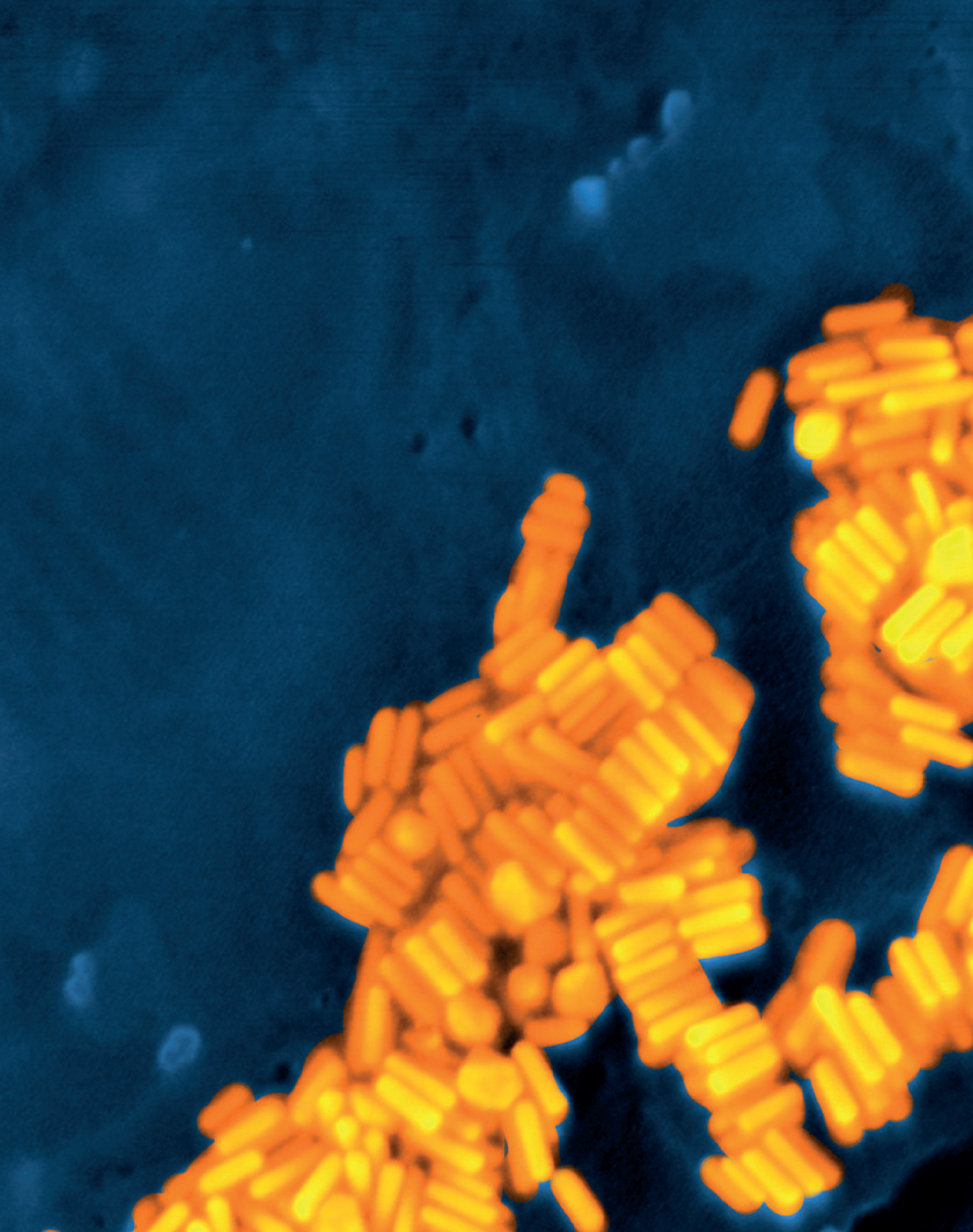
An Old Man in Military Costume, painted by Rembrandt in 1630-31, is not only a compelling portrait of an old man wearing a cloak, a neck protector (known as a gorget) and a feathered cap, it is also an analytical challenge: beneath the painting of the old man lies a second, hidden painting. How can analytical science reveal the underlying image without causing any damage to the upper painting? The answer is X-rays (and gamma rays) – and patience. In 1978, X-radiography first revealed the face of a man, rotated 180 degrees from the upper portrait. But who was he, how was he dressed, and what colors were used? Patience. In the early 1990s, neutron activation autoradiography (NAAR) was carried out and, although many of the NAAR images contained contributions from multiple elements, some tantalizing information was revealed: mercury (from the pigment vermilion, HgS) was used to paint the face, and he was wearing a cloak painted with a copper-containing pigment. But the details were fuzzy. More patience. In 2013, the painting was studied by macro-X-ray fluorescence (MA-XRF) scanning, which enabled complete distribution maps of individual elements to be collected. The results allowed us to create a digital reconstruction of the underlying painting: a young man, wearing a cloak with a wide collar – perhaps also a gorget. But what, if anything, is he wearing on his head? Nothing is evident in the XRF maps, but they cannot detect the lower Z elements that comprise organic materials. Even more patience... Analytical science will, someday, provide us with a tool to answer this and other questions.



Reconstructing a hidden Rembrandt. a) An Old Man in Military Costume by Rembrandt van Rijn (about 1630–31, oil on panel, 65.7 x 51.8 cm, JPGM 78.PB.246, Photo credit: J. Paul Getty Museum, Los Angeles); b) X-radiograph of painting acquired in 2008 (rotated 180°); c) digital color reconstruction of underlying painting; macro-XRF element distribution maps of d) Cu-K, e) Hg-L and f) Pb-L X-ray fluorescence emission.

Collaboration

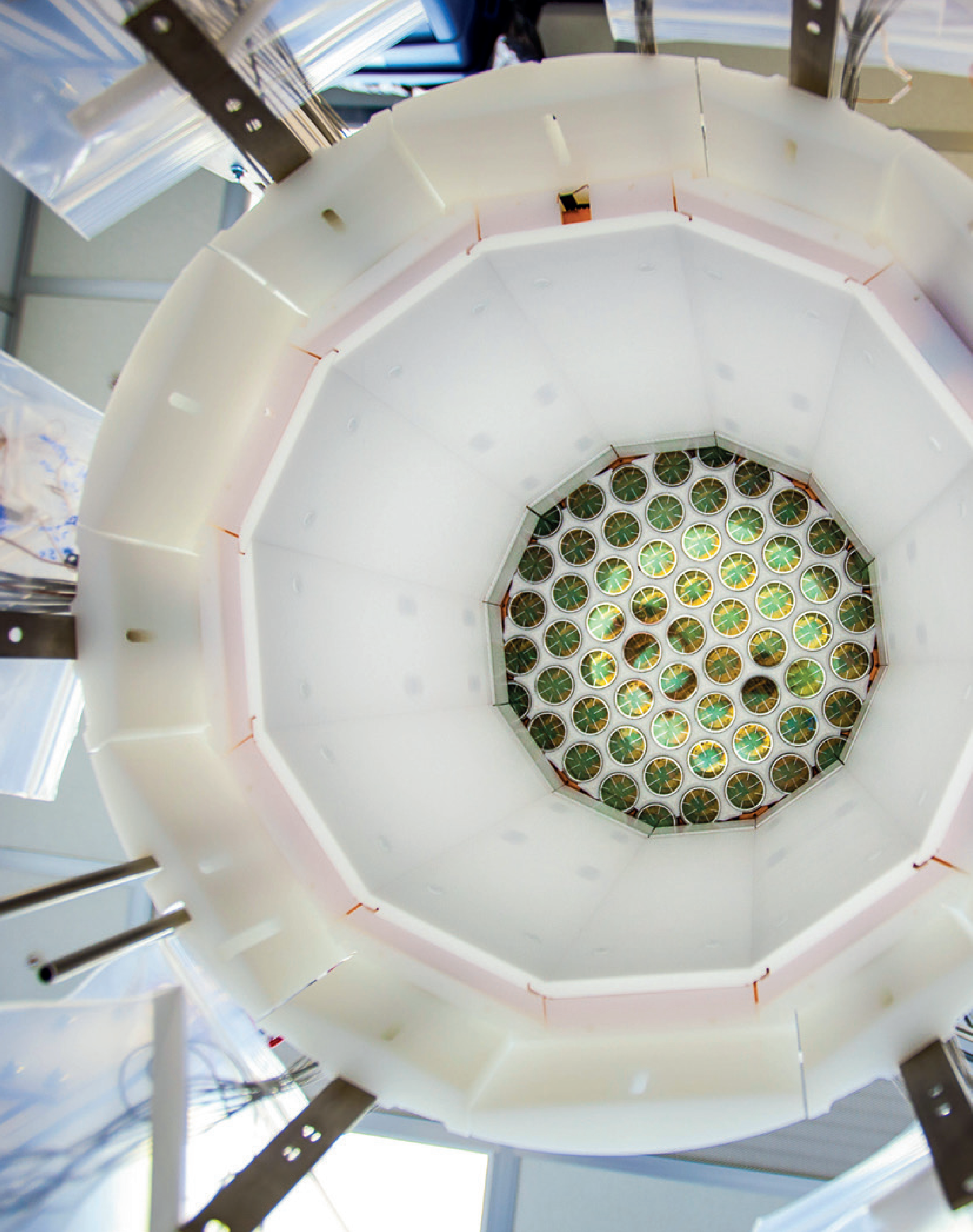
To gain a better understanding of the materials and methods used by one of the world's greatest artists, this, as with most cultural heritage research, was a collaboration between scientists, conservators and art historians: Karen Trentelman, senior scientist and leader of the Technical Studies research group at the Getty Conservation Institute; Koen Janssens and Geert van der Snickt, X-ray Analysis, Electrochemistry and Speciation, University of Antwerp; Joris Dik, Laboratory of Materials Science, Delft University of Technology; Yvonne Szafran, head of Paintings Conservation at the J. Paul Getty Museum; and Anne Woollett, curator of paintings at the J. Paul Getty Museum.

