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In the news

GCxGC identifies *Deepwater Horizon* oil onshore four years after spill

Comprehensive two-dimensional gas chromatography (GCxGC) is being used in a unique way to fingerprint oil, even four years after most of it has degraded, and to assess how it changes over time.

Scientists from Woods Hole Oceanographic Institution and Bigelow Laboratory for Ocean Sciences in USA have refined the methods typically used to identify the source of oil spills and adapted them for application on a longer time frame to successfully identify oil from the Macondo Well, the source of the Deepwater Horizon (DWH) spill in 2010.

"We were looking at two questions: how could we identify the oil on shore, now four years after the spill, and how the oil from the spill was weathering over time," said Christoph Aeppli, lead author of the study [1], who worked with his then-colleagues at Woods Hole Oceanographic Institution, and University of California, Santa Barbara, on the investigation and the report.

Using GCxGC, the researchers measured the levels of degradation in biomarkers, which were molecular fossils (Fig. 1). Each reservoir has specific amounts of different biomarkers, so oil biomarkers serve as identifiers, much like human fingerprints. When exposed for a long time to the environment, some biomarkers are altered due to natural processes. Oil consists of tens of thousands of compounds, and many of them can be degraded by bacteria or broken down by sunlight.

Resilience of specific biomarkers

This research was designed to determine the resilience of specific biomarkers and to see how they held up when exposed to environmental conditions on shore.

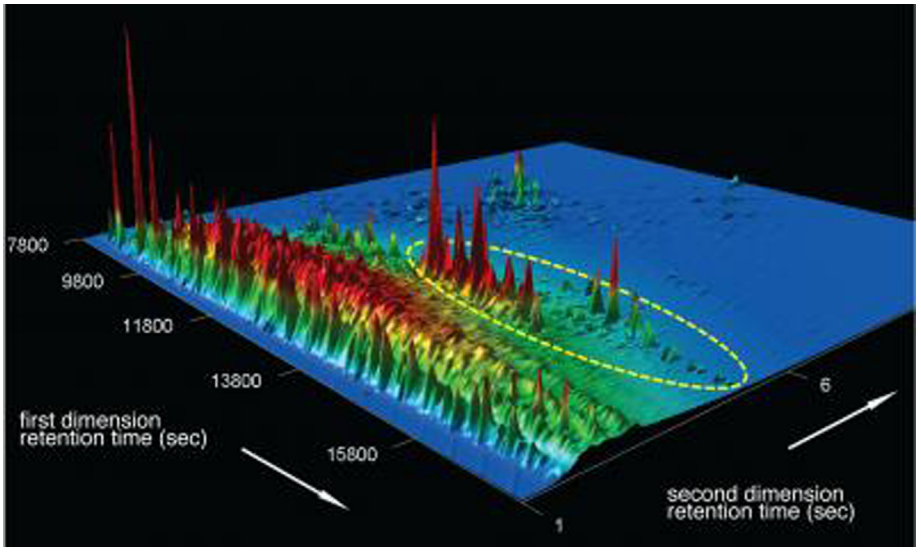

Fig. 1. Researchers used comprehensive two-dimensional gas chromatography (GCxGC) in their oil spill forensics to measure levels of degradation in biomarkers. The biomarkers here are shown inside the dotted line. (Credit: Christoph Aeppli, Bigelow Laboratory for Ocean Sciences).

"We found that some biomarkers – homohopanes and triaromoatic steroids (TASs), specifically – degraded within a few years following the Deepwater Horizon spill," said Chris Reddy, a scientist at Woods Hole Oceanographic Institution and co-author of the paper. "These biomarkers are not as resilient as once thought and they may provide a future window into determining how much, and how quickly, these oil components may linger in the environment when exposed to air, sunlight, and the elements.

The researchers sought to determine the specific source of the degradation of biomarkers. Through analysis of oil-soaked "sand patties" collected along the Gulf shore over a 28-month period, they found that most biomarker compounds were recalcitrant and could be used to identify DWH oil. However, other biomarkers degraded.

