

Shimadzu  
**Journal** VOL. **03** **ISSUE 1**

Environmental Analysis and more...





## Director's note



Dear Reader,

The year 2015 has started with the celebration of Shimadzu's 140th anniversary. We have been striving for these 140 years to offer the highest technologies and valuable solutions to meet our customers' various needs, guided by our corporate philosophy: "Contributing to Society through Science and Technologies". We established this year's new corporate slogan: "Design the future –Best for our customer–" and pledged to make every effort to fulfill customers' dreams. We, as a manufacturer, believe that collaboration with customers should generate innovative instruments and create valuable solutions that deliver true contributions to the world.

*Shimadzu Journal* has been highlighting various collaborative research projects as well as technical reports and applications from our library since its launch in October 2013. Previous issues have focused on the fields of food safety, pharmaceuticals, clinical research, material science and toxicology / forensics, and have showcased outstanding results from collaborations with leading experts in each field.

This latest issue focuses on environmental analysis and contains information from a collaboration with Professor Kevin A. Schug of the University of Texas at Arlington, USA. He and his team use our state-of-the-art analytical instruments to assess environmental waters. In addition, this issue contains much information on other applicable topics, as well as the latest news and applications.

For 140 years, Shimadzu has been developing instrumentation for a broad range of applications in a variety of markets. This history is rivaled only by the passion we have for the future and the sincere desire to establish high-quality relationships with you. Our goal is to exceed your expectations by providing meaningful solutions and exceptional service and support.

Thank you for being a part of Shimadzu's history and future. We hope this journal will be of great help to all of you, and we welcome your feedback.

Yours Sincerely,

**Teruhisa UEDA, PhD.**

General Manager, Analytical & Measurement Instruments Division



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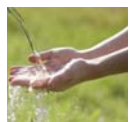
## Featuring Environmental Analysis



### Insight from Customer

#### **Professor Kevin A. Schug of the University of Texas at Arlington** \_\_\_\_\_ 4

We interviewed Dr. Kevin A. Schug, Associate Professor and Shimadzu Distinguished Professor of Analytical Chemistry in the Department of Chemistry and Biochemistry at the University of Texas at Arlington (UT Arlington). His research is mainly on the separation of bioactive chemical compounds with mass spectrometry techniques.



### Environmental Analysis

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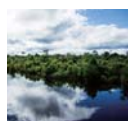
About 15% of Americans rely on their own private wells for their drinking water, but unlike public water systems, these are not subject to either state or federal regulations and are not regularly tested by experts. The use of multiple instruments to analyze groundwater has the advantages of describing groundwater samples more completely than individual measurements, validating measurements, and protecting against reporting false positives. To demonstrate this combinatorial analytical advantage, Shimadzu analytical instruments were used to characterize groundwater samples.



### Interview

#### **Contributing to Develop Environmental Technologies Based on Biodiversity** \_\_\_\_\_ 11

We interviewed professor Michihiko Ike from the Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, who is involved in cutting-edge research on environmental technologies based on biodiversity.



#### **Shimadzu Selection** \_\_\_\_\_ 13

These articles were selected by Shimadzu for this issue. The articles are from application notes and technical reports, relating to environmental analysis and feature a variety of instruments we produce. The cutting-edge technologies are also included. Please obtain the articles of your interest through the links on the titles.



### Environmental Analysis

#### **Hydraulic Fracturing and the Environment** \_\_\_\_\_ 15

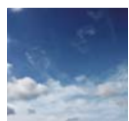
Hydraulic fracturing is a well-stimulation process used to improve recovery and production of oil and natural gas from unconventional petroleum deposits. Coal bed methane and gas shale are examples of unconventional petroleum deposits that require "fracking". When fracking a well, a large volume of water mixed with sand and chemicals is injected into the formation at pressures high enough to cause the rock to crack. The sand fills the fissures, creating channels that allow the gas to escape into the pipe. Coal bed methane gas deposits do not require as much water as shale gas deposits. Because shale "fracking" requires millions of gallons of water, there is genuine concern that the environment will be adversely impacted.



### Environmental Monitoring

#### **Global Monitoring of POPs in the Asian Coastal Region and International Conference of Asian Environmental Chemistry 2014 in Thailand** \_\_\_\_\_ 19

Environmental water contains a variety of elements, including those related to industrial and agricultural activity and urban waste. In efforts to manage these pollutants in Asia, the United Nations University (UNU) and Shimadzu Corporation jointly established a capacity-building initiative that would provide Asian countries with the analytical scientific knowledge and technology to monitor pollutants in the environment and better implement multilateral environmental agreements like the Stockholm Convention on POPs.



### Topics

#### **"Save the Energy" Project** \_\_\_\_\_ 22

In January 2010, Shimadzu started the "Save the Energy" project to strengthen our lineup of energy-saving products. This project promotes the development of products that offer the potential of significant energy savings and are consistent with a low-carbon society by achieving energy savings of at least 25 % through lower power consumption by the customer and lower operating costs.



### Topics

#### **Shimadzu awarded twice in Innovation Awards - the Analytical Scientist Innovation Awards 2014** \_\_\_\_\_ 24

Shimadzu is honored to be recognized by The Analytical Scientist Innovation Awards 2014 for two innovative analytical systems: iMScope Trio imaging mass microscope and the Nexera-e comprehensive two-dimensional liquid chromatograph.



### Product Information

#### **Nexera UC (Online SFE-SFC), 5D Ultra-e (LC-GCxGC-MS/MS), EPMA-8500G** \_\_\_\_\_ 25

## Interview with Prof. Kevin A. Schug



We interviewed with Dr. Kevin A. Schug, Associate Professor and Shimadzu Distinguished Professor of Analytical Chemistry in the Department of Chemistry and Biochemistry at the University of Texas at Arlington (UT Arlington). His research is mainly on the separation of bioactive chemical compounds with mass spectrometry techniques. Also, he is currently undertaking one of the most extensive investigations of the potential impact of industrial processes, such as unconventional drilling and hydraulic fracturing, on our environment. He and Shimadzu started collaborative work in 2012 when the Shimadzu Center for Advanced Analytical Chemistry was established.

**Dr. Schug, we greatly appreciate you taking time to talk with us.**

**At first, could you tell us the background of this collaborative research? Why did you choose Shimadzu as your partner?**

First, thank you for this opportunity to speak with you. It has been a real pleasure to work with Shimadzu, and I sincerely appreciate your efforts to tell our story. My interactions with Shimadzu actually began way back in 2000, when I was a graduate student at Virginia Tech. Our analytical group, headed by Prof. Harold McNair, regularly administered American Chemical Society short courses in gas chromatography, liquid chromatography, sample preparation, and other topics. Shimadzu was always willing to put instruments on site for these courses, and I was able to build a good relationship with a number of their technical and sales employees. In the end, I completed my dissertation research on the topic of adduct ion formation in electrospray ionization, using a Shimadzu QP8000a single quadrupole mass analyzer.

After my post-doctoral stay at the University of Vienna, I joined the faculty in the Department of Chemistry and Biochemistry at U.T. Arlington. Within a year or two, contact was made back to Shimadzu, and we were able to organize the acquisition of an LCMS-ITTOF, in 2007, through the Shimadzu Equipment Grants for Research Program. It was only one of a handful of such systems available in the country at that time, so we had a unique opportunity to perform cutting edge research that others could not, based on the powerful features of the instrument. Not long after that, we began discussions of a larger partnership. Much of the success of establishing what would ultimately be the Shimadzu Center for Advanced Analytical Chemistry and the Shimadzu Institute for Research Technologies at U.T. Arlington was due to our forward looking administration. It became quickly clear to those involved, that this partnership would be a big win for all involved. U.T. Arlington would acquire a wide range of

state-of-the-art instrumentation. Shimadzu would gain an active partner performing cutting edge research using their instrumentation. My laboratory could expand into a variety of different areas where some opportunities for research were present – namely, in trace analysis of compounds from biological fluids, using CoSense and triple quadrupole mass spectrometry, and into assessing the potential environmental impact of unconventional natural gas and oil processes, using a wide range of instrumentation. Clearly, one of the main reasons why our partnership has been successful is due to the personal relationships and support provided.

**Then could you outline the research and let us know what discovery and achievement have been made so far?**

Our research on trace quantitative analysis from biological fluids began through a collaboration with a local medical school, where they were piloting the clinical use of estrogens for the treatment of traumatic brain injury. They could use an immunoassay to quantify the level of estrogens in plasma, but no such validated method existed for trace quantification of estrogens in cerebrospinal fluid. We began with a traditional liquid-liquid extraction off-line sample preparation technique, but learned quickly that the workflow took too long to effectively handle a large number of samples. At that time, we were introduced to Shimadzu CoSense, which features the use of restricted access media for on-line sample preparation. We assembled the set-up in the lab with the help of Shimadzu personnel and set about developing more efficient methods. We have been successful in developing ultra-sensitive methods (low parts-per-trillion detection limits) for detection of estrogens in cerebrospinal fluid and in plasma. We have also carried out some fundamental studies on how best to optimize trapping efficiency on the MAYI trap restricted access media offered by Shimadzu. Our research on groundwater quality is unique. By this point, we have taken and analyzed over 800 well water samples in proximity to unconventional drilling and hydraulic fracturing activities. This is the largest effort to date of this kind. In 2011, we realized that very little work had been done to assess potential environmental impacts of this industrial activity, which has been so very important to the United States economy. It has been our goal to be objective and simply collect data that no one else was collecting. As an academic entity, we could remain wholly unbiased, and in fact we have done much of our work without outside support, beyond some funds provided by the University, and the availability of a large suite of analytical instruments based on the Shimadzu partnership. We have developed a core set of analytical techniques based on Shimadzu GC-MS, headspace GC-FID/BID, ICP-OES, and TOC/TN analyses. These methods borrow best practices from standard methods, but also build in a combination of targeted and untargeted strategies to allow for a comprehensive evaluation of water quality. In an early





report, we found evidence for indirect impact of unconventional drilling processes on water quality in North Texas. We are currently working on two manuscripts that report a survey of a larger section of North Texas, and a time-course study where samples were taken before, during, and after drilling activity in west Texas. We expect that these studies will bring vast new insights into the relationship between modern gas and oil extraction, and its potential environmental impact.

### Why are you interested in this research? What is the goal?

We are driven by the interest and desire to find new solutions to challenging analytical problems. We also want this effort to involve high impact problems. The clinical world brings significant analytical challenges, and it involves issues relevant to human health. Environmental analysis is not something I would have pictured our group doing five years ago, but it has now become a major research effort for us. Just like clinical work, there are real human impacts to environmental issues, and the work we are doing on groundwater quality brings us close together with individuals and their homes. The goal in that effort is to assess whether there are any deleterious effects of current practices of unconventional oil and gas extraction. As this is research that very few people are pursuing, it is that much more important to dedicate the time and resources to it. It is rewarding to work in areas that can make a difference, as well as provide optimal training for students so that they can carry the banner forward.

### How are our instruments helping you?

We could not do any of this work without our Shimadzu instruments. Not only that, the unique high performance features of many of the systems we use enable us to do some things that would be very difficult for others. I have always felt that Shimadzu was smart in the lines of instrumentation they develop. It is clear that you are not trying to fit completely in existing markets, but rather to set new markets with specialized instruments and solutions. For our pre-clinical and clinical work, we use the CoSense system coupled to highly sensitive triple quadrupole mass spectrometry. Only a few other manufacturers offer similar configurations, and thus, we can be quite unique in the methods that we develop; those methods also provide superior performance. For the groundwater work, we use a very diverse group of instruments. The fact that Shimadzu provides so many different choices gives us some flexibility to ensure that we can get the job done right and see the things we need to see in order to make reliable conclusions.