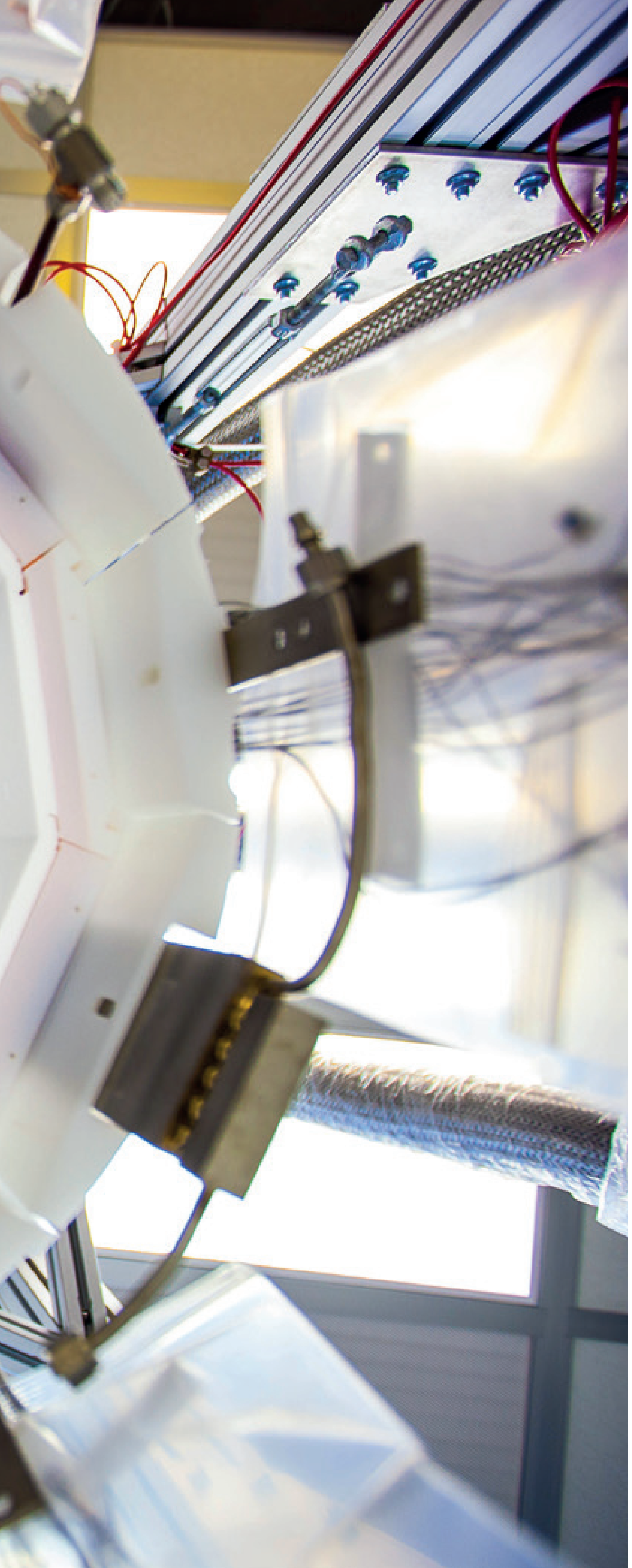


Air & Water

SPLAT!

At PNNL, scientists are collaborating with physical chemistry scientists to push the frontiers of quantitative imaging of natural and artificial nanoparticles, by using single particle laser ablation time-of-flight mass spectrometry – more affectionately known as SPLAT II. The photo shows a scanning electron microscope image of a gold nanorod array used to calibrate the SPLAT II system.
Photo credit: PNNL





Kept in the Dark

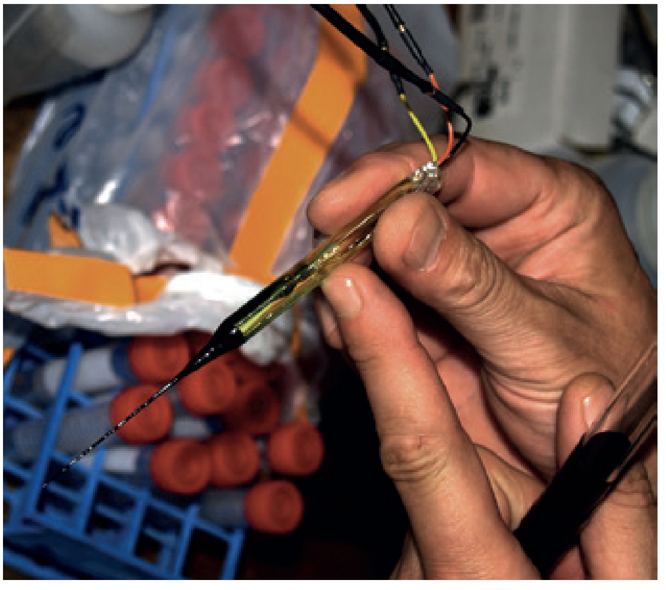
Photomultiplier tubes at the top of the LUX detector. Scientists aim to use the 370 kg liquid xenon time-projection chamber to directly detect galactic dark matter in a laboratory – one mile beneath the earth's surface. "Welcome to my underground lair..."

Photo credit: Matthew Kapust/Sanford Underground Research Facility

Deep-Sea Sulfide Sensor

Custom-made sulfide sensor held by Dirk de Beer (Max Planck Institute for Microbiology) at NEPTUNE, Canada's Marine Technology Centre. The sensor, along with nine others, is used to study deep-sea sediment chemistry.