"This knowledge is helping us improve our oil spill forensics," said Aeppli. "It is providing a foundation for better, longer-term identification techniques that account for exposure of oil to wind, waves, sunlight, and microbial degradation over long times."

Aeppli, Reddy and colleague Dave Valentine from UC Santa Barbara will apply this new oil-fingerprinting technique to process tens of thousands of samples collected shortly after the DWH spill.

Contact:
Christoph Aeppli
Bigelow Laboratory for Ocean Sciences
Woods Hole, MA, USA
Tel.: +1 (207) 315 2567
E-mail: caeppli@bigelow.org.

Reference

[1] C. Aeppli, et al., Recalcitrance and degradation of petroleum biomarkers upon abiotic and biotic natural weathering of *Deepwater Horizon* oil, Environ. Sci. Technol. (2014) doi:10.1021/es500825q.

http://dx.doi.org/10.1016/j.trac.2014.06.001

Malaria has genetic 'barcode'

A new genetic "barcode" for malaria parasites could be used to track and to contain the spread of the disease, according to the London School of Hygiene & Tropical Medicine (LSHTM) [1].

Malaria kills around 600,000 people each year, and increased population mobility through international air travel carries further risks of re-introducing parasites to areas from which it is eliminated and dispersing drug-resistant parasites to new regions.

A highly predictive barcode in the genetic sequence of the malaria parasite *Plasmodium falciparum* can be used to identify the geographic origin of a parasite from a blood sample and to monitor its spread.

The LSHTM researchers analyzed the DNA of over 700 *P. falciparum* malaria parasites taken from patients in 14 countries in West Africa, East Africa, South East Asia, Oceania and South America. They found several short genetic sequences that were distinct in the DNA of parasites from certain geographic regions, and those allowed them to design a genetic barcode to be used in identifying the source of new infections.

"Being able to determine the geographic origin of malaria parasites has enormous potential in containing drug resistance and eliminating malaria," said lead author Taane Clark, Reader in Genetic Epidemiology and Statistics at LSHTM. "Our work represents a breakthrough in the genetic barcoding of *P. falciparum*, as it reveals very specific and accurate sequences for different geographic settings. We are currently extending the barcode to include other populations, such as India, Central America, southern Africa and the Caribbean, and plan to include genetic markers for other types of malaria, such as *P. vivax*."

For the first time, the researchers studied the DNA found in two parts of the parasite's cells outside the nucleus. The mitochondria (the power houses of the cell) and the apicoplasts (used in the metabolism of the cell) are inherited through maternal lines only, so their genes remain much more stable over generations, and have therefore often been used as tools to explore the origins of humans.

By identifying short sequences in the DNA of the parasite's mitochondria and apicoplasts, which were found to be specific for different geographic locations, the team were able to design a highly accurate genetic barcode (92% predictive), which is stable and geographically informative over time.

"By taking finger-prick bloodspots from malaria patients and using rapid gene-sequencing technologies on small amounts of parasite material, local agencies could use this new barcode to quickly and accurately identify where a form of the parasite may have come from, and help in programs of malaria elimination and resistance containment," said co-author Cally Roper, Senior Lecturer in Malaria Genetics at LSHTM.

This barcode is limited, as the LSHTM study lacked representation of the Indian sub-continent, Central America, southern Africa and the Caribbean, due to the scarcity of sequence data from these regions. Also, there is a need to study more samples from East Africa, a region of high genetic diversity, high migration and poor predictive ability.

Contact:
Cally Roper
London School of Hygiene and Tropical Medicine
London, UK
Tel: +44 (0)20 7927 2616
E-mail: cally.roper@lshtm.ac.uk

Reference

[1] M.D. Preston, et al., A barcode of organellar genome polymorphisms identifies the geographic origin of *Plasmodium falciparum* strains, Nat. Commun. 5 (2014) <http://dx.doi.org/10.1038/ncomms5052>.