### What are Shimadzu's strengths compared to other vendors (not limited to the instruments)?

I have always said that Shimadzu's greatest strength is its people and service. I have been in the role of a customer for Shimadzu and for many other companies, and I have always found that Shimadzu service has been the most helpful and reliable. I like the idea that I do not necessarily have to have a service person on site to get help with a problem. Oftentimes, a phone call yields a simple fix that we can quickly and inexpensively implement. Now that we are part of a larger partnership, we enjoy a much closer interaction with Shimadzu. This means that our students have regular contact with engineers, applications chemists, and sales/marketing personnel to get more out of their education. In a similar fashion, we get to work together many

times on projects of mutual benefit. I am happy to say that I have had, and I am sure will continue to have, very productive collaborations with Shimadzu Scientific Instruments in the United States and Shimadzu Corporation in Japan. I am even looking forward to future partnerships with other Shimadzu subsidiaries around other parts of the world. I could not imagine a better relationship to help enable my research, that of others at U.T. Arlington, and advance the education of our students in ways virtually impossible at other institutions.

### Finally, could you share any requests that you have with respect to analytical and measuring instrument vendors?

Keep doing what you are doing. Keep innovating. And, selfishly, keep us informed about the newest releases and solutions. I am always amazed at how you are constantly releasing new technology into the marketplace. Through the Shimadzu – U.T. Arlington partnership, we have remained on the cutting edge of research in analytical chemistry, and that is a very important place for us to be, as we continue to move towards Tier One research status. We have several instruments that are largely unique in North America. We appreciate the receptiveness that Shimadzu has had to our suggestions for new products and improvements to existing ones. Ultimately, not everyone needs exactly the same solution, and it is important to be able to work together with a vendor and partner who is willing to be flexible to help us achieve our goals. Thank you! I look forward to a rewarding and productive future in our continuing interactions.

### It was significant to know what you think about us and our collaboration. We will strive to meet your request more than ever. Thank you very much.





## His recent publications:

1. Beinbauer, J.; Liangqiao, B.; Fan, H.; Sebela, M.; Kukula, M.; Barrera, J.A.; Schug, K.A. Bulk derivatization and cation exchange restricted access media-based trap-and-elute liquid chromatography-mass spectrometry method for determination of trace estrogens in serum. *Anal. Chim. Acta* 2015, 858, 74-81.
2. Schug, K.A.; Sawicki, I.; Carlton Jr., D.D.; Fan, H.; McNair, H.M.; Nimmo, J.P.; Kroll, P.; Smuts, J.; Walsh, P.; Harrison, D. A Vacuum Ultraviolet Detector for Gas Chromatography. *Anal. Chem.* 2014, 86, 8329-8335.
3. Papouskova, B.; Fan, H.; Lemr, K.; Schug, K.A. Aspects of Trapping Efficiency And Matrix Effects in Development of a Restricted Access Media-Based Trap-and-Elute Liquid Chromatography-Mass Spectrometry Method. *J. Sep. Sci.* 2014, 37, 2192-2199.
4. Fan, H.; Papouskova, B.; Lemr, K.; Wigginton, J.G.; Schug, K.A. Bulk Derivatization and Direct Injection of Human Cerebrospinal Fluid for Trace Level Quantification of Endogenous Estrogens Using Trap-and-Elute LC-MS/MS. *J. Sep. Sci.* 2014, 37, 2010-2017.
5. Barnes, J.S.; Schug, K.A. Oxidative Degradation of Quercetin with Hydrogen Peroxide Using Continuous Flow Kinetic Electrospray · Ion Trap · Time of Flight Mass Spectrometry. *J. Agric. Food Chem.* 2014, 62, 4322-4331.
6. Nguyen, H.P.; Chandel, N.S.; DeBerardinis, R.J.; Schug, K.A. Hydrophilic interaction liquid chromatography · tandem mass spectrometry to detect and quantify dicarboxyethyl glutathione, a metabolic biomarker of fumarate hydratase-deficient cancer cell. *J. Sep. Sci.* 2013, 36, 3303-3309.
7. Fontenot, B.E.; Hunt, L.R.; Hildenbrand, Z.L.; Carlton Jr., D.D.; Oka, H.; Walton, J.L.; Hopkins, D.; Osorio, A.; Bjorndal, B.; Hu, Q.; Schug, K.A. An evaluation of water quality in private drinking water wells near natural gas extraction sites in the Barnett Shale Formation. *Environ. Sci. Technol.* 2013, 47, 10032-10040.
8. Barnes, J.S.; Foss Jr., F.W.; Schug, K.A. Thermally Accelerated Oxidative Degradation of Quercetin Using Continuous Flow Kinetic Electrospray-Ion Trap-Time of Flight Mass Spectrometry. *J. Am. Soc. Mass Spectrom.* 2013, 24, 1513-1522.
9. Yang, S.H.; Wang, E.H.; Gurak, J.A.; Bhawal, S.; Deshmukh, R.; Wijeratne, A.B.; Edwards, B.L.; Foss Jr., F.W.; Timmons, R.B.; Schug, K.A. Affinity Mesh Screen Materials for Selective Extraction and Analysis of Antibiotics using Transmission Mode Desorption Electrospray Ionization Mass Spectrometry. *Langmuir* 2013, 29, 8046-8053.
10. Tedmon, L.; Barnes, J.S.; Nguyen, H.P.; Schug, K.A. Differentiating Isobaric Steroid Hormone Metabolites Using Multi-Stage Tandem Mass Spectrometry. *J. Am. Soc. Mass Spectrom.* 2013, 24, 399-409.

## Analysis of Groundwater Quality Using GC-MS, HS-GC-FID, TOC/TN Analysis, ICP-OES, and a Multi-parameter Probe in a Complementary Fashion



Jonathan Thacker<sup>1</sup>, Doug D. Carlton Jr.<sup>1,2</sup>, Zacariah L. Hildenbrand<sup>2,3</sup>, Brian E. Fontenot<sup>2,4</sup>, Kevin A. Schug<sup>1,2</sup>

<sup>1</sup> Department of Chemistry & Biochemistry, The University of Texas at Arlington, Arlington, TX 76019

<sup>2</sup> Affiliate of Collaborative Laboratories for Environmental Analysis and Remediation, The University of Texas at Arlington, Arlington TX 76019

<sup>3</sup> Inform Environmental, LLC (Dallas, TX)

<sup>4</sup> Independent Consultant



### 1. Introduction

In the United States, the Environmental Protection Agency (EPA) sets regulations and recommends guidelines for public water systems.<sup>1</sup> About 15% of Americans rely on their own private wells for their drinking water, but these are not subject to either state or federal regulations and are not regularly tested by experts, unlike public water systems.<sup>2</sup> The chemical analysis of groundwater can be utilized to assess possible contamination as well as inform on possible health risks associated with its consumption. The use of multiple instruments to analyze groundwater has the advantages of describing groundwater samples more completely than individual measurements, validating measurements, and protecting against reporting false positives. To demonstrate this combinatorial analytical advantage, a Shimadzu QP2010 Ultra gas chromatograph- mass spectrometer equipped with a Shimadzu AOC-20i / s autosampler and autoinjector (GC-MS), a Shimadzu GC-2010 plus equipped with a flame ionization detector (FID) and a Shimadzu AOC-5000 plus headspace autosampler (HS-GC-FID), a Shimadzu TOC-L outfitted with a TNM-L total nitrogen module and a Shimadzu ASI-L autosampler (TOC/TN), a Shimadzu ICPE-9000 inductively coupled plasma- optical emission spectrometer equipped with a mini-torch nebulizer, a CETAC ASX-520 Autosampler (Teledyne Technologies Incorporated; Omaha, NE, USA), and argon plasma (ICP-OES), and a YSI Professional Plus multiparameter meter (YSI Incorporated; Yellow Springs, OH, USA) were used to characterize groundwater samples. These instruments and associated methods have been applied to analyze approximately 1000 groundwater samples over a 1-year period in regions undergoing unconventional oil and gas (UOG) production in the USA.

### 2. General Groundwater Quality Parameters

At each sampling site, groundwater was purged for approximately 20 – 30 minutes (until temperature, oxidation/reduction potential, and pH values had stabilized) from a water well before collection. The YSI multiparameter probe was used to measure general groundwater quality parameters, including temperature, pH, conductivity, dissolved oxygen, oxidation/reduction potential, and turbidity.<sup>3</sup> These data may be used to support measurements from more detailed analytical techniques.

### 3. Metals Analysis with the ICPE-9000

There are a variety of metal ions known or suspected to cause health problems that are regulated by the EPA. The Shimadzu ICPE-9000 ICP-OES was used to measure concentrations of various metal ions. Samples were acidified to a 2% by volume nitric acid solution and then filtered as needed. Quantification was performed via standard addition to account for varying matrices among the groundwater samples. High or low cumulative concentrations of metal ions determined by ICP-OES could be validated by their correlation with conductivity measurements. 100 groundwater samples from the Barnett Shale of North Texas were analyzed by ICP-OES and the multiparameter probe. Fig. 1 displays the relationship between the sum of estimated concentrations of 64 metal elements determined by ICP-OES and conductivity for 100 groundwater samples. These data suggest that a relatively high conductivity measurement in groundwater can be a general indicator of a high total metals concentration.

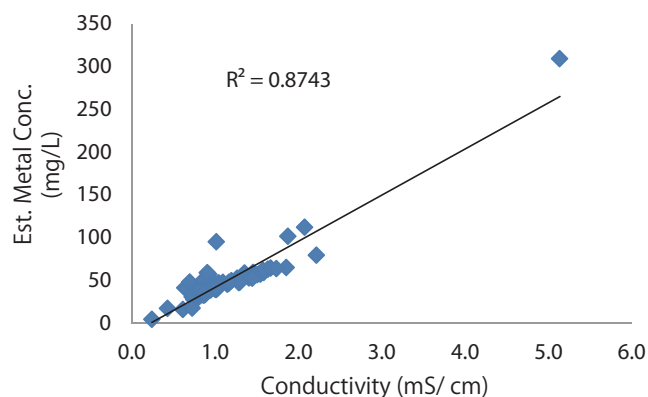


Fig. 1 Total concentration of metal elements determined by ICP-OES and its correlation with measured bulk conductivity in 100 groundwater samples.

## 4. Analysis of Volatile and Semi-Volatile Organic Compounds using a GCMS-QP2010 Ultra

The EPA regulates many organic compounds known or suspected to be harmful to the environment or human health. In addition, organic compounds identified in groundwater may help determine the source of contamination. For example, specific compounds thought to be used in unconventional drilling techniques such as hydraulic fracturing. The Shimadzu QP2010 Ultra GC-MS equipped with a SHRXI-5MS (30 m x 0.25 mm x 0.25  $\mu$ m) column was used to simultaneously target compounds that might be present in

groundwater in the event of contamination from UOG activities, while also screening for other volatile and semi-volatile organic compounds in an untargeted fashion.<sup>3</sup> Samples were prepared by extracting 5 mL of ground water with 2 mL of ethyl acetate. Table 1 and Table 2 display the MS program used and selected SIM ions for compounds of interest, respectively. Fig. 2 displays an example GC-MS chromatogram using this method on DI water spiked with several compounds.

