[CASE STUDY]

IMS and APGC Advance the Discovery of Emerging Environmental Pollutants

Memorial University of Newfoundland's investment in state-of-the-art Waters instrumentation enables researchers to simultaneously detect tens of thousands of compounds present in complex environmental and biological samples with the ultimate goal of identifying emerging contaminants.

ENVIRONMENTAL RESEARCH AT MEMORIAL UNIVERSITY OF NEWFOUNDLAND

Researchers at the Memorial University of Newfoundland (MUN), Canada, are dedicated to research excellence that is both locally relevant and internationally significant. One such area with a substantial global impact is the identification of emerging environmental contaminants using a combination of state-of-the-art mass spectrometry (MS), multidimensional separation techniques and computational chemistry. The Jobst Research Group at MUN investigates how these pollutants impact the environment and human health, and then works collaboratively with partners in industry and government to guide the development of safer chemicals and effective regulatory interventions.

Under the helm of Dr. Karl J. Jobst, Assistant Professor in the MUN Department of Chemistry, researchers collaborate with clinician scientists, chemical biophysicists, computational chemists, epidemiologists, and experts in public health, to identify novel contaminants that are associated with adverse health outcomes at all stages of life. After serving in positions at the Ontario Ministry of the Environment and Environment Canada, Dr. Jobst joined the MUN faculty in 2019 to further his research in detecting emerging pollutants. His team believes this work is a crucial step towards establishing guidelines to limit exposure, as well as preventing health outcomes that result from pollution.

At MUN, researchers collaborate to identify novel contaminants that are associated with adverse health outcomes at all stages of life. Photo credit: Memorial University Newfoundland.

WORKING WITH WATERS

While the technical capabilities of the Waters™ Instrumentation certainly play a big role in the Jobst Research Group's recent ground-breaking work, Dr. Jobst also credits the help of the Waters team. The support from Waters personnel in getting the new instrumentation up and running quickly in the laboratory has sped up the process of some truly exciting discoveries. He explains:

"We had excellent training and support from Waters, so the instrument integrated almost seamlessly into the lab environment. It's one thing to purchase an instrument with certain specifications. It's another to have good technical support and training to back you up as you bring the instrument online. I'm lucky to work with talented graduate and undergraduate students who also were trained by Waters, and they've already produced a lot of interesting results. The instrument was installed in December 2021, and by spring of 2022, we had the results for our first couple of publications on studies we conducted using the instrument. The entire process went very smoothly."

"The bigger picture of our work is characterizing anthropogenic chemicals that pose a risk to human health and the environment. Our goal is to find these compounds and to work with colleagues who can help us determine their potential harms or adverse effects. As a chemist, I'm pro-chemical because chemistry enables our way of life. However, science has proven that a small fraction of these chemicals can harm the environment and our health. With the advancement of high-resolution mass spectrometry (MS) and ion mobility mass spectrometry (IMS), now we have technologies to keep up with the number of emerging pollutants and work towards limiting any negative impact they may have."

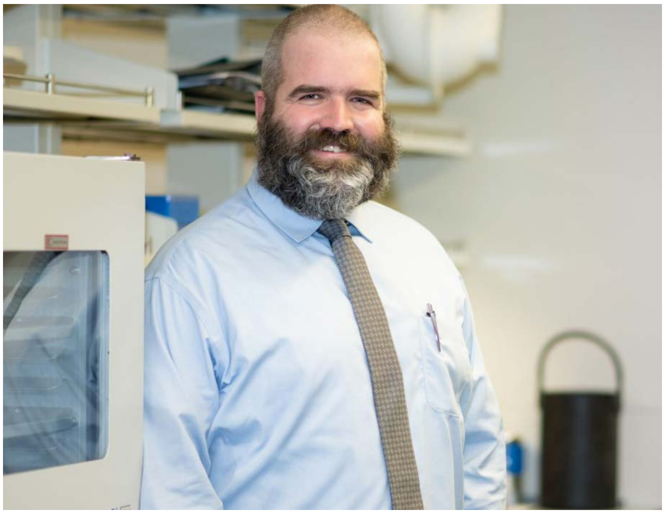
DR. KARL J. JOBST
Assistant Professor in the MUN Department of Chemistry

The Jobst Research Group is charting new territory in their work with help from recent investments in Waters SELECT SERIES™ Cyclic IMS™ and Waters Atmospheric Pressure Gas Chromatography (APGC™) Ionization Technology.