SiMPs increase power of MRI

Silicon mesoporous particles (SiMPs) that contain even smaller particles of iron oxide could make magnetic resonance imaging (MRI) a far more powerful tool to detect and to fight disease [1].

Scientists at Rice University and The Methodist Hospital Research Institute (TMHRI), Houston, Texas, USA, led an international team of researchers in creating composite particles that can be injected into patients and guided by magnetic fields. Once in position, the particles may be heated to kill malignant tissues or trigger the release of drugs at the site.

The team, led by Rice chemist Lon Wilson and TMHRI scientist Paolo Decuzzi, was searching for a way to overcome the challenges presented by iron-oxide nanoparticles (Fe_3O_4-NPs) that are good at some things but not others, depending on their size.

Fe_3O_4-NPs can be manipulated with magnets, provide excellent contrast under MRI, create heat when triggered and degrade quickly. But they cannot do all that simultaneously and team needed a way to decouple the functions from their sizes.

The answer was to package thousands of Fe_3O_4-NPs – with magnetic cores as small as 5 nm across – inside larger particles. The researchers made two such nanoconstructs, embedding Fe_3O_4-NPs in silicon mesoporous particles (SiMPs) (Fig. 2) and discoidal polymeric nanoconstructs (DPNs). They knew

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   Trends Anal. Chem. 30 (2011) 204.
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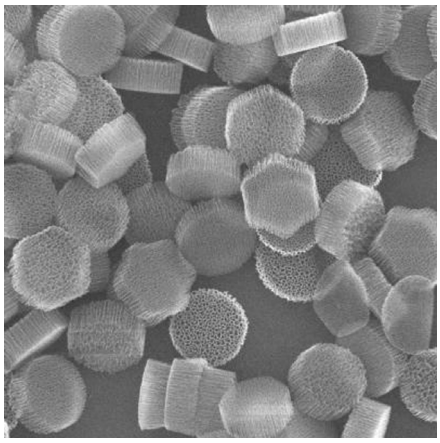

Fig. 2. Silicon mesoporous particles (SiMPS), about 1 µm across, contain thousands of much smaller particles of iron oxide. The SiMPs can be manipulated by magnets and gather at the site of tumors, where they can be heated to kill malignant tumors or trigger the release of drugs. The particles were created by an international team led by scientists at Rice University and The Methodist Hospital Research Institute in Houston, Texas, USA. (Credit: Wilson Group/ Rice University).

from previous research that sub-µm-sized SiMPs and DPNs naturally accumulate within the blood vessels of the tumor.

Fe_3O_4-NPs enhance the ability to position and hold the particles in place with magnets.

"They get attracted by the magnet," said lead author and Rice graduate student Ayrat Gizzatov, "and that induces another dipole-dipole magnetic interaction among the particles and increases their interparticle communication mechanism."

Tests showed Fe_3O_4-NPs made the nanoconstructs 10 times better than traditional contrast agents with what amounted to significantly lower doses of iron than used in current practice.

The new research also showed that, as a general principle, confining MRI contrast agents (e.g., Fe_3O_4-NPs) in geometric structures enhances their relaxivity – the property that makes the agents appear in MRI images. The shorter the relaxation time, the greater the contrast in the image.

While the particles are too big to target specific proteins, Gizzatov said it might also be possible to modify them with elements that will increase their accumulation in tumors.

Contact:
Professor Paolo Decuzzi
The Methodist Hospital Research Institute
Houston, Texas, USA
Tel.: +1 (713) 441-7316
E-mail: pdecuzzi@houstonmethodist.org

Reference
[1] A. Gizzatov, et al., Adv. Funct. Mater. (2014) doi:10.1002/adfm.201400653.

Test detects defective prions in blood

An assay can detect prions in blood samples from humans with variant Creutzfeld-Jakob Disease (vCJD) and in animals at early stages of the (asymptomatic) incubation phase [1].

The first cases of vCJD (which became known as Mad Cow Disease in humans) occurred in the late 1990s and were thought to be the consequence of eating beef products contaminated with defective prions. Since then, several cases of secondary infections caused by transfusions with blood from donors, who subsequently developed vCJD, have been reported, so raising concerns about the safety of blood and blood products.