Photo credit: Ocean Networks Canada (Flickr)



Mössbauer Magic

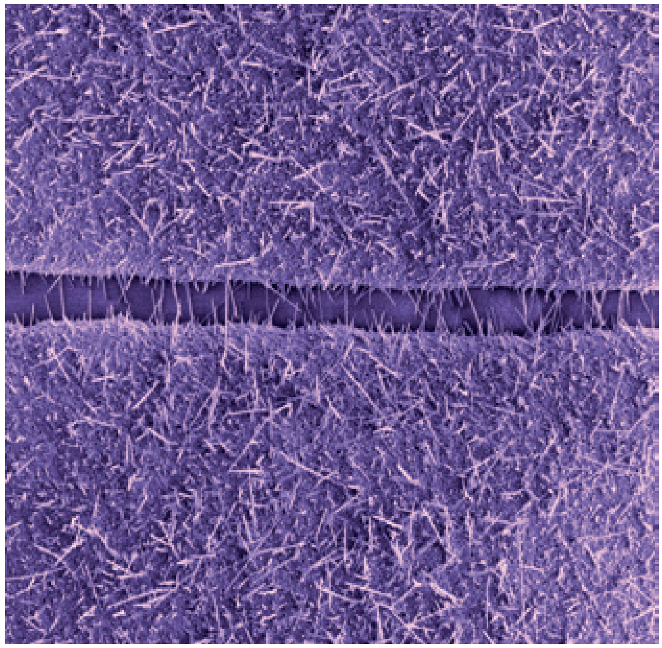
Environmental Molecular Sciences Laboratory (EMSL) scientists use a highly sensitive Mössbauer spectrometer to investigate valence state, coordination number, and crystal field strengths for a wide range of samples.

Photo credit: EMSL (CC 4.0)

Bridging the Gap

Adaptation of a scanning electron microscopy image of copper oxide nanowires that bridge the gap between neighboring copper microstructures in a carbon monoxide nanosensor.

Photo credit: Okinawa Institute of Science and Technology



Sea Change

Portable spectroscopy instrumentation is being used to analyze the deterioration processes caused by the sea in various construction materials at the Galea Fort, Getxo, Basque Country, Spain.

Photo credit: Hector Morillas, IBeA research group, Department of Analytical Chemistry, University of the Basque Country

Pigeon Patrol

Pigeons donned tiny pollution sensor vests and took to the skies of London to measure ozone and nitrogen dioxide as part of a collaboration between marketing company DigitasLBi and Plume Labs. Here the pigeons are unleashed...

Photo credit: Plume Labs

Awe & Wonder

Radioactive Probe

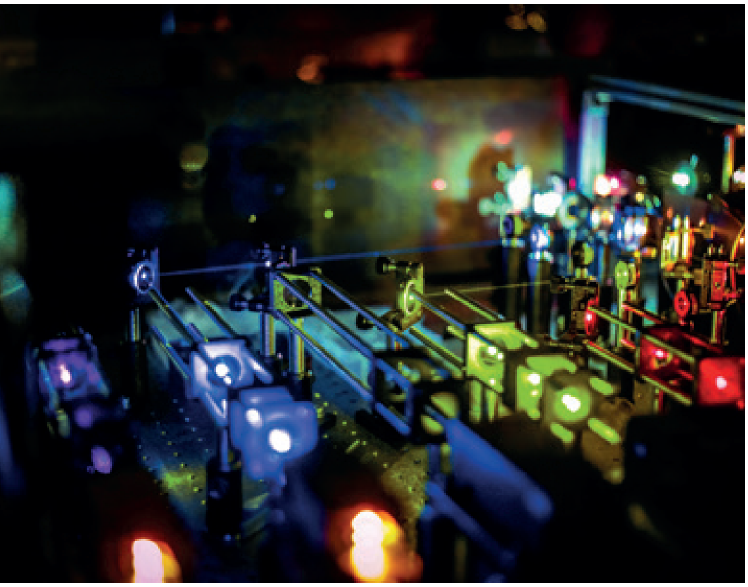
Investigating the chemistry of the inner surface of nuclear fuel cladding for radioactive materials with an X-ray Photoelectron Spectrometer.

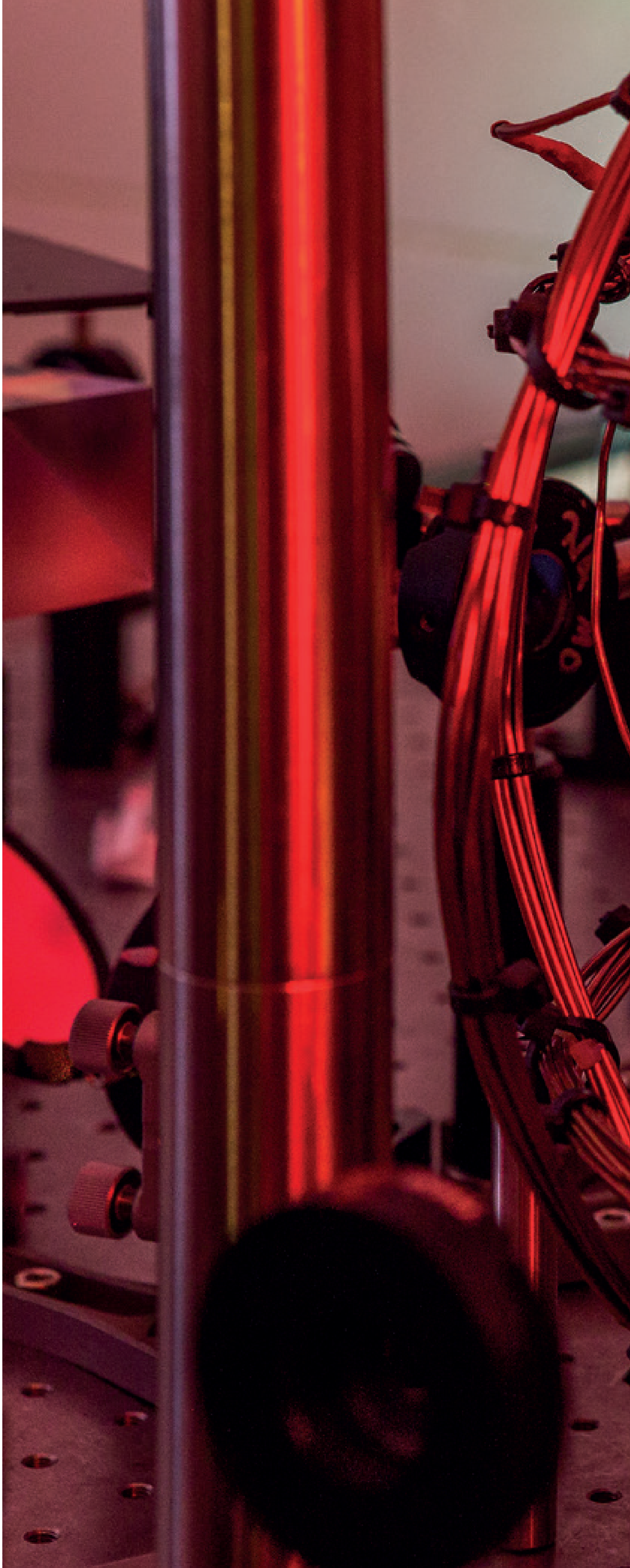
Photo credit: Canadian Nuclear Lab

Bright Lights, Big City?

Scientists at MIT have developed a super-resolution imaging technique (pictured), which uses a combination of multi-colored lasers and mirrors to track transient phenomena; for example, enzyme clustering on genes.

