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The race is on for low-cost PFAS sensors

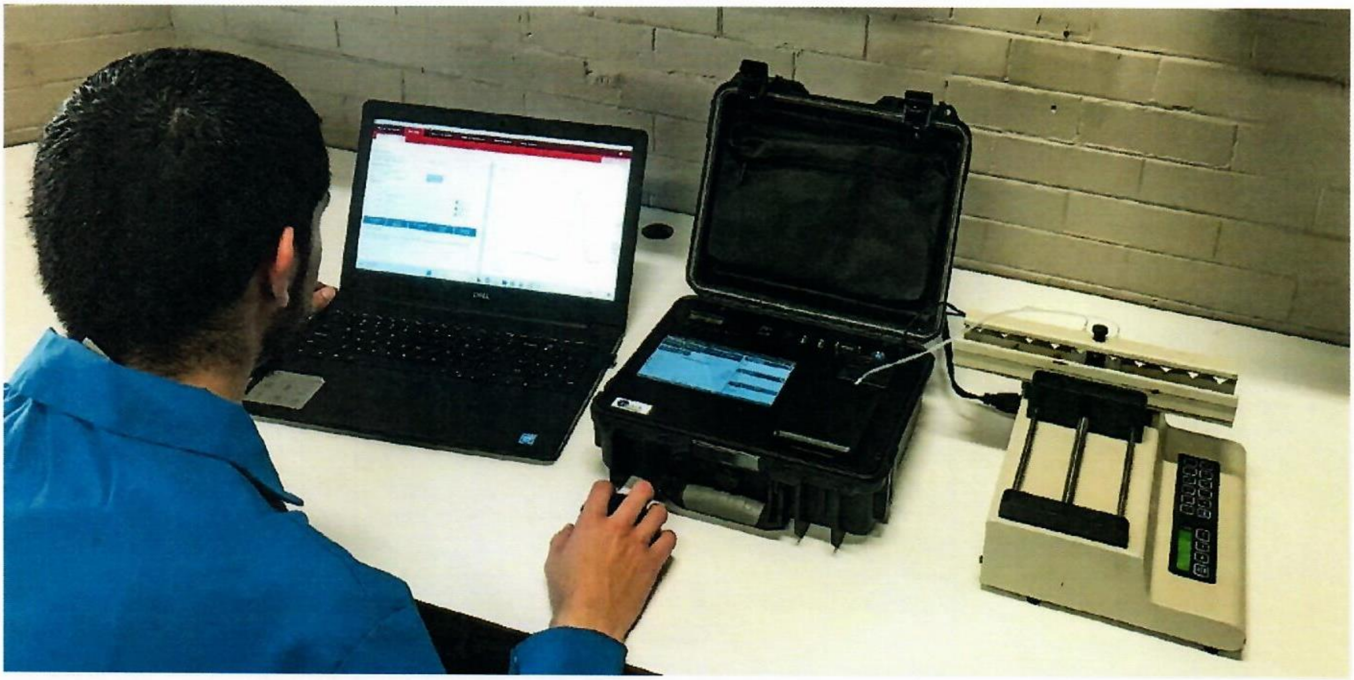
Researchers seek to improve the selectivity and sensitivity of field-deployable devices

BRITT E. ERICKSON, C&EN STAFF

For some scientists, the quest to develop an easy-to-use, low-cost sensor for detecting per- and polyfluoroalkyl substances (PFAS) in drinking water is personal. “I bought a new house, and I got this letter that said apparently we had PFAS in our water and we needed a reverse osmosis system,” says Sagnik Basuray, a chemical and materials engineer at the New Jersey Institute of Technology.

In brief

Testing for per- and polyfluoroalkyl substances (PFAS) in drinking water is big business, and it's about to get a lot bigger because of new limits proposed by the US Environmental Protection Agency for six of the so-called forever chemicals. Many researchers are hoping to cash in on the growing demand for PFAS testing by commercializing low-cost, portable sensors that can rapidly screen water for the contaminants. Scientists are excited about what these sensors can do, but it will likely be a few years before a commercial product is available. First, researchers must improve the sensitivity so they can detect PFAS at the low part-per-trillion limits proposed by the EPA. And they need to improve the selectivity of sensors to be able to differentiate between the thousands of PFAS on the market. The stability of field-portable sensors over time is also a challenge.