To develop the assay, Olivier Andréoletti, from the Ecole Nationale Vétérinaire de Toulouse, France, and colleagues first optimized a method called protein misfolding cyclic amplification (PMCA). The method mimics in a test tube the process by which misfolded (toxic) prions propagate, and the researchers determined experimental conditions that enabled efficient PMCA amplification of the vCJD agent in the blood.

Having defined such conditions, they showed that the assay can detect vCJD in asymptomatic but infected animals in the early phase of the incubation period. They examined blood samples collected from infected sheep and macaques (because vCJD-infected macaques are considered the best model of the human disease). In both models, the assay accurately identified infected animals and detected the presence of vCJD prions in blood from macaques shortly after the initial infection (and several years before the onset of clinical disease).

Samples from human vCJD patients are rare, and none exists from individuals at the preclinical stage of the disease. To test the assay in human blood, the researchers obtained samples from vCJD patients and non-infected controls and analyzed them blind in two different laboratories. The assay correctly and consistently identified three of the four vCJD affected patients, and yielded no false-positive result in any of the 141 healthy controls. The negative result in one of the vCJD samples raised the question of the potential absence of vCJD agents in the blood of certain patients diagnosed with the disease.

"The blood-borne transmission of vCJD is a major concern for blood transfusion banks, plasma derived products manufacturers and public health authorities," commented the authors. "A vCJD blood-screening test would represent an ideal solution for identifying donors or blood donations that might be at risk."

Contact:
Olivier Andréoletti
Interactions Hôtes Agents Pathogènes
Ecole Nationale Vétérinaire de Toulouse
Toulouse, France
Tel.: +33 677-182-184
E-mail: o.andreoletti@envt.fr

Reference
[1] C. Lacroux, et al., Preclinical detection of variant CJD and BSE prions in blood, PLoS Patholog 10 (6) (2014) e1004202. <http://dx.plos.org/10.1371/journal.ppat.1004202>.

Kirkbright invites applications for 2015 Award

The Gordon F. Kirkbright Bursary is open to applications for the 2015 Award.

A prestigious annual award, it enables a promising student or non-tenured young scientist of any nation to attend a recognized scientific meeting or to visit a place of learning.

The fund for this bursary was established in 1985 as a memorial to Professor Gordon Kirkbright, in recognition of his contributions to analytical spectroscopy and to science in general.

Although the fund is administered by the Association of British Spectroscopists (ABS) Trust, the award is not restricted to spectroscopists.

The closing date for entries is 31 December 2014.

For further information, please contact John Chalmers at:

E-mail address: vibspecconsult@aol.com

Graduate student wins 2014 Award

The Gordon F. Kirkbright Bursary Award for 2015 went to third year graduate student Jozef Lengyel of the J. Heyrovský Institute of Physical Chemistry of the Academy of Sciences of the Czech Republic in Prague, Czech Republic, for visiting Berlin for his project (see proposal below).

Lengyel's research interests focus on the molecular clusters with a particular emphasis on atmospheric and biological implications using molecular beam techniques, advanced mass spectrometric methods and different laser spectroscopic methods.

To date, Lengyel (Fig. 3) has co-authored 11 scientific publications in peer-reviewed journals.

Fig. 3. Jozef Lengyel, Winner of The Gordon F. Kirkbright Bursary Award 2014.

Successful proposal for 2014 Award

The study of atmospheric aerosols attracts considerable attention because of its influence on atmospheric chemistry and climate. In our laboratory in Prague, we implement several experimental methods ranging from mass spectrometric techniques to photofragment kinetic energy spectroscopy. Their combination in one experiment can provide unprecedented comprehensive information on the chemical composition, nucleation and reactivity of aerosols. Recently, we have investigated pickup and nucleation processes of nanometer-sized aerosols and ice particles [1,2]. The experiments revealed the dominant role of the nitric acid molecule as the nucleation center. Besides, HNO_3 acidic dissociation was suggested in complexes with more than four water molecules in agreement with earlier experiments and *ab initio* calculations.