ENVIRONMENTAL CONTAMINANT DETECTION AND IDENTIFICATION

Growing concerns about the ability of some chemicals to persist in the environment over extended periods and accumulate in both humans and wildlife have bolstered efforts to identify and regulate these substances known as persistent organic pollutants (POPs). Because environmental contaminants can encompass a wide range of chemical compounds with diverse structures and properties, identifying unknown contaminants becomes more difficult when they do not fit into established categories or are structurally novel. Many contaminants also exist in minute concentrations, requiring highly sensitive analytical techniques to identify them accurately.

MS stands as the prevailing technique for discerning environmental contaminants, where the nature of a pollutant molecule is inferred through the behavior of its associated ion.



Dr. Karl J. Jobst (pictured) and his team use the Waters SELECT SERIES Cyclic IMS to investigate how pollutants impact the environment and human health. Photo credit: Memorial University Newfoundland.

The Jobst research group focuses on investigating this ion chemistry and developing innovative methods to selectively ionize and detect hazardous chemicals. With recent investments in Waters instrumentation, the laboratory now possesses cutting-edge equipment capable of concurrently identifying tens of thousands of compounds within complex environmental and biological samples. Dr. Jobst explains:

"There's a renaissance in trying to find new chemical contaminants in the environment, and that's largely powered by the availability of new hardware. With recent developments in high-resolution MS and IMS, we now have advanced technologies that allow us to actually keep up with the number of emerging pollutants."

PFAS

Some of the more well-known chemical compounds of concern are per- and polyfluoroalkyl substances (PFAS), which have been widely used since the 1940s in industry and everyday household products, because they persist in the environment and bioaccumulate in humans and wildlife. Despite these concerns, the identities of most PFAS in environmental and biological samples are unknown today. Dr. Jobst describes the problematic nature of these compounds:

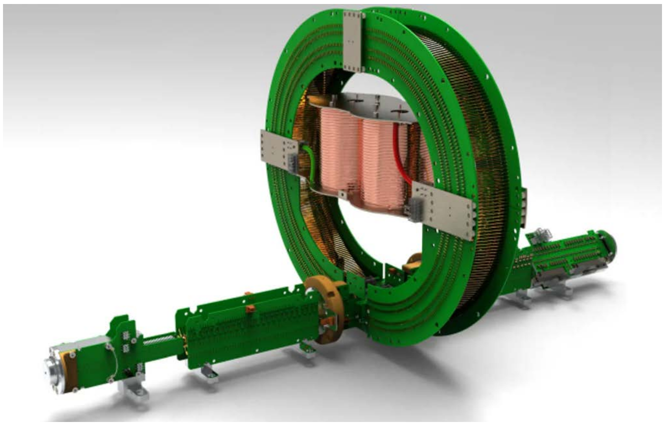
"We can find chemicals originally produced in industrial parts of Canada and the United States that have travelled to very remote regions. Some of these chemicals are found in the blood of virtually every human being on the planet. It's in our interest to identify and quantify these compounds, as well as try and find out what new pollutants are coming down the pipeline."

When Dr. Jobst began establishing his new research group, he invested in the Waters SELECT SERIES Cyclic IMS, which combines novel cyclic ion mobility separation (cIMS) with state-of-the-art high performance and time-of-flight MS, to aid his team in expanding this work in environmental contaminants. The instrument enables selection of ions by both mass and mobility, a unique and enabling functionality of cIMS that provides unparalleled flexibility and capabilities for research studies in both academia and industry.

"The Waters SELECT SERIES Cyclic IMS offers a great advantage in its mobility resolving power. The capability of cIMS has been extremely important for our work because it's allowed us to identify PFAS that would not be discovered by any other technique or strategy, to my knowledge."