Photo credit: MIT

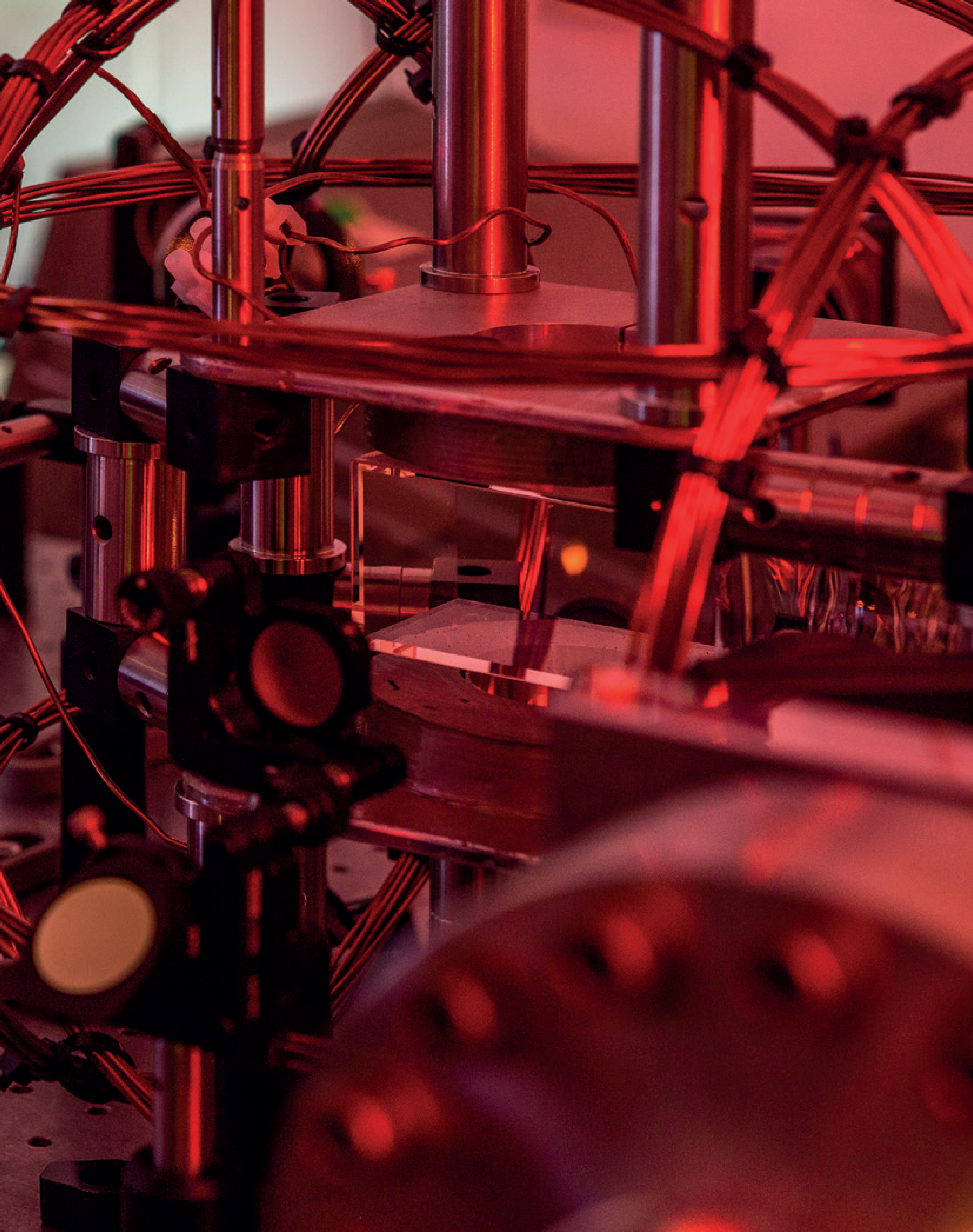




Absolute Zero

Bose–Einstein condensates (BECs) are quite chilly – typically less than a billionth of a degree above zero Kelvin (just above -273.15 ˚C). The small orange cloud to the right of the center of the image is the laser-trapped BEC. BECs are extremely sensitive to tiny changes in the Earth's magnetic field or gravity, so they could have potential utility in navigation systems. Now, physicists from Australian National University (ANU), University of Adelaide and UNSW ADFA (University of New South Wales at the Australian Defence Force Academy), have passed the task of trapping and super cooling atoms with three lasers onto an artificial intelligence system. "I'm sorry Dave, I'm afraid I can't do that."

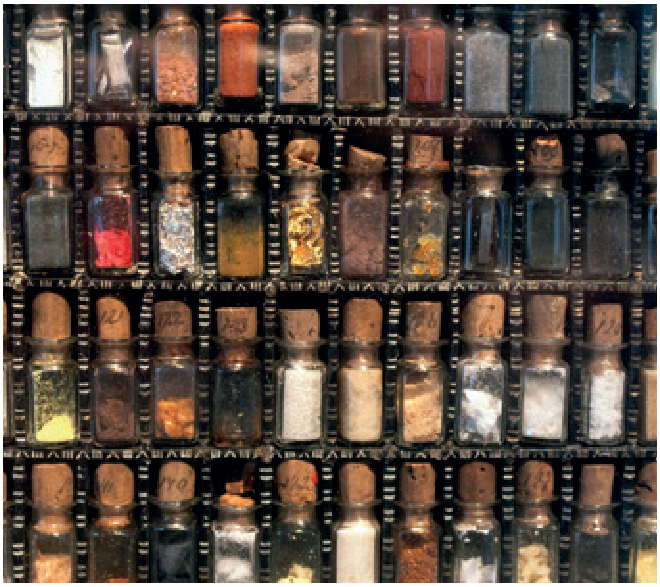
Photo credit: Stuart Hay, ANU



Chemistry Test

A collection of chemical elements and compounds from 1875-1900. Without resorting to your analytical toolbox, care to make any predictions of the contents? Answers on a postcard, please.

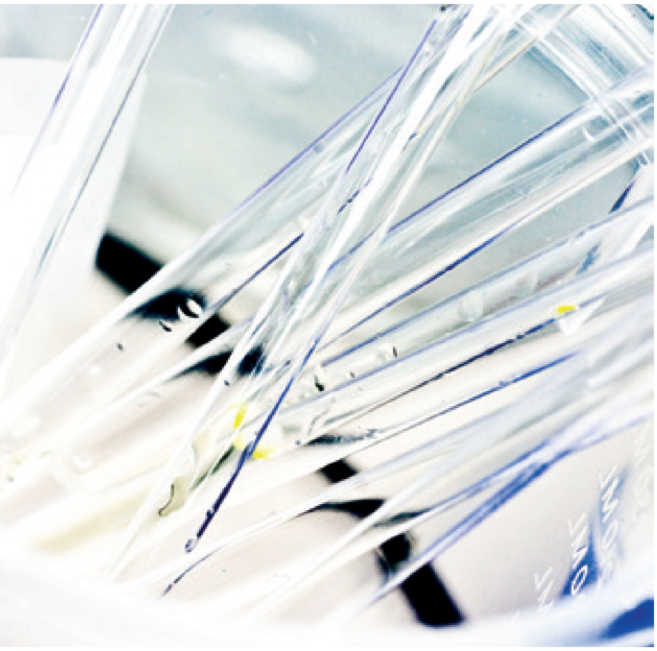
Photo credit: Hans Splinter (Flickr)

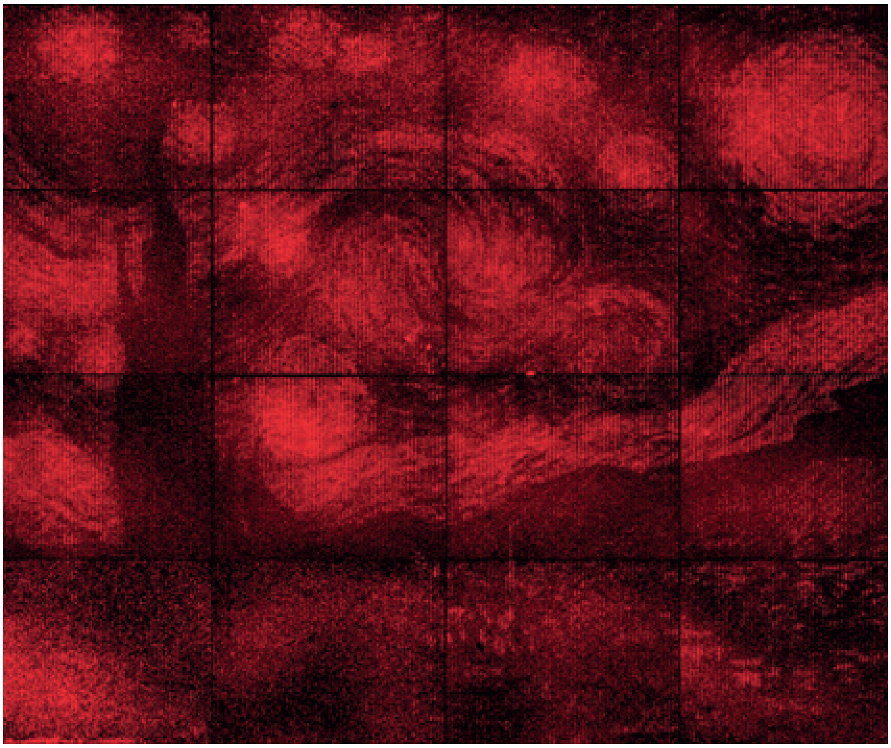


Macro NMR

Overexposed close up of tubes used for nuclear magnetic resonance spectroscopy.