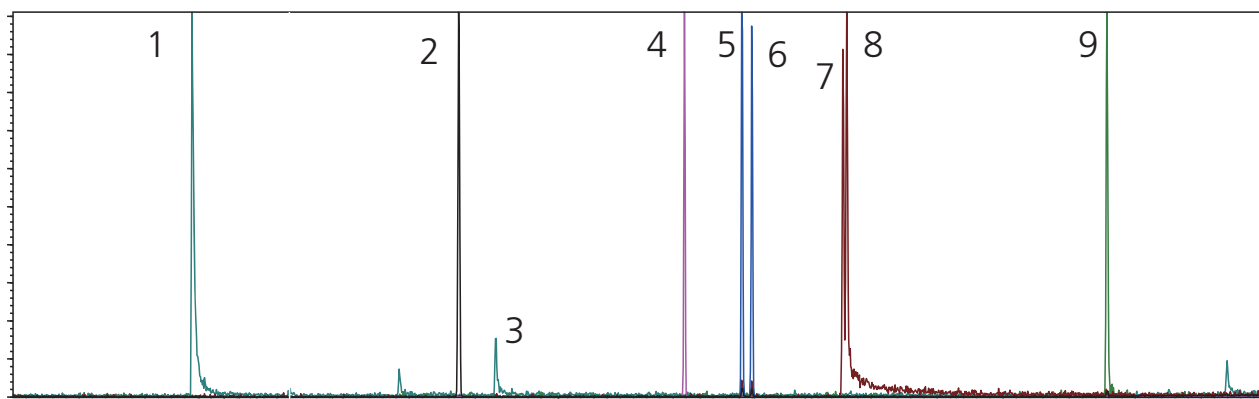


Fig. 2 GC-MS chromatogram. 1: ethylene glycol, 2: p-xylene, 3: ethylene glycol butyl ether, 4: naphthalene, 5: 2-methylnaphthalene, 6: 1-methylnaphthalene, 7: 2-naphthol, 8: 1-naphthol, 9: bisphenol A

### Analysis Conditions

Instrument: GCMS- QP2010 Ultra  
 Column: SHRXI-5MS, 30 mL. x 0.25 I.D., df: 0.25  $\mu$ m  
 Column oven temp.: 40 °C (3 min.)  $\rightarrow$  (20 °C/min.)  $\rightarrow$  70 °C (0 min.)  $\rightarrow$  (40 °C/min.)  $\rightarrow$  330 °C (2 min.)

### [GC]

Carrier gas: He  
 Carrier gas control: Linear velocity, 35 cm/s  
 Split ratio: 20:1  
 Injection port temp.: 300 °C  
 Injection volume: 2  $\mu$ L

### [MS]

Acquisition mode: Scan/ SIM  
 Interface temp.: 260 °C  
 Ion source temp.: 260 °C

Table 1 MS program

Start time (min.)	End time (min.)	Acqu. mode	Event time (sec.)	m/z
0.60	2.25	Scan	0.20	40.00-100.00
0.60	2.25	SIM	0.10	31.10, 55.10, 29.10
2.88	5.78	Scan	0.20	40.00-200.00
2.88	5.78	SIM	0.10	78.10, 56.10, 31.10, 45.10, 91.10, 44.10
5.78	6.35	Scan	0.20	40.00-200.00
5.78	6.35	SIM	0.10	91.10, 57.10, 29.10, 105.10, 44.00
6.35	7.30	Scan	0.20	40.00-250.00
6.35	7.30	SIM	0.10	45.10, 57.10, 59.10, 68.10, 73.00, 91.10, 105.15, 103.00
7.30	8.50	Scan	0.20	40.00-300.00
7.30	8.50	SIM	0.10	128.10, 142.15
8.50	11.00	Scan	0.20	40.00-400.00
8.50	11.00	SIM	0.10	45.10, 144.15, 213.10
11.00	13.00	Scan	0.20	40.00-400.00



Table 2 Selected SIM ions for compounds of interest

Compound	CAS Number	SIM Ion	Compound	CAS Number	SIM Ion
Acetaldehyde	75-07-0	29.10	Mesitylene	108-67-8	105.15
Acetophenone	98-86-2	105.10	Methanol	67-56-1	31.10, 29.10
Benzene	71-43-2	78.10	1-Methylnaphthalene	90-12-0	142.15
Benzyl Chloride	100-44-7	91.10	2-Methylnaphthalene	91-57-6	142.15
Bisphenol A	80-05-7	213.10	Naphthalene	91-20-3	128.10
2-Butoxy Ethanol	111-76-2	57.10	1-Naphthol	90-15-3	144.15
n-Butanol	71-63-3	56.10	2-Naphthol	135-19-3	144.15
Cumene	98-82-8	105.10	1,2-Propanediol	57-55-6	45.10
Dimethyl Formamide	68-12-2	44.10	n-Propanol	71-23-8	31.10
d-Limonene	5989-27-5	68.10	Propargyl Alcohol	107-19-7	55.10
Ethanol	64-17-5	31.10, 29.10	Toluene	108-88-3	91.10
Ethylbenzene	100-41-4	91.10	1,2,4-Trimethyl Benzene	95-63-6	105.10
Ethylene Glycol	107-21-1	31.10	m-Xylene	108-38-3	91.10
2-Ethyl Hexanol	104-76-7	57.10	o-Xylene	95-47-6	91.10
Glutaraldehyde	111-30-8	44.10	p-Xylene	106-42-3	91.10
Isopropanol	67-63-0	45.10, 29.10			

### 5. Alcohol Analysis using GC-2010 Plus and AOC-5000 Headspace Sampler

Low boiling point compounds may have a poor peak shape and separation or may not be detected when analyzed by the GC-MS method. This is primarily due to their elution before, during, or near the solvent, ethyl acetate, and/or the signal being confounded by certain compounds with ions generated from atmospheric gases. Fig. 3 and Fig. 4 display a HS-GC-FID chromatogram of a groundwater sample containing ethanol and methanol and a side-by-side comparison of a GC-MS and a HS-GC-FID chromatogram of solutions containing various concentrations of methylene chloride, respectively. Low molecular

weight alcohols and other volatiles were detected using the Shimadzu GC-2010 Plus equipped with a ZB-BAC2 column, 30m x 0.32 mm x 1.2 μm (Phenomenex, Inc., Torrance CA, USA).<sup>3</sup> Headspace sampling directly from the groundwater samples was chosen to minimize extraction solvent and matrix interferences with the chromatography. The use of the FID eliminates atmospheric background which can convolute identification of light alcohols by MS. 2 mL of 0.25 M sodium chloride solution were added to 5 mL of groundwater in a 20 mL screw-top headspace autosampler vial.

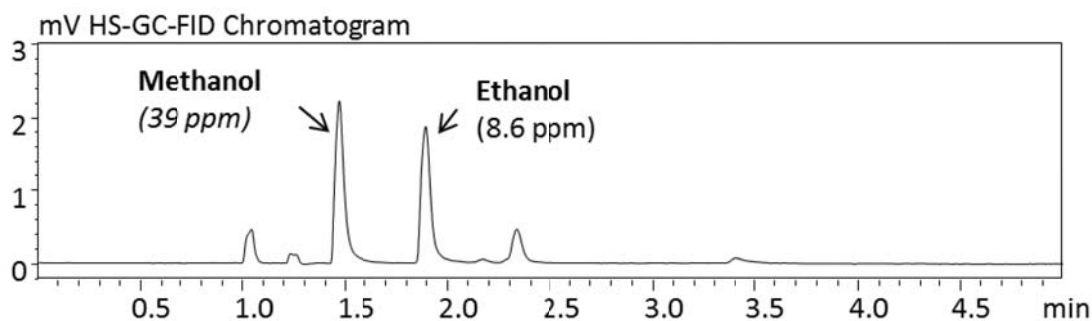


Fig. 3 HS-GC-FID chromatogram of a groundwater sample containing methanol and ethanol

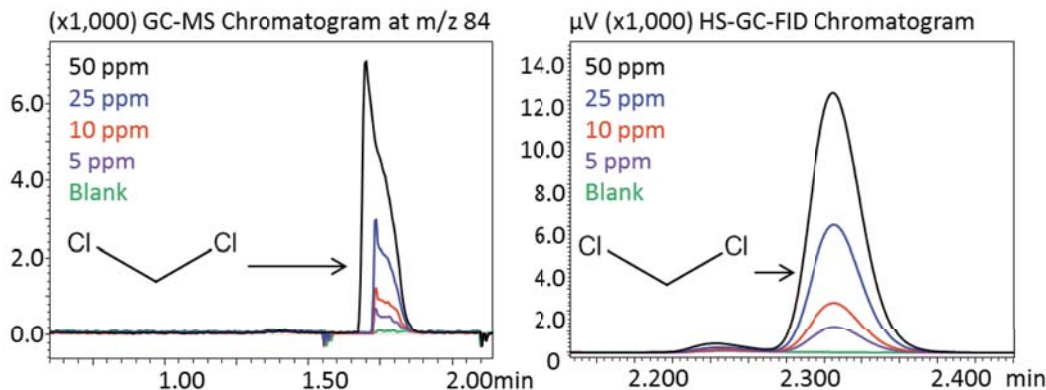


Fig. 4 GC-MS and HS-GC-FID chromatograms of methylene chloride

The headspace autosampler can be transferred to a GC-MS for identification of unknown compounds detected by HS-GC-FID. Analysis of compounds with a boiling point significantly higher than 90 °C may not be suitable for headspace sampling.

## Analysis Conditions

Instrument: GC-2010 Plus

Column: ZB-BAC2, 30 m L. x 0.32 mm I.D., df:1.2 µm

Column oven temp.: 40 °C (4.5 min.) → (30 °C/min.) →130 °C (2 min.)  
→(35 °C/min.) →200 °C (0.5 min.)

Carrier gas: He FID temp.: 200 °C

Carrier gas control: Linear velocity, Agitator temp.: 90 °C  
50 cm/s Agitator time: 15 min.

Split ratio: 10:1 Syringe temp.: 90 °C

Injection port temp.: 200 °C

Injection volume: 750 µL

## 6. TOC/ TN

Carbon and nitrogen content of the water were measured with the Shimadzu TOC-L outfitted with the TNM-L total nitrogen module. Samples were filtered with a 0.45 µm PTFE Luer lock syringe filter as needed and filled a 40 mL volatile organic analysis autosampler vial. Total Carbon (TC), Inorganic Carbon (IC), Nonpurgable Organic Carbon (NPOC), Purgable Organic Carbon (POC), and Total Nitrogen (TN) were measured. When TC-IC was below 2 ppm, NPOC+POC was used for reporting TOC per manufacturer suggestions. In all other cases, TC-IC was used for TOC.

TOC and TN are valuable to validate the presence of organic compounds and amines or other nitrogen-containing organic compounds determined by a more detailed analytical method. A non-zero TN value does not confirm nitrogen-containing organic compounds, as TN is also sensitive to nitrate, nitrite, and ammonia. Agricultural contamination of groundwater results primarily in an increase of halogenated and nitrogen-containing compounds<sup>4</sup>, while UOG contamination would result in the introduction of carbon or carbon and nitrogen-containing compounds, depending on the phase of the extraction operation. The detection of compounds GC-MS/ HS-GC-FID should be accompanied by nonzero TOC values. Many caveats such as analyte response factors and volatility, can account for the lack of graphical linearity of the GC and TOC measurements from sample to sample. In addition to validating more targeted analytical methods, TOC/ TN can be utilized as an indicator for contaminated groundwater samples.<sup>5</sup> It may be efficient to screen many samples with TOC/ TN before applying more detailed and costly methods. A positive correlation between HS-GC-FID and TOC data was found for an arbitrary set of 14 groundwater samples selected for evaluation. Four out of five of the samples with the highest total HS-GC-FID peak areas had the highest TOC/ NPOC values.

## 7. Summary

Research involving the chemical analysis of groundwater is likely to be highly scrutinized due to the potential for risks associated with health and environmental impacts. Although the measurement of general parameters such as conductivity and Total Organic Carbon (TOC) may have analytical utility on their own, they can be even more valuable for supporting findings using more targeted analytical techniques such as ICP-OES and GC-MS.

## 8. Acknowledgments

The authors would like to thank the Shimadzu Institute for Research Technology (SIRT) and the Shimadzu Center for Advanced Analytical Chemistry (SCAAC) at The University of Texas at Arlington for use and support of the aforementioned analytical instruments. They would also like to thank Shimadzu Scientific Instruments, Inc. (Columbia MD) for the use of the TOC instrument featured in this work.