DR. KARL J. JOBST
Assistant Professor in the MUN Department of Chemistry

In a unique configuration, the Jobst Research group uses the SELECT SERIES Cyclic IMS with APGC ionization to reveal the presence of unknown PFAS based on the ratio of their mass and collision cross section (CCS). One recent study used gas chromatographic cyclic ion mobility mass spectrometry (GC-cIMS) on indoor dust samples. The results revealed chlorofluoro n-alkane compounds without prior knowledge of their occurrence, suggesting the presence of an emerging class of "forever chemicals" that contaminate the indoor environment.[1]



The Jobst Research group are using the SELECT SERIES Cyclic IMS to explore the relationship between CCS and drift, unwrapping the chromatographic cyclic ion mobility data and recovering ion mobility displacement information.

Another study reports on the discovery of fluorotelomer ethoxylates (FTEO) in indoor dust and industrial effluents using GC-cIMS. Alarmingly, the highest concentrations were observed in samples collected from healthcare facilities, consistent with the potential use of these compounds as stain repellents and in anti-fog products; such sprays are used to prevent condensation on eyeglasses. These results suggest that FTEOs may well be widespread pollutants that are more persistent than previously thought.[2]

Dr. Jobst explains how his team uses CCS measurements from the Waters SELECT SERIES Cyclic IMS with APGC ionization to discover undocumented pollutants, and their potential environmental impacts, without prior knowledge of their occurrence or structure:

"The mass versus CCS plots really helped us find these compounds. One of the most commonly used approaches to identify PFAS nowadays uses negative mass defect to recognize when PFAS are present in the sample. And that works well for legacy PFAS compounds, but it didn't work for the FTEO compounds that we've recently reported on. I don't think that discovery would have been made without this instrumentation. I believe that they would have only been discoverable by GC-MS. They don't ionize all that well with liquid chromatography (LC) coupled with MS, so it was kind of serendipitous that we're able to find these compounds. I was quite surprised with the number of PFAS that we were able to observe by GC-MS and didn't see by LC-MS. This configuration may be the only way to find these types of compounds."

Yet identifying the compound is just the first step. In some cases, the scientific understanding of a contaminant may still be evolving, leading to uncertainties regarding its health and environmental impacts.

"It's one thing to interpret the spectrum and come up with a structure proposal. But that must be followed up with additional experiments to confirm the identity. Ultimately, we want to quantify those compounds so we can better understand the potential impacts on the environment and why those compounds are there in the first place."

DR. KARL J. JOBST
Assistant Professor in the MUN Department of Chemistry

MICROPLASTICS

With grants from the Natural Sciences and Research Council (NSERC) and the Government of Canada's New Frontiers in Research Fund (NFRF), the Jobst Research Group is also conducting research on microplastics, which can enter the human body through ingestion of contaminated food and water or inhalation of airborne particles. While the full extent of the health impacts of microplastic exposure on humans is still being studied, there is growing concern about potential risks as they can accumulate in tissues and organs, potentially causing inflammation, oxidative stress, and other adverse effects.

Recent work by Dr. Jobst and his team found concentrations of size-resolved particles of common plastics, such as polyethylene, polypropylene, polystyrene and polymethylmethacrylate, in indoor air samples. The concentrations of indoor microplastics exceed those measured in the outdoor environment by several orders of magnitude, which suggests that the indoor environment could be the main source of exposure. While plastics remain essential for modern life, the potential risks associated with exposure to microplastics particles, as well as their additives and decomposition products, underline further need for their study.[3]

"Our preliminary results suggest we are exposed to a significant concentration, on the order of 100 to 200 µg per day, of polystyrene and other plastics. A significant portion of particulate matter below 2.5 µm in size is composed of plastic. Until now, no one really knew how much of these plastics were in indoor air. There are lots of measurements in the marine environment, especially of particles that are relatively large, exceeding 5-10 µm. But not the very small particles, the ones that can get into your lungs and potentially pass into your blood stream. Next, we'll work with colleagues to do exposure experiments to understand the potential effects. That thread of research has just started."

DR. KARL J. JOBST
Assistant Professor in the MUN Department of Chemistry

The Waters SELECT SERIES Cyclic IMS combines cIMS with high performance time-of-flight MS.