Photo credit: inF! (Flickr)

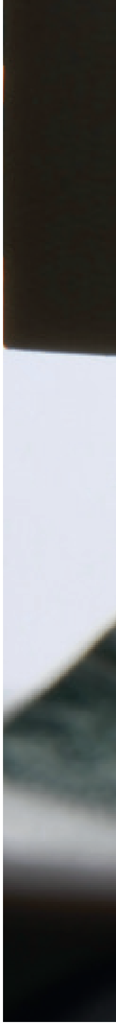


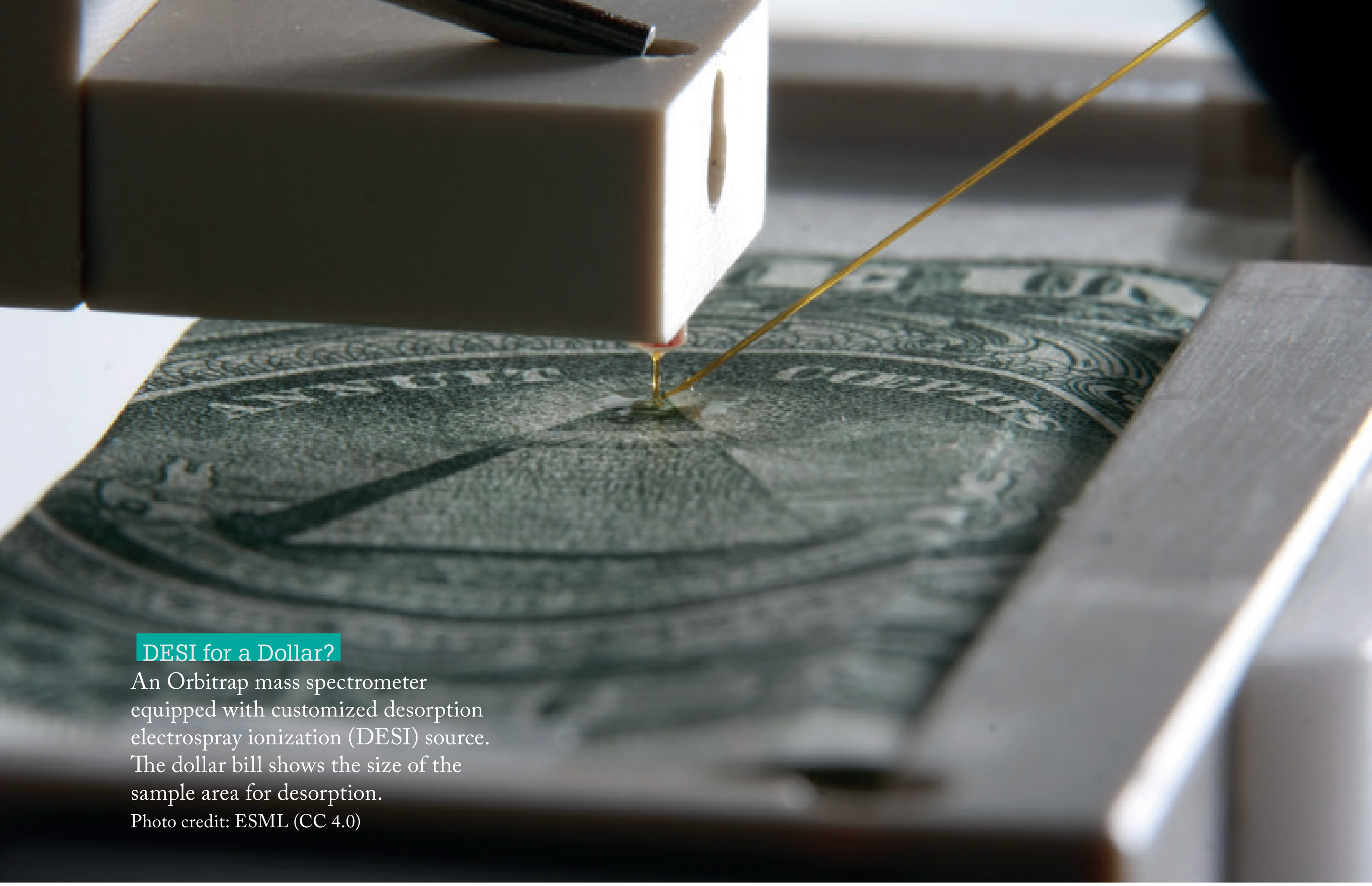


The Starry Night

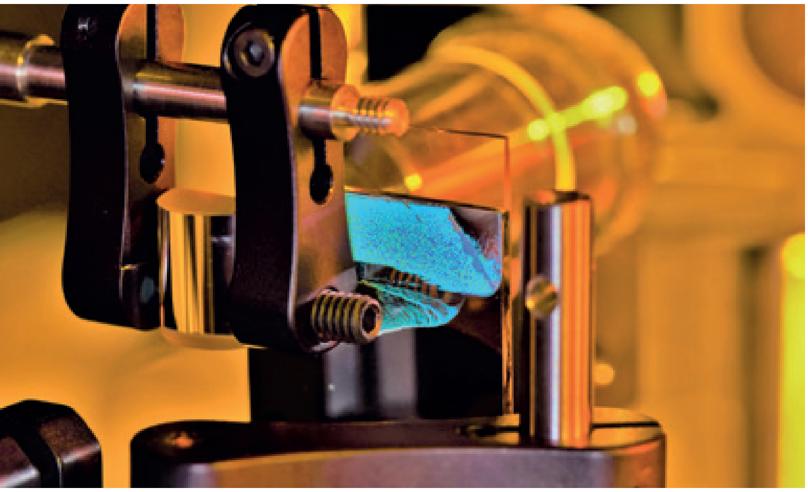
Using folded DNA to precisely place glowing molecules within microscopic light resonators, researchers at Caltech have created one of the world's smallest reproductions of Vincent van Gogh's The Starry Night. The monochrome image – just the width of a dime across – was a proof-of-concept project that demonstrated, for the first time, how the precision placement of DNA origami can be used to build chip-based devices, such as computer circuits, at smaller scales than ever before.