## 9. References

- <sup>1</sup> US EPA. Drinking Water Contaminants. <http://water.epa.gov/drink/contaminants/index.cfm#one> (accessed October 28, 2014).
- <sup>2</sup> US EPA. Private Drinking Water Wells. <http://water.epa.gov/drink/info/well/> (accessed October 28, 2014).
- <sup>3</sup> Fontenot, B. E.; Hunt, L. R.; Hildenbrand, Z. L.; Carlton, D. D., Jr.; Oka, H.; Walton, J. L.; Hopkins, D.; Osorio, A.; Bjorndal, B.; Hu, Q. H.; Schug, K. A. An Evaluation of Water Quality in Private Drinking Water Wells Near Natural Gas Extraction Sites in the Barnett Shale Formation. *Environ. Sci. Technol.* **2013**, *47*, 10032-10040.
- <sup>4</sup> Almasri, M. N.; Kaluarachchi, J. J. Modeling Nitrate Contamination of Groundwater in Agricultural Watersheds. *J. Hydrol.* **2007**, *343*, 211-229.
- <sup>5</sup> Boyer, E.W.; Clark, J.; Madden, M.; Rizzo, D.E. The impact of Marcellus gas drilling on rural drinking water supplies. The Center for Rural Pennsylvania. 2012.

## Contributing to Develop Environmental Technologies Based on Biodiversity



The Earth's ecosystem comprises a diverse variety of plants and animals. Due to the benefits we enjoy from these ecosystems, there is increased interest, including internationally, in biodiversity conservation, sustainable use and equitable sharing of genetic resources and associated benefits. To expand on this topic, we interviewed professor Michihiko Ike, from the Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, who is involved in cutting-edge research on environmental technologies based on biodiversity.

### Firstly, could you please tell us about your research work?

My research mainly involves developing technologies for cleaning up wastewater and soil by carefully using the forces of nature, such as plants and microorganisms. Nature and other earth systems are fundamentally very robust and, unless we do something quite extreme, nature tends to clean itself to keep the environment in constant balance. Furthermore, the plants responsible for a part of this work generate their own energy through photosynthesis and are able to propagate themselves. Therefore, they are almost like a perpetual motion machine. As an engineer, I have been focused on developing equipment that can utilize the ability of plants and microorganisms to decompose pollutants and so on.

In the past, my work mainly involved so-called "end-of-pipe" wastewater treatment systems, which are analogous to our veins. More recently, I have been thinking about integrating a kind of manufacturing, in the form of collecting and recirculating natural resources, which is analogous to our arteries.

### Specifically what types of methods are involved?

Take rare earth metals, for example. Due to advances in scientific technology, this class of substances is being used in massive quantities. However, though they are extremely useful to modern industry, they also cause environmental pollution when concentrated and discharged in effluents and gas emissions. As a result, these elements, such as selenium, nickel, and antimony, are already subject to established environmental standards or other regulatory limits.

In particular, selenium is an essential nutrient for humans, if taken in very small quantities, and also offers a diverse range of industrial applications, such as for semiconductor synthesis or in materials used in photocopier photoconductive drums. However, discharged water from refinery plants contains high concentrations of selenium and coal-fired power plants emit it as well. Therefore, there is concern that selenium is having a negative effect on the water and soil environments.

Currently, removing selenium from the environment requires an extremely expensive physicochemical process that consumes a large amount of energy. However, it ends up not being recycled, but rather either diluted to a non-harmful level or landfilled.

In sharp contrast to the physicochemical process, microorganisms are able to detoxify and recycle the substance at a low cost and modest energy consumption. Certain microorganisms collect the selenium and accumulate it in their body. Therefore, we utilize that characteristic. There are also microorganisms that consume hazardous cadmium at the same

time and synthesize a semiconductor substance called cadmium selenide. Such facts demonstrate the remarkable potential of a new manufacturing method that converts wastewater containing toxic metals into high value-added materials while treating.



### I am starting to think that microorganisms are an ideal catalyst of purification and resource recovery, but does it have any problems?

The various actions by the microorganisms are collectively referred to as metabolism. The metabolites that result from this process sometimes include troublesome substances that can require special processing measures. Microorganisms can often produce intermediate metabolites that are chemically difficult to predict and can be quite difficult to process. For example, when microorganisms decompose a type of detergent called nonylphenol ethoxylate, an accumulation of even more toxic metabolites may occur. This is known as an endocrine disrupter and has resulted in the sex of fish changing from male to female.

The microorganisms clean up the detergent, but generate a separate risk. Therefore, whenever microorganisms are used to decompose chemical substances, they must be investigated to determine whether or not their metabolites contain toxic substances. Essentially, this is similar to the process of investigating the adverse side effects of drugs. It is also important to investigate the growing environment and types of food that promote microorganism metabolism or result in complete decomposition.

In the selenium research mentioned earlier, we also have to verify whether the microorganisms absorbed all of the selenium dissolved in the water.



## It requires investigation of extremely large number of different parameters.

During these investigation and analysis stages, we use LC and GC systems from Shimadzu Corporation to analyze a wide variety of chemical substances. We don't have the luxury of owning every type of analytical instrument available, so sometimes we borrow an EDX system or other instruments from a separate laboratory in Osaka University. Since we are trying to determine an unknown process, we are very grateful for the almost consultant-like technical advice Shimadzu provides regarding the methods we should use for analysis.

Recently, we have also been focused on researching the relationship between floating plants and microorganisms. We have confirmed a phenomenon where very powerful chemical decomposing microorganisms are concentrated at the root area of floating aquatic plants, and we are now researching ways to utilize them for treating wastewater or purifying the environment. This concentration of microorganisms at the root of these plants is not a coincidence, but is probably due to a reaction to some sort of communication substance secreted from the plant, such as vitamins, proteins, amino acids, or sugars. By analyzing this intermediary substance in order to identify it, we hope to build a more efficient cleaning system. Chemical analysis will provide an important key for that as well. There are still several hurdles we need to clear before we achieve a practical system, but we intend to continue researching this as technology that would be particularly useful.

intermediary substance in order to identify it, we hope to build a more efficient cleaning system. Chemical analysis will provide an important key for that as well. There are still several hurdles we need to clear before we achieve a practical system, but we intend to continue researching this as technology that would be particularly useful.

## What do you foresee researching in the future?

I think research will need to be more predictive. Thirty years ago there were probably only a handful of people that viewed CO<sub>2</sub> emissions as a problem. However, the global warming phenomenon could have been predicted from a careful analysis of several factors, including social and economic progress. In my field, I think we need to gain a solid understanding of how the natural and human worlds work by thoroughly analyzing the ecosystems of water and soil. By doing so, we can discover the next approaching risk as early as possible, and thereby take actions to change economic or other activities in the human world, for example. As long as we are researching the extremely complicated ways in which the natural world works, I am sure we will continue to rely on help from Shimadzu Corporation. Note that by "utilizing" biodiversity we mean something slightly different from activities to simply protect nature. For example, protecting a plant simply because it is unique to a particular area is difficult to justify, making it also difficult for local governments to spend public funds to protect it. However, if the roots of that plant attract microorganisms that clean the water, so that it clearly demonstrates an added value of decomposing harmful pesticides and chemical substances, then protecting it is easier to justify. If the utilization of biodiversity results in systems that allow future generations to also enjoy the services provided by the ecosystem, then perhaps there is hope for an equitable distribution. However, in actuality, the expression "utilizing" biodiversity seems a little presumptuous and lately I am starting to feel that we are being too careless or exploitative with plants and microorganisms for the sake of environmental protection. By creating an inferior environment without regard to what they may prefer and utilizing a part of their innate will to live, maybe we are simply protecting them selfishly for

the parts that are useful to us. In that sense, I feel a little bad for those living organisms (laughs).

## That is certainly a very interesting perspective. Thank you so much for talking with us today.



### Dr. Michihiko Ike

Professor of Engineering  
Division of Sustainable Energy and Environmental Engineering,  
Graduate School of Engineering, Osaka University

After completing his master's program at the Osaka University Graduate School of Engineering and working in a corporate job, Dr. Ike joined Osaka University as an assistant professor in 1990. After then serving as associate professor, he has held his current position since 2006. During that period, he received a grant from the Ministry of Education, Science and Culture to work as a researcher at the Technical University of Hamburg-Harburg in Germany in 1998 and 1999.

# Shimadzu Selection

These articles were selected by Shimadzu for this issue. The articles are from application notes and technical reports relating to environmental analysis and feature a variety of instruments we produce. The cutting-edge technologies are also included. Please obtain the articles of your interest through the links on the titles.



## Selection 1 New Technology

### On-line LC-GCxGC-MS/MS: A Powerful Unified Separation-science Tool

This Technical Report demonstrates the potential of the on-line combination of HPLC, cryogenically modulated comprehensive GCxGC, and MS/MS. The selectivity of the HPLC dimension enabled the separation of chemical classes; each fraction, transferred to the GCxGC instrument via a syringe-based interface, was subjected to a specific programmed temperature vaporizer (PTV) GCxGC-MS/MS for untargeted or targeted analysis.



## Selection 2 Environmental Analysis

### High-Sensitivity Analysis of Nonylphenol in River Water Using GC-MS/MS

Nonylphenol (NP) is used as a raw material for the production of surfactants, and as an antioxidant used to protect rubber and plastics, etc. However, in recent years, it has been specified as a substance that can cause endocrine disruption in the environment. We investigated the use of a high m/z selectivity GC-MS/MS for analyzing NP. By optimizing the MS/MS analytical conditions, selective detection of thirteen 4-NP isomers was achieved with high sensitivity. Further, in the analysis of NP in river water, which typically contains many contaminants, analysis was possible without adversely affecting identification accuracy, even when omitting the cleanup procedure that may reduce the recovery rate.



## Selection 3 Environmental Analysis

### Rapid Analysis of 2,4-DNPH-Derivatized Aldehydes and Ketones Using the Prominence-i with a Shim-pack Column

This application news presented a rapid analysis of 2,4-DNPH-derivatized aldehydes and ketones using the LC-2010 integrated HPLC with a Shim-pack FC-ODS column. As the goal of this study was to obtain a shorter analysis time than the previous method, we investigated the run conditions using the new Prominence-i integrated HPLC with a 2.2  $\mu\text{m}$  particle size Shim-pack XR-ODS column. Presented here are the results of simultaneous analysis of thirteen 2,4-DNPH-derivatized aldehyde and ketone standards run on a conventional 5  $\mu\text{m}$  particle column, and an example of rapid analysis with a 2.2  $\mu\text{m}$  particle column.



## Selection 4 Environmental Analysis

### Analysis of Anionic Surfactants by Prominence-i and RF-20Axs Fluorescence Detector

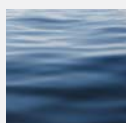
According to the Ministerial Ordinance on Water Quality Standards, an HPLC method using a fluorescence detector has been adopted as the test method for anionic surfactants. Since either the RF-20A or RF-20Axs fluorescence detector can be connected to the new Prominence-i integrated high-performance liquid chromatograph, the combination of integrated operability and high-sensitivity fluorescence detection is possible. This application news presents an example of the analysis of five anionic surfactants using the Prominence-i integrated HPLC with the RF-20Axs high-sensitivity fluorescence detector.



## Selection 5 Environmental Analysis

### Simultaneous Determination of Polycyclic Aromatic Hydrocarbons Using the Prominence-i Integrated High Performance Liquid Chromatograph

Many polycyclic aromatic hydrocarbons exhibit fluorescence, and can therefore be detected with high selectivity and high sensitivity using a fluorescence detector. However, of the sixteen polycyclic aromatic hydrocarbons designated as "priority pollutants" by the U.S. Environmental Protection Agency (EPA), acenaphthylene alone does not exhibit fluorescence. The Prominence-i, which incorporates a UV detector, can be connected to the RF-20Axs fluorescence detector, permitting simultaneous analysis of all sixteen polycyclic aromatic hydrocarbons. Here, using two analytical methods, one with the wavelength switching mode and the other using simultaneous measurement at multiple wavelengths, we introduce an example of simultaneous analysis of the 16 PAHs.



## Selection 6 Environmental Analysis

### High-Sensitivity Analysis of Ammonia, Methylamine, and Trimethylamine in Environmental and Energy Fields

The dielectric barrier discharge ionization detector (DID) permits detection of nearly all compounds, except for helium and neon, at higher sensitivity than that possible with TCD and FID detectors. Here, we introduce examples of analysis at the ppm level of ammonia and methylamine in water, and of trimethylamine in water by GC-DID.