On the other hand, Winter's group in Berlin is investigating liquid-jet photoelectron spectroscopy for exploring the electronic structure of complex system, such as HNO_3 or H_2SO_4, in water [3,4]. The dissociation of these acids at the surface of aqueous solution can be quantified and the ratio of dissociated and undissociated acid (degree of dissociation) can be determined using X-ray photoelectron spectroscopy (XPS).

This proposal focuses on chemical reactivity occurring on ice and water in a variety of forms, from low-temperature water clusters and aerosol particles to bulk at the room temperature. We will focus on the following questions: Can we study the elementary processes (such as acidic dissociation) in the presence of solvent molecules at the detailed molecular level? What is the influence of the local environment experienced by the contaminants? Does it differ on/in the solid aerosols vs. on/in the liquid-vapor interface? We plan to target these questions by a combination of techniques available in both groups.

The mixed aerosols in molecular beams can be produced by two methods: pickup of acids to pure ice aerosols results in acid molecule at the surface; while coexpansion from acid vapor yields the acid located inside the aerosol. The chemical reactivity will be determined by mass spectrometry [1] and the spectroscopy of kinetic energies of photofragments using velocity map imaging method. The formation of zwitterionic structure can be revealed, e.g., by analysis of kinetic energy of the H atom from the H_3O radical [5]. XPS will be used to determine the electronic structure of the complex system at the surface and in bulk of the liquid water jet. The experiments will be supported by the theoretical calculations. Each of these approaches alone can provide a deep insight into a particular studied phenomenon, yet their application in a concerted manner within the project will provide an unprecedented depth of knowledge about the studied complex systems.

References

[1] J. Lengyel, A. Pysanenko, J. Kočišek, V. Poterya, C.C. Pradzynski, T. Zeuch, P. Slavíček, M. Fárník, Nucleation of mixed nitric acid–water ice nanoparticles in molecular beams that starts with a HNO_3 molecule, J. Phys. Chem. Lett. 3 (2012) 3096.

[2] J. Lengyel, J. Kočišek, V. Poterya, A. Pysanenko, P. Svrčková, M. Fárník, D. Zaouris, J. Fedor, Uptake of atmospheric molecules by ice nanoparticles: pickup cross sections, J. Chem. Phys. 137 (2012) 034304.

[3] T. Lewis, B. Winter, A.C. Stern, M.D. Baer, C.J. Mundy, D.J. Tobias, J.C. Hemminger, Does nitric acid dissociate at the aqueous solution surface? J. Phys. Chem. C 115 (2011) 21183.

[4] A.M. Margarella, K.A. Perrine, T. Lewis, M. Faubel, B. Winter, J.C. Hemminger, Dissociation of sulfuric acid in aqueous solution: determination of the photoelectron spectral fingerprints of H_2SO_4, HSO_4^-, and SO_4^{2-} in water, J. Phys. Chem. C 117 (2013) 8131.

[5] V. Poterya, J. Fedor, A. Pysanenko, O. Tkáč, J. Lengyel, M. Ončák, P. Slavíček, M. Fárník, Photochemistry of HI on argon and water nanoparticles: hydronium radical generation in $HI(H_2O)_n$, Phys. Chem. Chem. Phys. 13 (2011) 2250.

Raman microscopy and imaging win awards

Research groups from the USA, France and Germany won the top three awards for scientific papers in 2013 that featured results acquired with a WITec instrument.

Scientists from all over the world submitted more than 60 publications. A jury

chose the three winning papers on selection criteria that included the impact of the scientific results and the innovation of the techniques applied.

Yufeng Hao won Gold Award for his work on graphene in Rodney Ruoff's research group at the Department of Mechanical Engineering and the Materials Science and Engineering Program, University of Texas, USA. The group successfully collaborated with Luigi Colombo's laboratory from Texas Instruments (TI) and published their work in *Science* [1]. A confocal Raman image of the publication was also chosen as the cover image for that issue of *Science* (Fig. 4). The scientific paper convinced the jury by demonstrating the beneficial application of confocal Raman imaging for high-impact graphene research. Hao (Fig. 5) had just moved from TI to New York to start a new position at Columbia University where he continues his work.