DATA STRATEGIES

Analyzing complex data obtained from environmental samples requires expertise in data interpretation and pattern recognition. Yet the presence of multiple compounds and interferences in environmental matrices can complicate the identification process, requiring extensive data processing and advanced statistical analysis. Modern mass spectrometers can provide information on tens of thousands of chemical compounds, but the inability to identify every compound can limit researchers. As a result, Dr. Jobst and his team are working on how to focus on the small fraction of data points that are likely persistent organic pollutants or emerging contaminants. Dr. Jobst describes these challenges:

"In an ideal world, we would be able to identify every compound present in a sample automatically and accurately, but that's just not possible with the current methodologies. The next best thing is to develop data reduction strategies that help us focus on the chemicals that are most likely to be pollutants. Ion mobility has really helped us in that respect, and to be honest, I'm surprised it hasn't been exploited more. If we measure the mass of a molecule along with its size and shape, then we can use that information to filter the data and really focus on persistent and bioaccumulative pollutants that are likely harmful. This strategy allows us to reduce the data set by orders of magnitude."

Again, the capabilities of the Waters SELECT SERIES Cyclic IMS have played a key role in this work.

"Once we've tentatively identified the compounds, the precision of the Waters SELECT SERIES Cyclic IMS allows us to confirm the identity of the compounds. Ultimately, we can use the system not only as a non-targeted tool, but in a targeted way to quantify those compounds, to establish their occurrence in the environment, and to better understand their use and why they're there. If we find an emerging class of compounds, and based on semi quantitative analysis, we determined that the concentrations are comparable to those of known pollutants, that might raise awareness to regulators and eventually help to adjust monitoring programs and regulations."

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Assistant Professor in the MUN Department of Chemistry

The Jobst Research Group is also interested in discovering new capabilities of the Waters SELECT SERIES Cyclic IMS instrumentation. Ion mobility resolution increases with the length of the mobility device and therefore with the number of passes. The team has begun to explore the relationship between CCS and drift with the Cyclic to unwrap the chromatographic cyclic ion mobility data and recover ion mobility displacement information. One recent study demonstrated that "wrap-around" can be mitigated by comparing drift times measured during single- and multipass experiments and extrapolating the number of passes experienced by each ion. This straightforward calculation results in the "unwrapping" of cIMS data so that the experiments can be interpreted in a nontargeted way while also reaping the benefit of peak capacities that rival those achieved using other comprehensive two-dimensional separations.[4]

Dr. Jobst explains the rationale behind this work:

"It's a problem that we wanted to solve to gain greater functionality of our instrument and ultimately use it to find new pollutants. It's about playing with the Cyclic and seeing what it can do. Most users only send the ions around 5–10 times. We wanted to see if there was any benefit to sending the ions around 100 times, even if the ions "wrap-around". The data suggests that if you send the ions around over 100 times, the precision of the measurement improves dramatically. It's a way of acquiring highly precise CCS measurements. I think users of the instrument will want to know that, and it will ultimately benefit my group's work on identifying unknown compounds."

NEXT STEPS

Even with so many projects on the go in the laboratory, the Jobst Research Group is already looking ahead at what else they can do with their new instrumentation. That includes expanding on their PFAS identification work by collaborating with other scientists and applying the technology to new samples.

"We have a study that will be published soon on fully characterizing industrial wastewater samples, and we're seeing many more examples of these non-ionic PFAS. We'll work with colleagues who can do exposure studies to better understand how these compounds can affect ecosystems and impact human health."

DR. KARL J. JOBST
Assistant Professor in the MUN Department of Chemistry

Yet the identification process is just the beginning, as the team's long-term goal is providing the research necessary to update regulatory frameworks on emerging contaminants, which can be a complex and time-consuming process. Existing regulatory frameworks tend to not be well-suited to addressing newly discovered contaminants. Regulatory gaps commonly exist in terms of testing methodologies, exposure limits, risk assessment procedures, or enforcement mechanisms.

"There is a bit of a cat and mouse game between regulators, industry and academia. When a compound is recognized as being harmful, it's often regulated, and the industry will often agree to stop producing it. But then they will replace it with something that is not always less likely to be harmful, and the cycle continues. Our goal here at MUN is to build a lab that can find these contaminants before they become a global problem."

DR. KARL J. JOBST
Assistant Professor in the MUN Department of Chemistry

It's an ambitious goal that will certainly keep Dr. Jobst's team busy for the foreseeable future. He comments, with an air of sanguinity:

"Ultimately, by the end of my career, if we can actually finish the game and get a comprehensive list of all the contaminants that are present in the environment, then I would say I'm done, and I can probably retire."

References

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