#### Selection 7 Environmental Analysis

### Analysis of Multiple Elements in Drinking Water by ICPE-9820

Conducting safety inspections for drinking water is the responsibility of each country according to their respective regulations. Typically, there are many target elements included in the test, such as N, Ca, etc., which are present at the mg/L level or greater, and toxic trace elements such as Pb and Cd, which are normally present at the µg/L level or less. Here, using the Shimadzu ICPE-9820 multi-type ICP atomic emission spectrometer and an ultrasonic nebulizer, we conducted analysis of river water, typically the source of tap water.



#### Selection 8 Environmental Analysis

### Analysis of Heavy Metals in Sewage Sludge and Sewage by ICPE-9820

In recent years, the increase of sewage sludge generated in the sewage treatment process has become a problem. For the purposes of waste reduction and recycling, following incineration, sewage sludge is being re-used as cement material, civil engineering material, fertilizer, etc. However, the reuse of sewage sludge, from the standpoints of environmental protection and potential health hazards, requires that its toxic heavy metal content is carefully examined. Here, using the Shimadzu ICPE-9820 multi-type ICP atomic emission spectrometer, we conducted analysis of processed water from a sewage treatment plant, in addition to sewage sludge ash.



#### Selection 9 Environmental Analysis

### Content Analysis of Toxic Elements in Soil by ICPE-9800 Series

Contaminated soil not only leads to contamination of untreated drinking water through permeation into river water and rainwater, it adversely affects health when the soil itself is directly ingested. Therefore, assessment of soil toxicity using a defined method is required. The apparatus used for the analysis is required to accurately measure those elements at trace concentrations equivalent to or lower than the reference values. Here, using the Shimadzu ICPE-9800 series multi-type ICP atomic emission spectrometer, we conducted content analysis of soil.



#### Selection 10 Environmental Analysis

### High-Speed X-Ray Diffraction Analysis of Asbestos (Chrysotile) Using Wide-Range High-Speed Detector

Asbestos is a material that has long been widely used as a building material due to its excellent heat and acid resistance. However, its use has gradually been banned because of widespread recognition of its adverse health effects. Here, we introduce an example of high-speed quantitative analysis of chrysotile, one kind of asbestos, using the new OneSight wide-range high-speed detector.



#### Selection 11 Environmental Analysis

### Quantitative Analysis of Pyrethroids in Soil Using Triple Quadrupole LC-MS/MS

Pyrethroids are insecticides used worldwide for both household and farming applications. Traditionally, pyrethroids are measured by Gas Chromatography with or without mass spectrometry. Here, we present a method using LC-MS/MS to show that LC-MS/MS can measure these compounds traditionally analyzed by GC. This report illustrates a simultaneous analysis of 15 pyrethroids using the Shimadzu LCMS-8050 with ultrafast polarity switching.



#### Selection 12 Environmental Analysis

### High Speed Analysis of Haloacetic Acids in Tap Water Using Triple Quadrupole LC-MS/MS

Haloacetic acids (HAAs), by-products of water disinfection, are formed from naturally-occurring organic and inorganic materials in water that react with the disinfectants chlorine and chloramine. A LC-MS/MS method, which is capable of direct injection of water samples, for measuring HAAs has been developed to replace previously used methods requiring tert-butyl-methyl ether liquid extraction and diazomethane derivatization prior to GC analysis, thus reducing the effort required for sample preparation.



#### Selection 13 New Technology

### Structural Analysis of Glycosphingolipids by LC-IT-TOF-MS

A method for detection and structural characterization of glycosphingolipids (GSLs) based on LC-IT-TOF-MS is introduced and the results of analysis of GSLs containing sialic acid in mouse thymocytes, CD4T and CDT8 cells are described as an example of its application. Even at trace levels and in a mixture, both carbohydrate chain and lipid structures were characterized, and previously unknown information could be obtained. The development of a new analytical tool is in progress and applicable future challenges are discussed.



# Hydraulic Fracturing and the Environment



William Lipps, PhD, Shimadzu Scientific Instrument Inc.

## 1. Introduction

Hydraulic fracturing is a well stimulation process used to improve recovery and production of oil and natural gas from unconventional petroleum deposits. Coal bed methane and gas shale are examples of unconventional petroleum deposits that require “fracking”. When fracking a well, a large volume of water mixed with sand and chemicals are injected into the formation at pressures high enough to cause the rock to crack. The sand fills the fissures creating channels that allow the gas to escape into the pipe. Coal bed methane gas deposits do not require as much water as shale gas deposits. Because shale “fracking” requires millions of gallons of water, there is genuine concern that the environment will be adversely impacted.

Fig. 1 illustrates the five stages of a fracking operation<sup>1</sup>. These are:

- 1) Acquire enough water needed for the hydraulic fracturing of the well. This could be up to 5,000,000 gallons of water.
- 2) Mix the chemicals with the water.
- 3) Inject the water plus chemicals into the well.
- 4) Recover the flow-back water and production water (hydraulic fracturing wastewater)
- 5) Treat and dispose of the wastewater

Step 1 notes that the fracking operation needs to acquire millions of gallons of water. This water may be withdrawn from relatively clean fresh groundwater or surface water supplies and contaminated with fracking chemicals and salts dissolved from the formation. Some petroleum companies are starting to recycle flow-back water, but most of them still dispose of it by deep well injection.

Mixing the chemicals with fresh water could result in spills at the mixing site. If mixing zones are not lined or contained there is the possibility of ground and surface water contamination from a spill.

## 2. The major components in “fracturing” fluids and how to analyze for them

### Sand

Sand is used to keep the fractures open so that gas can flow through.

Sand is defined as a particle size distribution ranging from 60 to about 2000 microns. The best “sands” for use in hydraulic fracturing are perfectly spherical ceramics with a very narrow grain size distribution to maximize porosity. The selection of material and grain size plays a key role in hydraulic fracturing.<sup>2</sup> Instruments, such as the Shimadzu SALD-2300 can be used to accurately and precisely measure grain size distribution between 0.017 and 2000 microns in samples from very low to high concentrations of suspended particles.

### Surfactants

Surfactants are used as a wetting agent that, when used along with other chemicals, can significantly increase to productivity of a well.<sup>3</sup> Unlike many other techniques used to monitor surfactants, the Shimadzu LCMS-8040 can be used to simultaneously analyze anionic, amphoteric, and non-ionic surfactants in very complex environmental samples.<sup>4</sup> Simpler and less expensive methods, such as Standard Methods 5540<sup>5</sup> determine surfactants as “groups” that can be extracted and measured using a spectrophotometer such as the Shimadzu UV-1800.

### 3. KCL, Guar, and Cross-linkers

Cross linkers are usually boron or zirconium compounds that are used to “link” guar gum molecules together. The guar is a water soluble polymer used to thicken the fracking fluid and hold the sand in suspension as it is carried through the pipe and into the fractures made in the shale. Addition of potassium prevents negatively charged carboxymethyl groups on the polymer from repelling each other allowing the polymer to occupy less space than it would if potassium had not been added.<sup>6</sup> Potassium or Sodium Chloride is also added to the fracking solution to prevent, or minimize, swelling of clay minerals.<sup>7</sup> Boron, sodium, and potassium along with other trace metals, such as iron, calcium, and magnesium, are readily determined by Inductively Coupled Argon Plasma Atomic Emission Spectroscopy (ICAP-AES) methods, such as USEPA Method 200.7<sup>8</sup>. Because the drilling solutions are prepared containing very high salt content,

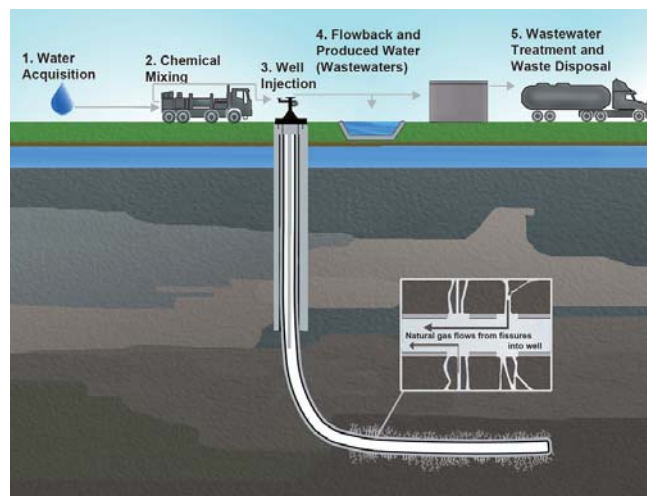


Fig. 1 Five Stages of a fracking operation

it is important to use an ICP-AES that is capable of aspiration of high salt solutions without clogging the nebulizer or excessive memory effects that may occur. The Shimadzu ICPE-9000 employs a vertical torch arrangement with a high salt nebulizer and self-draining spray chamber. The ICPE-9000 software and potential for both axial and radial orientation of the spray chamber make it possible to analyze both trace and very high concentrations of analyte with very little dilution.

#### 4. Scale Inhibitor

If the concentration of calcium and/or barium is high enough, and the conditions are right, they can precipitate with carbonate or sulfate to form scale. The formation of scale inside the pipe or within the rock fractures decreases gas production. The addition of phosphonates or ammonium chloride as ingredients of the fracking solution helps to minimize scale. Simple colorimetric tests combined with visible spectrophotometers, such as the Shimadzu UV-1800 can be used for measurement of scale inhibitors.

#### 5. Acid

Hydrochloric acid and various organic acids, such as citric acid, are used in the fracking solution to dissolve remnants of cement left behind from the drilling process or to dissolve the calcite and hematite cement that binds the individual mineral grains of the shale together. Since hydrochloric acid is composed of the hydrogen and chloride ions it is impossible, other than by pH or a neutralization titration, to determine the concentration of hydrochloric acid in the fracking solution. A Shimadzu organic acid HPLC system with a UV or conductivity detector can be used to determine concentrations of organic acids.

#### 6. Friction Reducer

High molecular weight polyacrylamide blended with petroleum distillates is added to the fracking solution to create laminar flow and decrease the total energy (horsepower) required to pump the solution down-hole<sup>9</sup>. The petroleum distillate may contain aromatics hydrocarbons, such as benzene, toluene, ethylbenzene, and xylenes (BTEX). USEPA method 624<sup>10</sup> is a gas chromatography coupled with mass spectrometry method capable of accurate determination of BTEX along with multiple other volatile organic compounds in very complex matrices. The Shimadzu GCMS-QP2010SE coupled with an EST Purge and Trap sample concentrator can be used for the analysis of volatile organics in fracking water samples.

#### 7. The potential environmental impact of fracking on US water supplies

As the injected water flows through the formation it dissolves existing minerals and carries with it the interstitial water. The fracking solution chemistry differs from the formation water and can dissolve elements, such as uranium, that were trapped in the formation<sup>11</sup>. When the fracking water returns back to the surface it carries with it some of the interstitial formation water, and any trace inorganic and/or organic compounds that may have dissolved. As little as 10% to up to 100% of the fracking water returns to the surface as the fracking wastewater<sup>12</sup>. This wastewater is collected into pits and disposed of. It is the flow-back water from the fracking process and the large volumes of produced water that pose the largest risk of environmental contamination<sup>13</sup>. Because of the very high salt content of the water, it is difficult to treat by conventional wastewater treatment procedures. Because the water contains very high salt concentrations, most methods normally used to analyze wastewater may not be applicable for testing fracking wastewater without modification<sup>14</sup>. Table 1<sup>15</sup> is an example of some typical fracking solution flow-back water analyses.

Other constituents that may be present in flow-back water are surfactants, glycols, methanol, and polyacrylates that are major ingredients added to the stimulation water mixture. These compounds are not on the "regular" EPA method lists routinely used when screening drinking water, groundwater, or wastewater for environmental compliance. Existing methods, such as EPA SW846 Method 8015 Non Halogenated organics by Gas Chromatography<sup>16</sup>, may not have sufficient sensitivity or selectivity in the complex matrices.