The Silver Award winners were researchers from the Centre de Biophysique Moléculaire, CNRS, France. Frédéric Foucher and Frances Westall showed comprehensive Raman imaging studies of microfossils from Norway, Canada, and Australia [2]. The jury honored Foucher and colleague for their successful application of (3 D) Raman imaging as part of their compelling scientific work.

The Bronze Award went to the research group of Maike Windbergs at the Department of Biopharmaceutics and Pharmaceutical Technology, Saarland University, Germany for a paper [3] with her group member Birthe Kann on pharmaceutical research that demonstrated the successful use of confocal Raman microscopy for the investigation of rough samples in combination with optical profilometry.

WITec has announced the PaperAward 2015 for publications published in 2014. Researchers from all fields of applications and both academia and industry are invited to submit their publications featuring results acquired with a WITec instrument to papers@witec.de.

Fig. 4. Image used on cover of *Science* to illustrate paper by Gold Award winner Yufeng Hao [1].

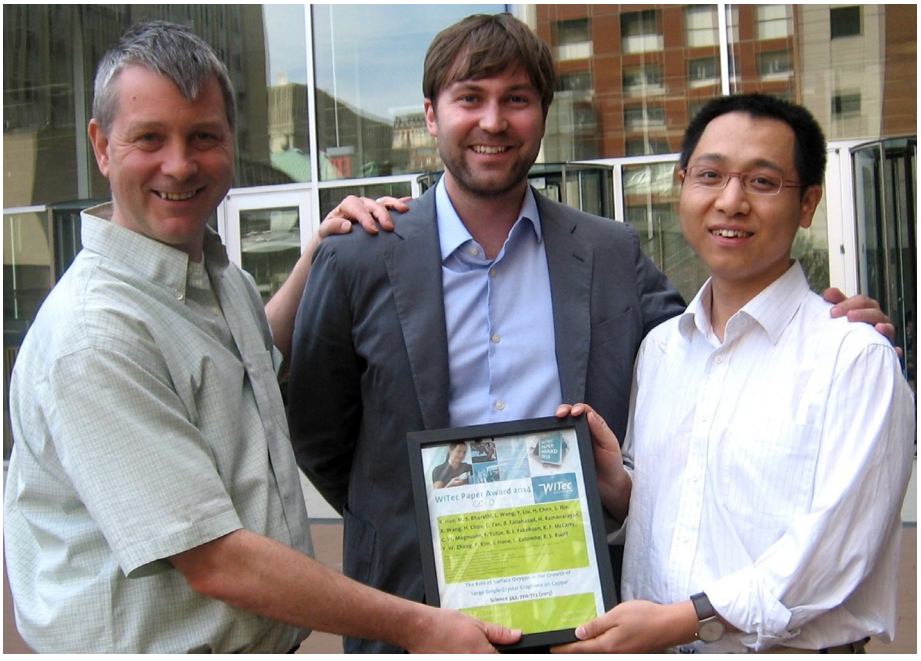

Fig. 5. Gold Award winner Yufeng Hao (right) and James Hone (left) in front of Columbia University in New York, USA. Hao and colleagues receive the award certificate in gold and a €500 ($US)Amazon gift card from Tavis Exzell, Regional Sales Manager at WITec USA (middle).

References

[1] Y. Hao, M.S. Bharathi, L. Wang, Y. Liu, H. Chen, S. Nie, et al., The role of surface oxygen in the growth of large single-crystal graphene on copper, Science (Washington, DC) 342 (2013) 720–723. doi:10.1126/science.1243879.

[2] F. Foucher, F. Westall, Raman imaging of metastable opal in carbonaceous microfossils of the 700-800 ma old Draken Formation, Astrobiology 13 (2013) 57–67. doi:10.1089/ast.2012.0889.