Photo credit: Ashwin Gopinath





DESI for a Dollar?
An Orbitrap mass spectrometer equipped with customized desorption electrospray ionization (DESI) source. The dollar bill shows the size of the sample area for desorption.
Photo credit: ESML (CC 4.0)



The Crystal Maze
Microscale granular crystal in a laser ultrasonic experimental setup. University of Washington mechanical engineers are the first to observe and analyze dynamics of two-dimensional microscale granular crystals. The little understood materials could be used in diverse applications – from signal processing to disease diagnosis to micro-meteorite shielding for spacecraft and better bulletproof vests.
Photo credit: University of Washington

Food & Drink

Sponsored by KNAUER

...Measuring Maple

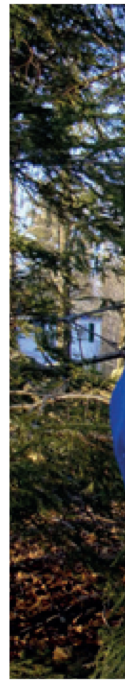
Acer Climate and Socio-Ecological Research Network (ACERnet) aims to investigate the impact of climate change on maple syrup. Maple samples are lyophilized, dissolved in methanol, filtered, then analyzed with reagent-based spectrophotometry and LC-MS to quantify overall and individual phenolic constituents in the maple sap, such as vanillin and coumarin, that contribute to its quality.

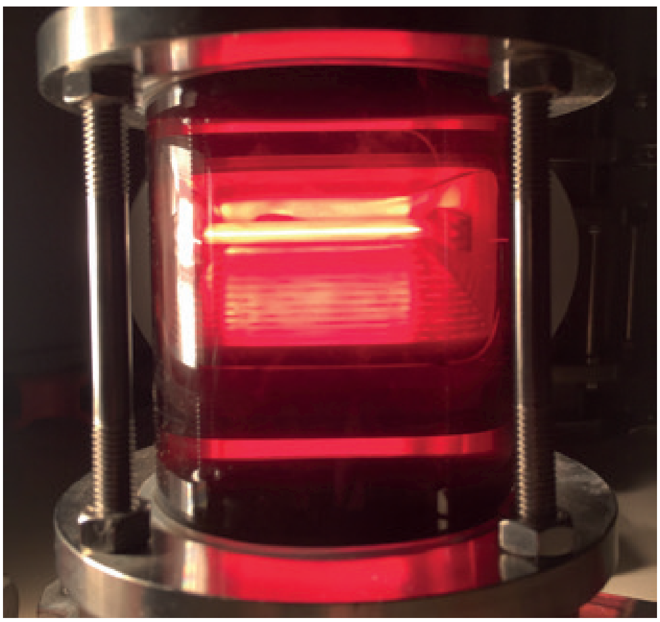
Photo credit: Joshua Rapp, ACERnet

A Real Corker!

Spoiling in wine is often caused by the presence of 2,4,6-trichloroanisole (TCA).
These new NDTech machines use gas chromatography to scan each cork for TCA in 20 seconds, which, according to the company, is significantly less than the 14 minutes for standard gas chromatography technology.

Photo credit: Amorim

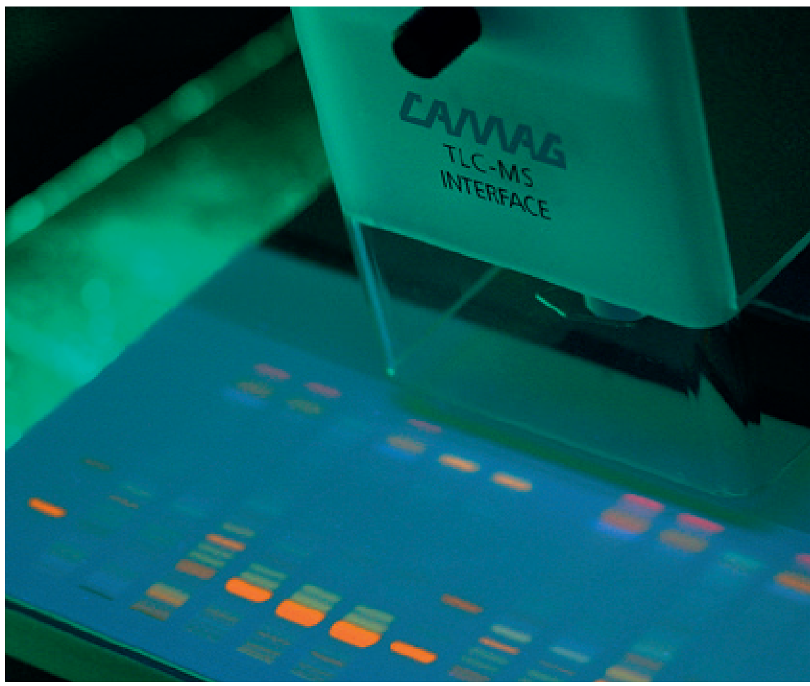




Yo Ho Ho and a Reactor of Rum

Bryan Davis, founder of the Lost Spirits Distillery, has developed a reactor that mimics the aging effect in spirits – cutting the processing time by up to 20 years. This image shows part of the table top reactor, which uses high intensity light to break up the polymers in the oak and dissolved in solution.

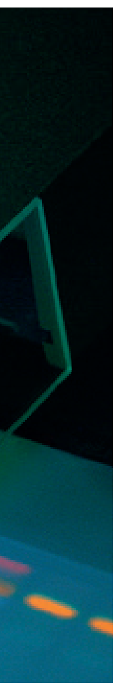
Photo credit: Bryan Davis, Lost Spirits Distillery

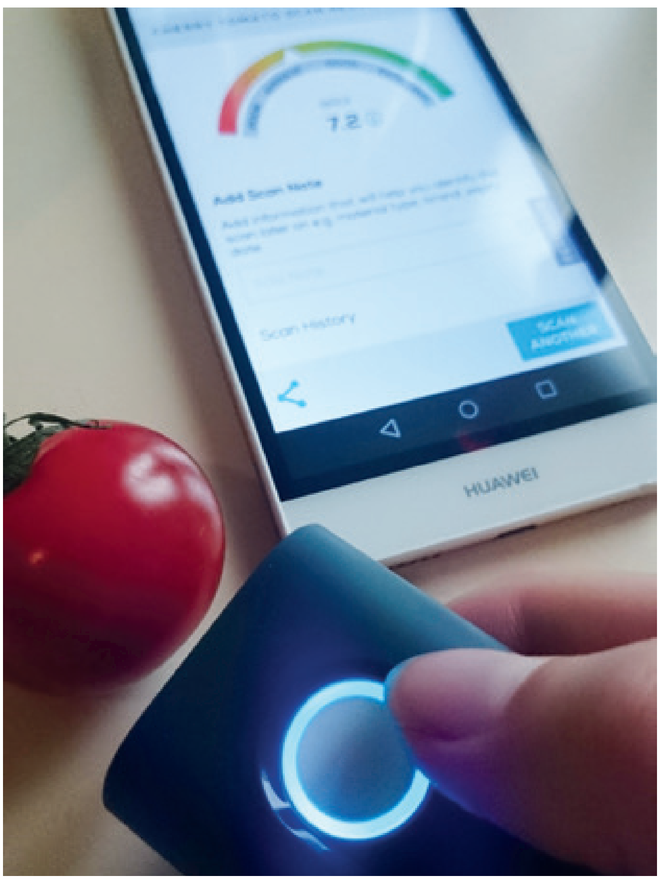


Much Needed TLC

Oak Ridge National Laboratory researchers use high-resolution, thin-layer chromatography coupled with mass spectrometry to separate compounds in ginkgo biloba leaf extracts.

Photo credit: Oak Ridge National Laboratory





Sampling Sap...

A member of the ACERnet team collects sap from trees by inserting a spile (small metal peg). A small amount of sap is then collected in a plastic vial and stored in a freezer until the end of the season.

Photo credit: Joshua Rapp, ACERnet

A Nice Cup of Cocoa

QuEChERs extract of raw cocoa beans for pesticides residue analysis. At the end of the clean up, the extracts are placed in autosampler vials ahead of injection into GC and/or HPLC with mass spectrometry.

Photo credit: JayPiDee (Flickr)

You Say Tomato

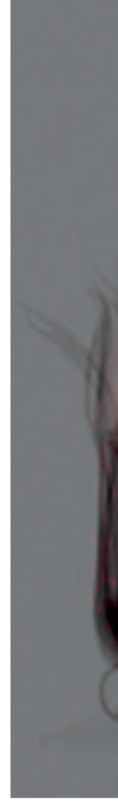
Determining the quality of a cherry tomato with a near-infrared spectrometer-based food scanner (SCiO, ConsumerPhysics, Tel Aviv, Israel) and the 'Tomato Selector' App on a smart phone. Such affordable food scanners could change the way consumers judge the quality of their food.