#### 8. Drinking Water

Drinking water supplies such as rivers, lakes, or shallow wells could be contaminated by flow-back and production water in the event of spills, improperly lined storage ponds, or leaking well casings from disposal by underground injection. Since the maximum allowable level for TDS in drinking water is 500 mg/L and chloride has a high solubility and mobility in the environment, drinking water contamination can be quickly detected by a sudden increase in chloride concentration. With the exception of potential contaminants for which there are no existing approved drinking water methods, all approved methods are capable of analyzing drinking water supplies. See Table 2 for a listing of Maximum Contaminant Levels (MCL) for primary drinking water contaminants, and Table 3 for a listing of MCLs for secondary contaminants<sup>17</sup>.

Table 1 Example of Flow Back Water Analysis

Component	Concentration (mg/L)
pH	6.6 (S.U)
Alkalinity as CaCO <sub>3</sub>	140
Total Dissolved Solids (TDS)	67,300
Total Suspended Solids (TSS)	100
Total Organic Carbon (TOC)	63
Biochemical Oxygen Demand (BOD)	3
Oil & Grease	< 5
Sodium as Na	18,000
Calcium as Ca	4,950
Magnesium as Mg	560
Barium as Ba	690
Iron as Fe	40
Chloride as Cl <sup>-</sup>	41,850
Bicarbonate as HCO <sub>3</sub> <sup>-</sup>	74

Table 2 Primary Drinking Water Contaminants and MCLs

Contaminant	MCL (mg/L)
Antimony	0.006
<b>Arsenic</b>	<b>0.010</b>
<b>Barium</b>	<b>2</b>
Beryllium	0.004
Cadmium	0.005
Chromium	0.1
Copper	1.3
Cyanide (free)	0.2
Fluoride	4.0
Lead	0.015
Mercury	0.002
Nitrate	10
Nitrite	1
Selenium	0.05
Thallium	0.002
Acrylamide	Zero
Alachlor	0.002
Atrazine	0.003
<b>Benzene</b>	<b>0.005</b>
Benzo(a)pyrene	0.0002
Carbofuran	0.04
Carbon Tetrachloride	0.005
Chlordane	0.002
Chlorobenzene	0.1
2,4-D	0.07
1,2-Dichloro-3-Dibromopropane	0.0002
o-Dichlorobenzene	0.6
p-Dichlorobenzene	0.075
1,1-Dichloroethane	0.005
1,1-Dichloroethylene	0.007
Cis 1,2-Dichloroethylene	0.07
Trans 1,2-Dichloroethylene	0.1
Dichloromethane	0.005
1,2-Dichloropropane	0.005
Di(2-ethylhexyladipate)	0.4
Di(2-ethylhexylphthalate)	0.006
Dinoseb	0.007
Dioxin	Zero
Diquat	0.02
Endothall	0.1
Endrin	0.002
Epichlorohydrin	Zero
<b>Ethyl Benzene</b>	<b>0.7</b>
Ethylene Dibromide	Zero
Glyphosate	0.7
Heptachlor	0.0004
Heptachlor Epoxide	0.0002
Hexachlorobenzene	0.001
Hexachlorocyclobutadiene	0.05
Lindane	0.0002
Methoxychlor	0.04
Oxamyl	0.2
PCB's	0.0005
Pentachlorophenol	0.001
Pichloram	0.5
Simazine	0.004
Styrene	0.1
Tetrachloroethylene	0.005
<b>Toluene</b>	<b>1</b>
Toxaphene	0.003



2,4,5-TP	0.05
1,2,4-Trichlorobenzene	0.07
1,1,1-Trichloroethane	0.005
Vinyl Chloride	0.002
<b>Xylenes</b>	<b>10</b>
<b>Gross Alpha</b>	<b>15 pCi/L</b>
<b>Gross Beta</b>	<b>4 millirem per year</b>
<b>Radium 226 + Radium 228</b>	<b>5 pCi/L</b>
<b>Uranium</b>	<b>30 ug/L</b>

Table 3 Secondary Drinking Water Contaminants and MCL's

Contaminant	MCL (mg/L)
Aluminum	0.05 – 0.2
<b>Chloride</b>	<b>250</b>
Copper	1
<b>Color</b>	<b>15 CU</b>
Fluoride	2
<b>Foaming Agents (Surfactants)</b>	<b>0.5</b>
<b>Iron</b>	<b>0.3</b>
<b>Manganese</b>	<b>0.05</b>
<b>pH</b>	<b>6.5 – 8.5</b>
Silver	0.1
<b>Sulfate</b>	<b>250</b>
<b>Total Dissolved Solids (TDS)</b>	<b>500</b>
Zinc	5

The contaminants in bold are those that have been reported in<sup>18</sup>, or are likely to occur in water supplies that have been impacted with production or back-flow water. Most of the contaminants in the USEPA drinking water primary and secondary pollutants list are industrial chemicals, such as chlorinated solvents and pesticides that are not very likely to be detected in oil-field water. Contaminants, such as methane or ethylene glycol, are not on the list and unless specifically tested for will not be reported even if they are present. Also, there are no USEPA approved methods for parameters such as methane or ethylene glycol. Water systems (and laboratories) must use EPA approved methods to demonstrate compliance with drinking water regulations. Shimadzu Instruments, such as the GCMS-QP2010SE and the ICPE-9000 are fully capable of analyzing fracking water impacted drinking water supplies for volatile organics by EPA Methods 524.2, 524.3, and 524.4, and for trace metals by EPA 200.7 and 200.5.

## 9. Conclusion

Shale gas deposits are deep below the earth's surface and recovery of gas is expensive and requires millions of gallons of water mixed with chemicals, known as "fracking solution". Most fracking solution stays underground or returns to the surface mixed with formation water, also known as production water. The shale gas recovery operation risks environmental contamination of drinking water and surface water as a result of poorly lined waste ponds, poorly designed wells, or chemical spills. Since the fracking and production water solutions are very high in Total Dissolved Solids and chloride ion, contamination of wells can be rapidly and easily detected. Analysis of the fracking water itself is possible with highly sophisticated instruments, such as those available from Shimadzu. Currently approved drinking water methods are sufficient to monitor drinking water and source water supplies. One of the problems may be that drinking water target organic analytes are mostly chlorinated solvents and pesticides. These compounds are not used in fracking solutions. Methods for the analysis of methane, alcohols, and glycols should be developed.

## 10. References

- <http://www2.epa.gov/hfstudy/hydraulic-fracturing-water-cycle>; accessed May 12, 2014
- Mader, D.; Hydraulic Proppant Fracking and Gravel Packing; Elsevier; 1989
- [http://bergen.spe.no/publish\\_files/ODS2010\\_PG\\_Cole-Hamilton.pdf](http://bergen.spe.no/publish_files/ODS2010_PG_Cole-Hamilton.pdf); accessed May 12, 2014
- Simultaneous analysis of anionic, amphoteric and non-ionic surfactants using ultra-high speed LC-MS/MS; Paper PO-CON1212E;
- Rice, E.W., Baird, R.B., Eaton, A.D., and Clesceri, L.S.; Standard Methods for the Examination of Water and Wastewater 22nd Edition, APHA, AWWA, WEF; 2012
- <http://omrl.eng.ua.edu/Library/Manuscripts/CrosslinkingPapers/SPE90840/SPE90840-3.pdf>; accessed May 12, 2014
- [http://www.halliburton.com/public/cem/contents/Chem\\_Compliance/web/H02686.pdf](http://www.halliburton.com/public/cem/contents/Chem_Compliance/web/H02686.pdf); accessed May 12, 2014
- [http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007\\_07\\_10\\_methods\\_method\\_200\\_7.pdf](http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_200_7.pdf)
- <http://cdn.intechopen.com/pdfs-wm/44660.pdf>, accessed May 12, 2014
- [http://www2.epa.gov/sites/production/files/documents/12\\_Hayes\\_-\\_Marcellus\\_Flowback\\_Reuse\\_508.pdf](http://www2.epa.gov/sites/production/files/documents/12_Hayes_-_Marcellus_Flowback_Reuse_508.pdf)
- Impacts of Shale Gas Wastewater Disposal on Water Quality in Western Pennsylvania; Environ. Sci. Technol., 2013, 47 (20), pp 11849–11857
- <http://blogs.nicholas.duke.edu/thegreengrok/frackingwater/> accessed May 13, 2014
- [http://www.wef.org/uploadedFiles/Access\\_Water\\_Knowledge/Wastewater\\_Treatment/Fracking%20Factsheet%20Final\(1\).pdf](http://www.wef.org/uploadedFiles/Access_Water_Knowledge/Wastewater_Treatment/Fracking%20Factsheet%20Final(1).pdf) accesses May 13, 2014
- <http://www2.epa.gov/sites/production/files/documents/hf-report20121214.pdf> accessed May 13, 2014
- [http://www2.epa.gov/sites/production/files/documents/12\\_Hayes\\_-\\_Marcellus\\_Flowback\\_Reuse\\_508.pdf](http://www2.epa.gov/sites/production/files/documents/12_Hayes_-_Marcellus_Flowback_Reuse_508.pdf)
- <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8015c.pdf>; accessed May 13, 2014
- <http://water.epa.gov/drink/contaminants/> accessed May 18, 2014
- <http://www.uta.edu/news/releases/2013/07/Schug-water-well-contaminant-s-study.php>, accessed May 18, 2014

## Global Monitoring of POPs in the Asian Coastal Region and International Conference of Asian Environmental Chemistry 2014 in Thailand



Kei Machida and Satoshi Yamaki, Shimadzu Corporation

### 1. UNU-Shimadzu Partnership Project

Environmental water contains a variety of elements, including those related to industrial and agricultural activity and urban waste. These pollutants do not have borders. In particular, Persistent Organic Pollutants, or POPs, can remain in water for a very long time and enter the food chain, posing a real risk to human and ecological health. In efforts to manage these pollutants in Asia, the United Nations University (UNU) and Shimadzu Corporation jointly established a capacity-building initiative that would provide Asian countries with the analytical scientific knowledge and technology to monitor pollutants in the environment and better implement multilateral environmental agreements like the Stockholm Convention on POPs. This joint project of global environmental monitoring is now in the 19th year and about to complete its sixth phase. All items monitored were substances of great concern at that time, e.g. both ambient and indoor aldehydes, endocrine disrupting chemicals (EDCs), POPs, and brominated flame retardants. Under this UNU-Shimadzu partnership project, numerous environmental researchers have been trained using the latest analytical scientific techniques for monitoring these pollutants. In addition, an extensive network connecting academia, the private sector and government has been built across the region and internationally.

In the current phase encompassing the November 2012 to October 2015 period, the focus is on perfluorinated compounds (PFCs) monitoring in environmental water in the Asian coastal region. PFCs such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic

acid (PFOS) are highly stable chemical compounds widely used as water repellents, oil repellents and coating agents. These compounds do not decompose easily in the natural world due to their stability. Reports of their detection in rivers, tap water, and food, as well as in the atmosphere and in human blood have led to concern about their effects on the human body. PFCs were added to the POPs group at the Stockholm Convention in 2009.

### 2. Monitoring and Management of POPs in Asia (The Sixth Phase: 2012-2015)

Ten institutes from Asian countries (China, India, Indonesia, Korea, Malaysia, Pakistan, Philippines, Singapore, Thailand, and Viet Nam) are participating in the sixth phase of the UNU-Shimadzu partnership initiative as national project coordinators (NPCs) to monitor POPs in environmental water. In February 2013, Shimadzu provided NPCs with training on the simultaneous separation and detection of PFOS and PFOA in surface water sample using liquid chromatography-tandem mass spectrometry (LC-MS/MS). In addition, Shimadzu supplied and installed LC-MS/MS instruments (LCMS-8040) in China, Korea and Singapore in early 2014 so that analysis of water samples collected by the NPCs in both dry and wet seasons could be conducted. All of the analytical data and reports were submitted to the UNU, which presented some of the monitoring results as well as the quality assurance and quality control practices to the Stockholm Convention regional committee. This data could be an important source for evaluating the global POPs level.