[3] B. Kann, M. Windbergs, Chemical imaging of drug delivery systems with structured surfaces-a combined analytical approach of confocal Raman microscopy and optical profilometry, AAPS J. 15 (2013) 505–510. doi:10.1208/s12248-013-9457-7.

Collaboration advances biopharmaceutical analysis

To develop advanced analytical profiling platforms and applications to characterize biologic and biosimilar drugs, scientists at Thermo Fisher Scientific (TFS) and BioAnalytix, Inc., of Cambridge, MA, are combining their expertise.

Biologic drugs, such as therapeutic monoclonal antibodies, comprise extremely large and complex biomolecules, which represent one of the most significant areas in the pharmaceutical industry. Minor differences in biologic structure from drug to drug, or from manufacturing lot to manufacturing lot can profoundly affect the safety and efficacy profiles of these drugs.

Analytic workflows need to characterize the molecules accurately and to ensure reproducible consistency during their development, scale-up and manufacturing processes. Active in analytic system performance and precise biologic analysis, TFS and BioAnalytix are collaborating to develop advanced analytical profiling standards to support, to enable and to accelerate development of biologic and biosimilar drugs.

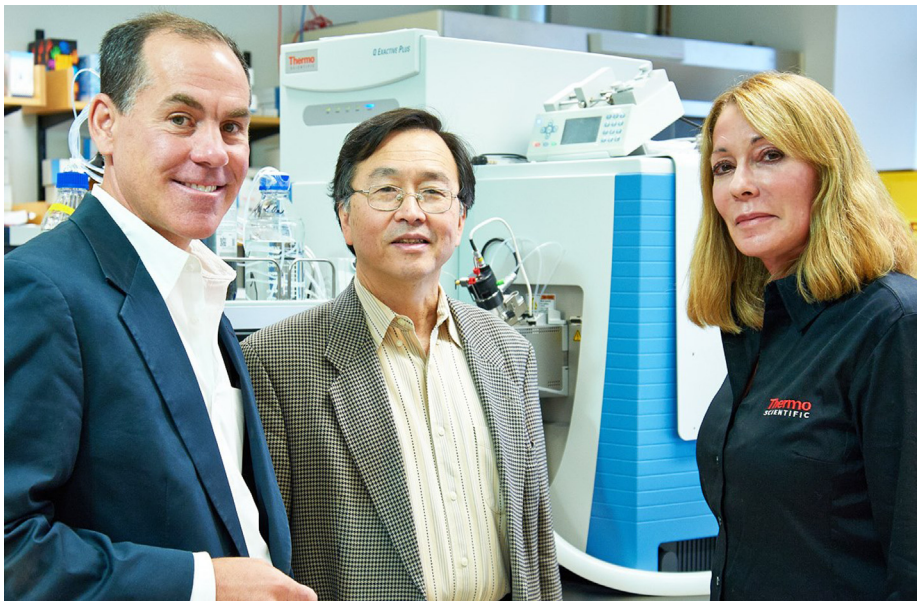

Fig. 6. Left to right: BioAnalytix President and CEO Kirt Poss, BioAnalytix Head of Analytical Science Shiaw-Lin (Billy) Wu, and Thermo Fisher Scientific's Mary Lopez.

BioAnalytix's team of biologic drug experts will use TFS's Orbitrap-based mass spectrometers, sample preparation, separation/enrichment, standards, reagents and software to develop advanced applications.

"In partnership with top pharmaceutical companies and technology leaders, like TFS, it is our goal to establish and to leverage leading analytical profiling standards in advancing the development, manufacture and regulatory approval of biologic and biosimilar drugs worldwide," said BioAnalytix President and CEO Kirt Poss (Fig. 6).

"This is an exciting real-world opportunity to showcase the ability of our technologies to provide unique, critical insights into protein structures," said TFS Vice-President, Marketing Ken Miller. "We have a long history of successful collaboration with BioAnalytix scientists, and we look forward to continuing this productive relationship."