Photo credit: Yannick Weesepoel, RIKILT

Health & Security

Fat Chance

Scientists aim to produce more efficient fuels and other bioproducts by using multi-omics approaches to understand the fundamental workings of cells in changing environments. This petri dish contains different mutant strain colonies of Yarrowia lipolytica, an oil-producing yeast.



Dandelion Clock

An X-ray image of two dandelions illustrates how gratings-based X-ray imaging provides information on small-angle X-ray scatter (red scale) as well as conventional absorption radiography (gray scale). Such enhancements to X-ray imaging may eventually help distinguish between explosives and benign materials for security screening or even improve medical imaging.

Photo credit: PNNL

Wheel of Fortunate Purification

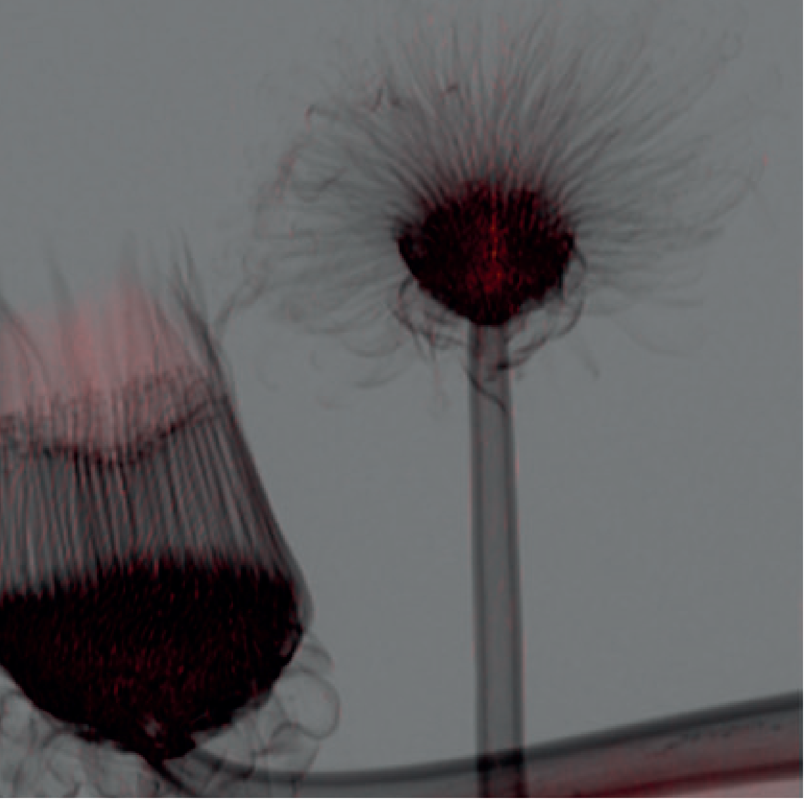
HPLC fractions from one of three protein purification steps in the preparation of respiratory Complex I from E.coli.

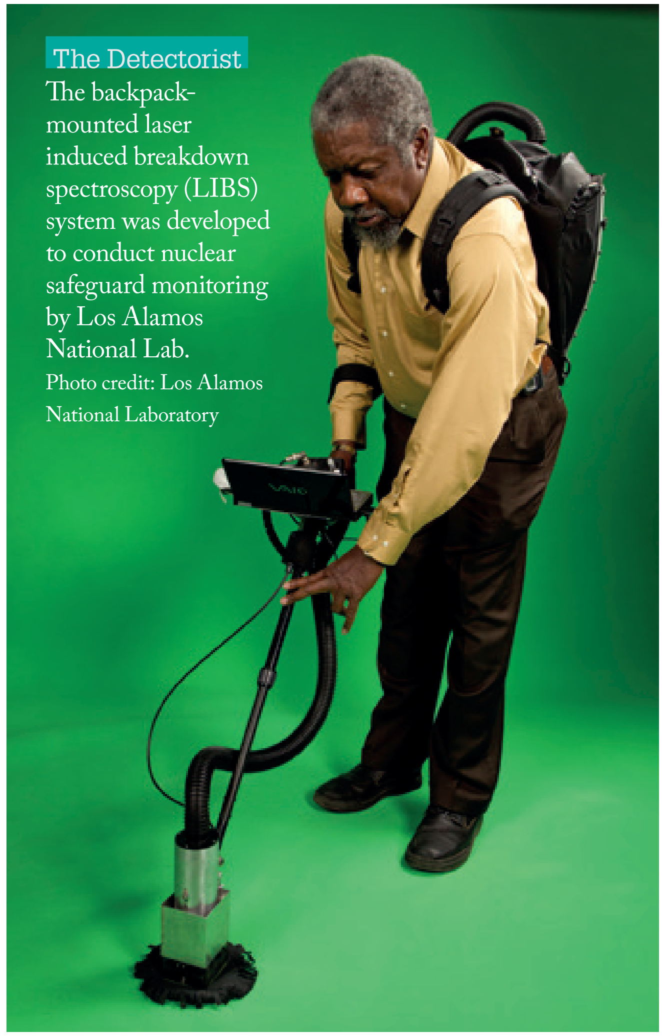
Photo credit: David Morgan (Flickr)

What's Up, Doc?

NASA Twins Study investigators are looking for metabolic changes in retired astronaut Scott Kelly and studying how it correlates to the food he ate during the One-Year Mission and Twins Study. Here, he watches a bunch of fresh carrots float in front of him while preparing to partake of their crunchy goodness on the International Space Station.

Photo credit: NASA

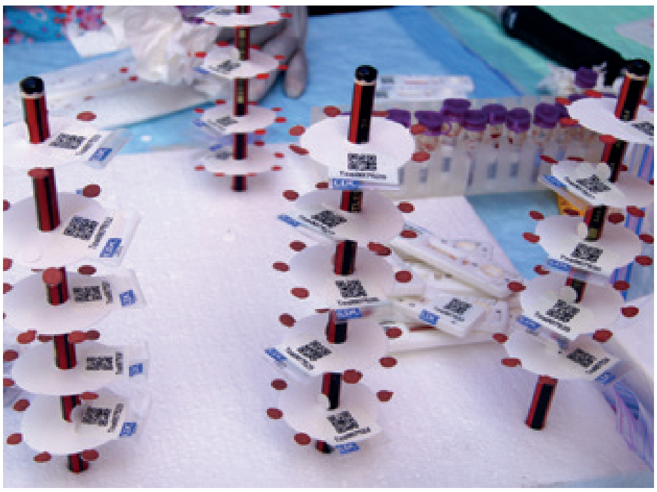


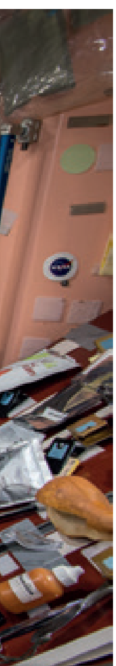


The Detectorist

The backpack-mounted laser induced breakdown spectroscopy (LIBS) system was developed to conduct nuclear safeguard monitoring by Los Alamos National Lab.