Project outline of the sixth Phase

Period	2012-2015
Target media	Environmental water
Target compounds	PFCs (perfluorinated compounds)
Target chemicals	PFOS/PFOA
Instrument	Shimadzu Nexera XR HPLC and LCMS-8040 triple quadrupole mass spectrometer
Method	ISO25101: 2009(E)
Participating national project coordinators (in alphabetical order)	Bharathidasan University (India) China-Japan Friendship Center for Environmental Protection (China) Chonnam National University (Korea) Department of Chemistry, National University of Singapore (Singapore) Environmental Management Center – PSARPEDAL (Indonesia) Environmental Research and Training Center (Thailand) Natural Sciences Research Institute, University of the Philippines (Philippines) Pakistan Council of Research in Water Resources (Pakistan) University of Malaysia (Malaysia) Viet Nam National University (Viet Nam)

### 3. International Conference of Asian Environmental Chemistry 2014

Disseminating the project activities and findings at relevant academic conferences is one of the objectives of the project. For this purpose, a UNU session was established as part of the scientific programs of the International Conference of Asian Environmental Chemistry (ICAEC) 2014 held from November 24th to 26th in Bangkok, Thailand. The ICAEC 2014 focused on the importance of preventing pollution by micro-pollutants and developing sound environmental management systems in South East Asia, East Asia and the South Pacific region. Recent research activities and observations of various environmental pollutions by micro-pollutants such as PCB, POPs, PPCP, VOC as well as E-waste were presented and discussed by more than 500 environmental chemists from about 20 countries.

The National Project Coordinators (NPCs) from eight countries joined the UNU session and presented their reports on the monitoring activities of PFOA and PFOS in their region that occurred during the first half term of the sixth phase of the project. The samples were collected from river water in each country during the wet and dry seasons of 2013 and 2014. The water samples were concentrated using a solid phase extraction cartridge and stored in a refrigerator. The final extracts were analyzed by electrospray ionization LC-MS/MS and the target compounds were detected using multiple reaction monitoring (MRM) using the Shimadzu LCMS-8040 installed in Singapore and Korea. The procedure was done with reference to the ISO25101:2009(E) analytical method.

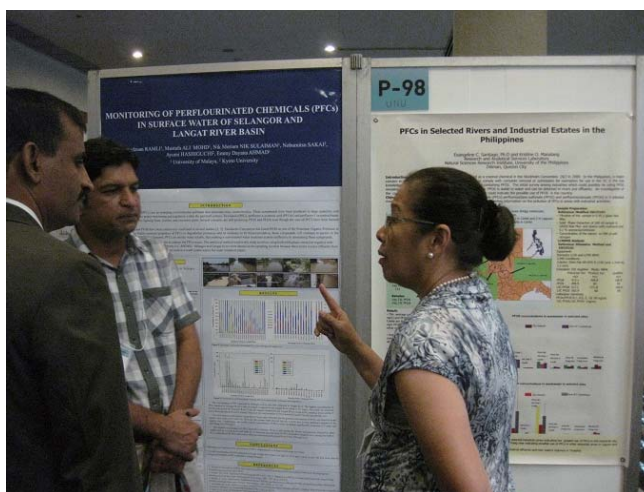
In India, samples were collected from the Kaveri, Vellar and Teamiraparani Rivers with sampling points randomly selected in industrial areas, urban centers and coastal areas. It was observed that PFOA concentration had increased when compared with past research references and the detection of PFCs in wet season was higher than in dry season. Korea reported on the analysis of PFOS and PFOA in water samples collected from rivers, agricultural areas and industrialized bays in Korea with the highest concentration being 33.2 ng/L for PFOS and 42.2 ng/L for PFOA. Singapore provided analysis results of PFOS/PFOA in water samples collected from 8 locations in river water, reservoir water and sea water. It observed that the major sources of PFCs in environmental water in Singapore come from municipal and industrial wastewater effluent. The highest concentration value was 19 ng/L for PFOS and 7.8 ng/L for PFOA. Contrary to India, the detected concentration in dry season was higher than in wet season. Thailand also reported monitoring results with samples collected from 25 locations in four main rivers, industrial areas and the sea. It presented that the industrial zone indicated high concentration in detection during wet season with 729.2 ng/L for PFOS and 118.7 ng/L for PFOA. Viet Nam presented concentration of 13 PFCs in surface water collected at 20 sampling locations from drainage systems in Hanoi city. The highest concentration was 1.65 ng/L for PFOS and 11.64 ng/L for PFOA in rainy season. Aside from oral presentations from India, Korea, Singapore, Thailand and Viet Nam during the UNU session, NPCs from the Philippines, Malaysia and Pakistan presented their results during poster sessions at the ICAEC 2014.

“So far more than 230 and 270 data were obtained for PFOS and PFOA, respectively,” said Dr. Osamu Ito, the United Nations University Institute for the Advanced Study of Sustainability (UNU-IAS). “Although it is still difficult to extract any clear trend across the countries from those limited number of data, there is

tendency that data reported by Thailand seem higher than those reported by India, Malaysia and Pakistan for PFOA. In addition, significant correlation was obtained between data obtained from 1st and 2nd sampling for PFOS, PFOA and PFOA/PFOS ratio, indicating consistency of measurement in each location. In order to make findings from the project convincible, it is necessary to show reproducibility through continuation of monitoring.”



UNU Session at ICAEC 2014



Poster presentation

### 4. UNU Project and Stockholm Convention on POPs

In addition to the NPCs' report, Dr. Yasuyuki Shibata of the National Institute for Environmental Studies in Japan outlined the global monitoring plan (GMP) activities of POPs under the Stockholm Convention. The Stockholm Convention is a global treaty designed to restrict the production and use of persistent organic pollutants in order to protect human health and the environment from these chemicals. The convention was adopted in 2001 and 12 chemicals were registered as POPs; an additional 11 chemicals have since been added. PFCs, the target compounds of the sixth phase of the UNU-Shimadzu partnership project, were listed under the Stockholm Convention in 2009.

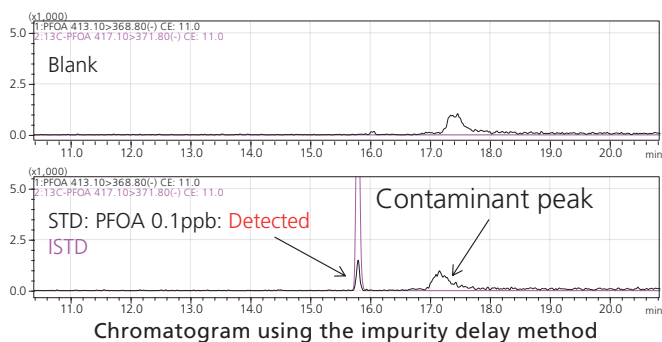
The GMP was established to evaluate the effectiveness of the Stockholm Convention and to provide a comprehensive framework for the collection of monitoring data on POPs from all regions, compilation of the regional reports and the development of

capacity-building activities. To facilitate the implementation of the GMP, the Stockholm Convention has established Regional Organization Groups (ROGs) for five UN regions. Dr. Shibata is working for the GMP as a member in the Asia & Pacific region. He remarked that some of the POPs monitoring data as well as the quality assurance and quality control information obtained under the UNU-Shimadzu partnership project have been reported at ROG meetings and could be important contributions to a global monitoring plan on POPs.

## 5. Shimadzu Applications

Simultaneous analysis of PFOA and PFOS in environmental water, in addition to the related compounds, can be performed by LC-MS/MS. The Shimadzu Ultra Fast LC-MS/MS series (UFMS series) enables trace-level analysis of environmental water using the Nexera XR LC-20 series and LCMS-8040 operated in the electrospray negative ionization mode. Water samples are passed through a solid phase extraction cartridge and eluted with suitable solvent. The concentrated samples are injected with a SIL-20AC XR autosampler. Appropriate MRM transitions are identified and optimized using the automatic instrument optimization function of Shimadzu LabSolutions software.

In addition, Shimadzu has developed an application illustrating a method for reducing background noise in order to increase sensitivity of target PFOS/PFOA. For highly sensitive detection of PFOS/PFOA, it is necessary to remove background contamination that exists in the mobile phase or instrument components. These impurities of PFOA may be detected at the same time as the target PFOA is injected. In order to separate the impurity PFOA, which was derived from the HPLC eluent or system, from the target PFOA in the sample, a delay column (35 mm x 4.0 mm i.d.) was installed between the mixer and the autosampler. In this system, the PFOA peak was detected in 15.8 minutes while the contaminant peak was detected in 17.2 minutes as shown in the left figure below. For the sixth phase of the UNU-Shimadzu partnership project, this impurity delay method was applied to samples of some countries for a performance check. For more details, please refer to: Shimadzu Application C81



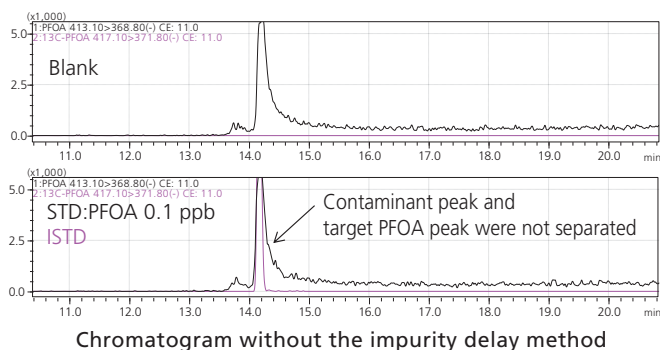
## 6. Acknowledgment

We kindly acknowledge all the UNU project members, especially Dr. Osamu Ito and Ms. Eiko Takashita of the UNU-IAS, Prof. Masatoshi Morita, Faculty of Agriculture, Ehime University, Dr. Yasuyuki Shibata of the National Institute for Environmental Studies, and the following NPC members of the UNU project for their contributions to the UNU Session of the ICAEC 2014.

- Prof. Babu Rajendran RAMASWAMY, Bharathidasan University, India
- Dr. Evangeline Custodio SANTIAGO, University of the Philippines, The Philippines
- Prof. Hian Kee LEE, National University of Singapore, Singapore
- Prof. Hyeon Seo CHO, Dr. Lam Hoang NGUYEN, Chonnam National University, Republic of Korea
- Dr. Ruchaya BOONYATUMANOND, Environmental Research and Training Center, Thailand
- Dr. Shakeel BADSHAH, Pakistan Council of Research in Water Resources, Pakistan
- Prof. Viet Hung PHAM, Hanoi University of Science, Vietnam (in alphabetical order)

## 7. References

- 1) Monitoring Pollution in Asia: A UNU-Shimadzu partnership for capacity building
- 2) ISO 25101: 2009, Water quality – Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) – Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry (2009)





## “Save the Energy” Project

In addition to supplying environmental measuring instruments and industrial equipment that reduce environmental loads, we also intend to strengthen our lineup of products that contribute directly to establishing a low-carbon society. In January 2010, we announced, both within and outside Shimadzu, the “Save the Energy” project, which we established to strengthen our lineup of energy-saving products. This project promotes the development of products that offer the potential of significant energy savings and are consistent with a low-carbon society by achieving energy savings of at least 25 %<sup>\*1</sup> through lower power consumption by the customer and lower operating costs. The project has resulted in reducing the power consumption of many products, and products with power savings of at least 25 % were identified as energy-saving products and certified under Shimadzu’s ECO-label system. By the end of fiscal 2013, this project resulted in developing and selling 34 energy-saving models. Among these, 27 models were analytical and measuring instruments, six were medical diagnostic imaging equipment, and one was an industrial machine.



This product is certified compliant with Shimadzu ECO-label standards.  
Energy savings: XX % lower energy consumption than previous Shimadzu models

$$*1 \text{ Energy saving rate} = \frac{a - b}{a}$$

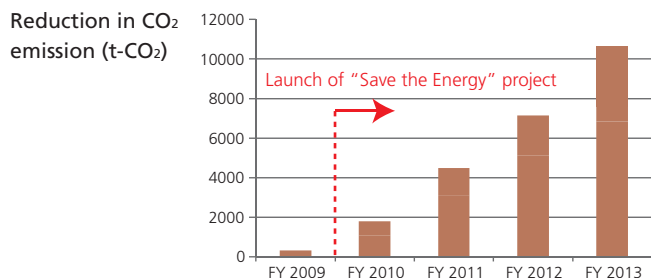
a: Power consumption of previous model  
b: Power consumption of new model

### Shimadzu ECO-Label (Power Saving) Certified Products Analytical and Measuring Instruments

Type	Model	Energy saving rate(%) <sup>*2</sup>	Type	Model	Energy saving rate(%) <sup>*2</sup>
Analytical and Measuring Instruments	GC-2025 gas chromatograph	29.3	Analytical and Measuring Instruments	DSES-1000 long-stroke displacement gauge for soft materials	45.2
	LC-20AP solvent delivery unit for preparative liquid chromatography	41.0		ECU1 series energy-conservation unit for Servopulser hydraulic units	59.4
	SIL-30AC <sub>MP</sub> autosampler for ultra high performance liquid chromatographs	27.9		ECU2 series energy-conservation unit for Servopulser hydraulic units	41.9
	SPD-M30A photodiode array detector for HPLC systems	35.4		EZ Test EZ-LX compact tabletop testers	57.8
	GCMS-QP2010 Ultra gas chromatograph-mass spectrometer	26.2		EZ Test EZ-SX compact tabletop tester	63.8
	GCMS-QP2010 SE gas chromatograph-mass spectrometer	27.3		MOC63u moisture analyzer	32.8
	GCMS-TQ8030 gas chromatograph-mass spectrometer	26.2		Radiography-specific 17-inch FPD	79.2
	GCMS-TQ8040 gas chromatograph-mass spectrometer	26.4		DAR-9000 digital subtraction angiography X-ray image processing unit	73.7
	IRTracer-100 Fourier transform infrared spectrophotometer	33.5	Medical Diagnostic Imaging Equipment	SDR-100 image processing unit (component in FLEXAVISION series systems)	56.3
	PDA-8000 spark optical emission spectrometer	43.3		Direct-conversion type 9-inch flat panel X-ray detector (component in BRANSIST safire angiography systems)	65.2
	EDX-8000 energy dispersive X-ray fluorescence spectrometer	44.1		Direct-conversion type 17-inch flat panel X-ray detector (component in SONIALVISION safire X-ray R/F systems) K-17 main panel assembly	75.8
	EDX-7000 energy dispersive X-ray fluorescence spectrometer	44.1		BRANSIST alexa angiography system	32.9
	SMX-800 microfocus X-ray fluoroscopy system	26.1	Industrial Machinery	MCXS anti-reflective coating system for solar cells	68.1
	TOC-L <sub>CSH</sub> total organic carbon analyzer	36.4			
	UH-200kNXh universal testing machine	81.3			
	UH-300kNXh universal testing machine	81.7			
	UH-F300kNXh universal testing machine	54.0			
	UH-500kNXh universal testing machine	81.9			
	UH-F500kNXh universal testing machine	54.3			
	UH-1000kNXh universal testing machine	81.8			
UH-F1000kNXh universal testing machine	61.6				

\*2 Energy savings rates were calculated based on operating products under the same conditions as the previous Shimadzu model. Actual energy savings may vary depending on operating conditions. Therefore, the indicated data is not intended as a guarantee of performance.

The total power consumption of the energy-saving models sold in fiscal 2013 was 44 % less than the energy that would have been consumed if the previous models had continued to be sold. Therefore, results far exceeded target savings. The energy-saving models sold in fiscal 2013 also reduced customer CO<sub>2</sub> emissions<sup>\*3</sup> by about 3,500 t-CO<sub>2</sub>. This is equivalent to about 8 % of the Shimadzu Group’s total CO<sub>2</sub> output of 44,472 t-CO<sub>2</sub> in fiscal 2013. Considering all the energy-saving models sold globally between fiscal 2010 and 2013, this project has reduced CO<sub>2</sub> emissions by over 10,000 t-CO<sub>2</sub>.



<sup>\*3</sup> CO<sub>2</sub> reductions assume that customers operate the products using Shimadzu's standard operating conditions.

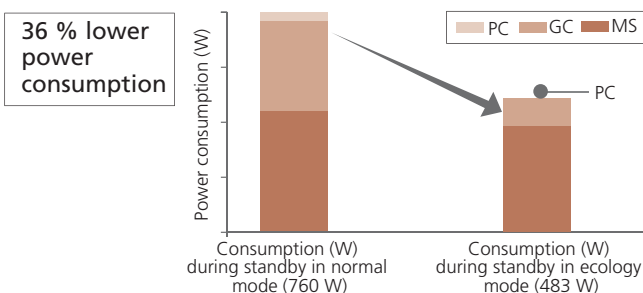
We are confident that by continuing to reduce the power consumption of products, we will contribute further to achieving a low-carbon society. Therefore, we intend to develop additional energy-saving models by deploying the technology used in current energy-saving products in other products throughout the company. We will also reduce the environmental impact of products by considering their entire product life cycle.

### GCMS-QP2010 Ultra Gas Chromatograph-Mass Spectrometer



The industry's first system with an ecology mode, the GCMS-QP2010 Ultra also helps save carrier gas and other resources

The gas chromatograph-mass spectrometer is a system that combines a gas chromatograph with a mass spectrometer. It can qualitatively and quantitatively analyze individual components in samples containing a large number of components by vaporizing the samples at a high temperature, separating each component, and then ionizing the components. It is used to measure trace components in substances from a wide variety of fields, including environmental testing, electronics and semiconductors, chemicals, pharmaceuticals, food products, residual pesticides, and the life sciences. The GCMS-QP2010 Ultra features the Ecology mode that reduces power consumption during the analysis standby mode by 36 %. Activating the Ecology mode automatically saves unnecessary power consumption in the gas chromatograph (GC), mass spectrometer (MS), and computer. Furthermore, it reduces the consumption of carrier gas (used to carry the sample into the instrument). The Ecology mode can also be entered automatically after a series of analyses is finished, enabling it to automatically save power and carrier gas after analyses are finished at night. As a result, using the Ecology mode for a year<sup>\*4</sup> could reduce power consumption by 26 % and CO<sub>2</sub> emissions by about 1.1 tons per unit.



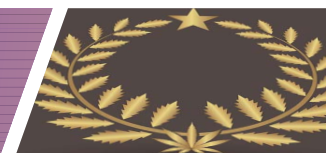
<sup>\*4</sup> Assuming the system is operated 6 hours a day for 260 days a year using Shimadzu's standard analytical conditions.

### UH-X/FX Series Hydraulic Universal Testing Machine Significantly less hydraulic oil required



Hydraulic universal testing machines are used to test the strength of materials and products by hydraulically applying a load. They can be used to perform a wide variety of tests, such as tensile, bending, compression, and cycle tests. They are essential for quality control and research and development of products and materials. The UH-X/FX Series machines are used for a variety of materials, but especially for testing the strength of concrete and metals. They are an essential testing machine in a diverse range of fields, such as for manufacturers in construction, steel, or automotive industries, for academic research laboratories, or government testing and inspection facilities. In 1955, Shimadzu was the first manufacturer to offer a domestically made universal testing machine. In the half-century since then, Shimadzu has continued to manufacture and sell universal testing machines and is currently the leading manufacturer in Japan, with about a 70 % market share in Japan and 10 % globally. The UH-X/FX series features a hybrid hydraulic unit that combines an AC servo motor and hydraulic pump to provide especially efficient control. The hybrid hydraulic unit is designed to only operate the pump when necessary, which reduces the amount of hydraulic oil required and significantly reduces the amount of electrical power consumed. The UH-500kNXh offers 82 % lower power consumption and requires only 40 liters of hydraulic oil, which is half the 80 liters required by the previous model. This helps reduce any environmental impact from discarding the oil.

## Shimadzu awarded twice in The Analytical Scientist Innovation Awards 2014



On December 23, The Analytical Scientist Innovation Awards (TASIAS) 2014 were published, celebrating a year’s worth of innovations and announcing 15 innovative advances. Shimadzu is honored to be recognized for two innovative analytical systems. The winner is the iMScope *TRIO* imaging mass microscope while the other selection is the Nexera-e comprehensive two-dimensional liquid chromatograph.

In the article, Rich Whitworth, the editor of The Analytical Scientist, said, “Our first TASIAS in 2013 set a worryingly high benchmark for all subsequent awards. I am delighted to report that the 2014 TASIAS easily hit that benchmark and feature 15 truly innovative advances,

many of which we expect to have game-changing implications in analytical science. Clearly, the TASIAS shine a light on the 15 winners, but we also hope that they demonstrate the innovation-rich nature of our field.”

The full TASIAS article can be found online, here: [Download pdf](#) (page 26, 30)

The 2014 TASIAS are also available in The Analytical Scientist print magazine, the iPad app, and in the downloadable PDF of the December issue.

### Winner: iMScope *TRIO*<sup>(\*)</sup>



[More information](#)

The judges of the TASIA 2014 described this system as “Combine light + MS microscopy = power” because of its revolutionary new technology of imaging mass spectrometry, a combination of an optical microscope with an imaging mass spectrometer.

(\*)This instrument is sold in all areas but North America.

### #7: Nexera-e



[More information](#)

The judges commented that it “Allows spatially resolved analysis using two complementary high resolution techniques. It is no longer just about what is in a sample, but also about where the molecules are, what are their neighbours, etc.”

## New Products

### Nexera UC

World's Foremost 'Unified Chromatography' System, which for the First-Time-Ever Showcases Complete Automation and Combines Automatic Sample Pre-treatment with Chromatographic Separation and Analysis



[Click here>>](#)

The Nexera UC system is designed to fulfil the measurement requirements of a wide range of applications, including monitoring pesticides in food products; drug delivery and search for disease biomarkers; additives in forming polymers; drug discovery research in pharmaceuticals and biopharmaceuticals along with cleaning validation.

#### Features

- Fully Automated On-line Sample Preparation and Analysis
- Even Labile Compounds Can be Analyzed without Degradation
- Extremely High Speed, Sensitivity, and Resolution

Note: The Nexera UC system was developed in collaboration between Shimadzu Corporation, Osaka University, Kobe University and Miyazaki Agricultural Research Institute, which is funded by the Japan Science and Technology Agency (JST).

### 5D Ultra-e

World-Leading 5D Ultra-e LC-GCxGC-MS/MS System Provides Five-Dimensional, Precise, Comprehensive Analysis of Extremely Complex Samples



[Click here>>](#)

The 5D Ultra-e (LC-GCxGC-MS/MS system) is a unique system that combines a comprehensive two-dimensional gas chromatograph and triple quadrupole mass spectrometer with an HPLC system connected online. This system is the only one of its kind in the world.

#### Features

- Consolidation of Technology for Maximizing the Capacity of Comprehensive 2D GC-MS
- Highly Selective MS/MS Detection

Note: This LC-GCxGC-MS/MS system was developed by the group led by Prof. Dr. Luigi Mondello at the University of Messina and Chromaleont S. r. l. in Italy and developed into a product by Shimadzu Corporation.



### EPMA-8050G

Achieving the World's Highest Level Sensitivity and Spatial Resolution



[Click here>>](#)

While maintaining excellent operability, this model is equipped with the latest field emission (FE) electron optical system, and achieves world-leading sensitivity and spatial resolution for an FE-EPMA instrument.

#### Features

- World's Highest Level of Spatial Resolution
- Large Current Ensures the World's Highest Level of Sensitivity
- Supports Automatic Analysis with Excellent Current Control Capabilities





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Printed in Japan, March, 2015