Photo credit: Los Alamos National Laboratory





We Are the Children

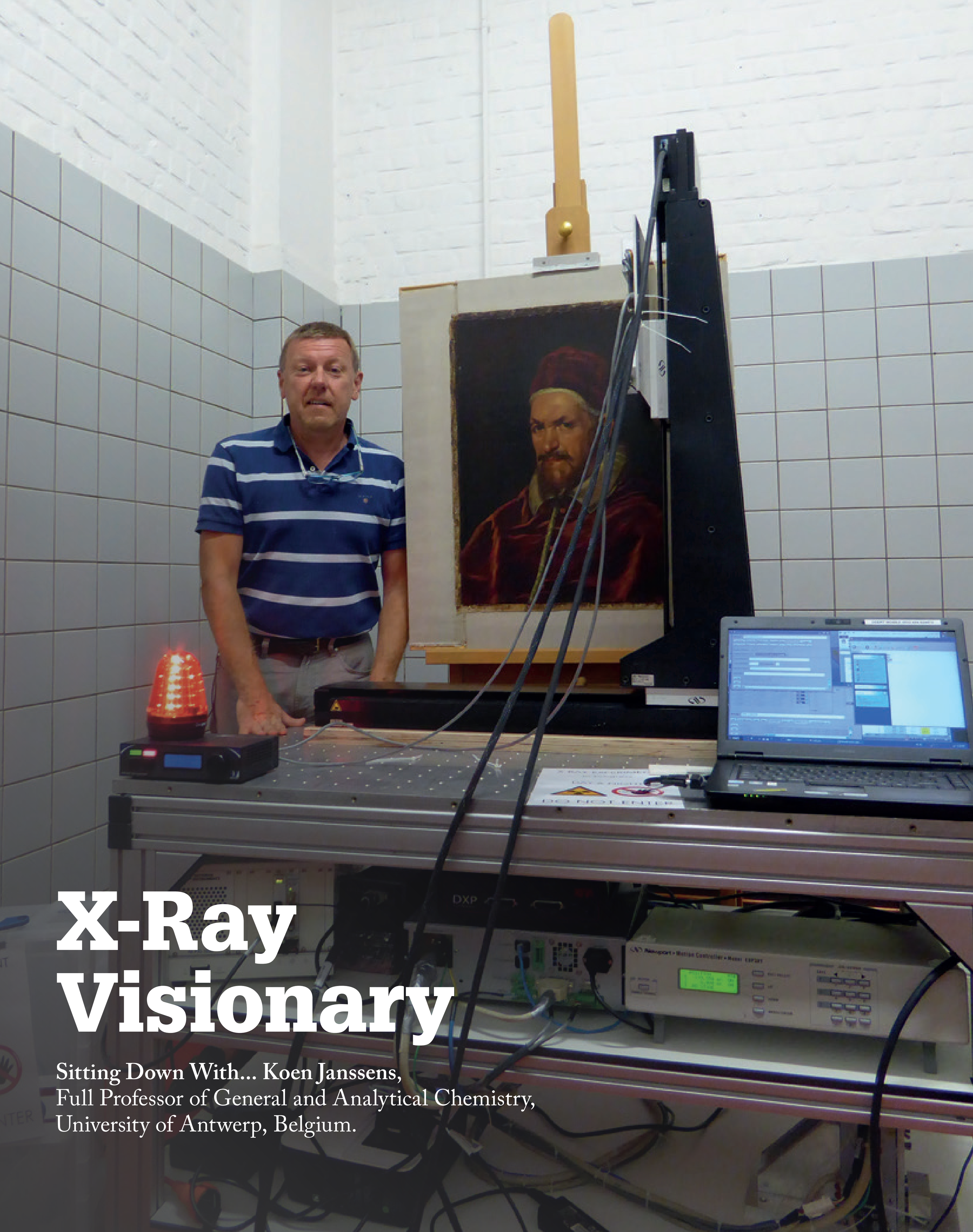
CDC epidemiologist Caitlin M. Worrell's photograph of a collection of dried blood samples, obtained from school children in Northern Haiti as part of a transmission assessment survey (TAS) being carried out in the Dondon Commune. The results of such surveys allows the national program to determine if mass drug administration has been successful in reducing the prevalence of lymphatic filariasis (LF).

Photo credit: Public Health Image Library (PHIL), Centers for Disease Control and Prevention (CDC)

Timeless HPLC

FDA research chemist Judy Regan purifies peptides using HPLC – in 1987.

Photo credit: US Food and Drug Administration



X-Ray Visionary

Sitting Down With... Koen Janssens,
Full Professor of General and Analytical Chemistry,
University of Antwerp, Belgium.

How did you get into X-ray techniques and art analysis?

X-ray-based techniques fit naturally into the world of art analysis because they allow non-destructive analysis of historical objects or materials. But I didn't start out in the art sector – in fact, I got into X-ray-based methods right at the very start of my career, during my master's thesis on automated data reduction of X-ray fluorescence spectra. My mentor at that time was Piet Van Espen, now part of our research group. In the early days, I was in history and the chemistry of historical materials. I started collaborating with archaeologists, which led to a more concrete project on the analysis of archaeological glass. It turned out that the city of Antwerp has a lot of historical glass from the 16th and 17th centuries, and we worked with a local archaeologist to trace the trade and local manufacture of glass.

And that led you to art?

I gradually became more interested in museum collections, especially historical museums, and finally ended up dealing with fine art objects. Again in Antwerp, there were art-historical Rubens specialists who were not only interested in how this master painted, but also in the materials he used. Another notable change was that about 15 years ago, miniaturization revolutionized the x-ray analysis world; the relatively large and cumbersome lab instrumentation had a new partner: portable and battery-operated X-ray fluorescence (XRF) equipment (the early forms of handheld XRF instruments). Because we could bring the instrumentation to the material to be examined, we were able to irradiate a square cm of a painting and figure out indirectly which pigments were used.

What's the added value of such measurements in the art world?

When I first started, people in the art-historical world were not terribly aware of the type of materials each painter was using. Such knowledge can be highly relevant in art authentication. Normally, painters of around the same time use the same set of pigments, so it's not possible to prove that a painting belongs to certain painter, but it's quite easy to prove the opposite: for example, if you find a type of yellow that can only have been used by a 19th century painter, it's not a Rubens! Such analysis can easily be performed with portable XRF – and, most importantly, it can be done in a non-destructive manner.

What kind of people do you have in your group?

Our group has around 25 people now and, perhaps most interestingly, my colleague Karolien de Wael is an electrochemist, who works on highly specific analyses – essentially using electrochemical sensors as detector. She is, of course, very familiar with redox reactions, which is what causes painters' pigments to change color. We combine her electrochemical experience and sensitive methods of detection with our high-end X-ray analysis experiments in paint samples. Normally, if you want to investigate whether a painter's pigment is going to undergo spontaneous reaction, you have to age it in an artificial aging chamber for several months; when it changes color, you can start analyzing the degradation process. With electrochemistry, we can dramatically speed up that kind of analysis. Four people in the group are dealing specifically with photo degradation, and three or four more researchers are interested in developing advanced analytical methods, usually combining several modes of analysis – or constructing mobile instrumentation we can take into museums. The rest of the group don't necessarily work on art analysis, but rather in food or environmental application areas.

What are your most rewarding research moments?

Well, the whole field is both rewarding and fascinating. We take our analytical equipment (often instrumentation we have developed ourselves) to the museum, and we really get up close with masterpieces – normally, you are not allowed to touch! And because we're working with X-rays, the works of art are usually moved somewhere private, like a conservation workshop. Then, we can be alone with very famous works of art – a unique moment of exclusive intimacy; you can talk directly to the art – or rather, via our instruments, the art works talk to us! Scanning usually takes several days, so it allows us to photograph and look at the work of art in a way that we will never experience again; it's a very stimulating aspect of these undertakings. Sometimes we discover completely unknown aspects of a work of art; for example, we may find that Rubens has decided to paint over something he didn't like or want. It's very exciting that, four hundred years later, we can make such decisions visible again. And that insight allows art historians to understand Rubens' frame of mind at the time – what he originally intended and why he decided to change his mind.

Such new knowledge must thrill art historians too...

It's great gift to give! The art historians we work with usually know these paintings very well indeed and may have been studying them for twenty years or more. By doing our chemical imaging analysis, we give them extra information that can sometimes completely change their view of the work, which is very rewarding for us also. Such enriching interactions really define the essence of analytical chemists – often working hard to achieve other people's goals.