A technician tests a field-portable electrochemical per- and polyfluoroalkyl substances analyzer being developed by 2Witech Solutions.

CREDIT: QINGWU WANG

Basuray has experience developing sensors for cancer, zoonotic diseases like bird flu, and environmental pollutants. When he received the letter about PFAS in his tap water, he started thinking about how to adapt his sensor platform to detect these prevalent contaminants.

Researchers like Basuray got interested in developing PFAS sensors because of contaminated drinking water in or near their homes. Many of them are now eager to commercialize their devices after the US Environmental Protection Agency's proposal in March to set limits for six of the chemicals in drinking water. They have portable technology that can detect ultralow levels of PFAS in water, but most acknowledge that it will be a few more years before such devices are ready to hit the market.

Often called forever chemicals because they are slow to break down, PFAS are known for their ability to resist oil and water. They are found in many household products, including raincoats, nonstick frying pans, and fast-food packaging. Little is known about the health effects of most of the thousands of commercial PFAS, but a few of them are considered harmful at extremely low levels.

For two of the most toxic PFAS—perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS)—the EPA proposed limits of 4 parts per trillion each in drinking water. The two chemicals are no longer used or produced in the US, but they contaminate drinking water throughout the country and worldwide.

It's challenging to detect PFAS at such low levels without the use of expensive laboratory-based techniques like liquid chromatography/tandem mass spectrometry. Laboratories typically charge a few hundred dollars to analyze a tap-water sample for PFAS, and it often takes weeks to get the results.

If the EPA finalizes its proposed limits for the six PFAS in drinking water, public water utilities in the US will be required to monitor for the chemicals and keep levels below the limits. Demand for low-cost, rapid sensors that can screen water samples for PFAS is expected to grow rapidly.

Many researchers see the growing demand as a business opportunity. But first they have some hurdles to overcome related to adaptability for field use, sensitivity, and selectivity.

The biggest challenge right now for PFAS sensors is sensitivity, says Mohamed Ateia Ibrahim, an environmental engineer with the EPA's Office of Research and Development. Some researchers claim that their devices have detection limits in the low part-per-trillion range, but most of them are not yet able to reach the EPA's proposed limits for PFOA and PFOS.

> "I'm really interested in getting things off of a benchtop and into the setting where they're useful."
>
> **—Rebecca Clark,** graduate student, Purdue University

Selectivity is also an issue because of the large number of PFAS in the marketplace, Ateia says. He is skeptical that any PFAS sensor can differentiate between all of them, despite some claims that they can be specific to individual PFAS. Researchers are also working to improve the stability of sensors to prevent the measurement signal from drifting over time.

PFAS are difficult to measure directly with any sensing device, let alone an inexpensive one. They are not active electrochemically or optically. So researchers have developed creative ways of measuring them indirectly.

Electrochemical approaches seem to have an edge over optical methods like fluorescence or surface plasmon resonance in terms of sensitivity. The most common electrochemical approaches use electrodes modified with molecularly imprinted polymers (MIPs) or metal-organic frameworks (MOFs) that capture PFAS. One group is investigating microelectrodes that monitor bubble nucleation induced by PFAS. Electronic sensors that measure the charge resulting from interactions between PFAS and novel sensing materials are also on the horizon. And efforts to integrate ultrasensitive single-particle nanosensors onto a portable platform are underway.

The magic of MIPs

MIPs can be tailored to attract and capture PFAS, so they are a popular choice for sensors. Several researchers are modifying the surfaces of electrodes with MIPs to make them suitable for detecting the fluorochemicals. Paolo

Ugo, a senior researcher at the Ca' Foscari University of Venice, and colleagues published some of the first results using the approach for detecting PFOS in water (*ACS Sens.* 2018, DOI: 10.1021/acssensors.8b00154). That work laid the foundation for other groups to build on.

The researchers in Italy modified a gold electrode by electropolymerizing *o*-phenylenediamine in the presence of PFOS as a template molecule. When the PFOS is stripped away, cavities the same size and shape as PFOS are left behind in the polymer matrix. Those cavities have a high affinity for the fluorochemical.

To generate a voltammetric signal, the researchers added the electroactive substance ferrocenecarboxylic acid to water. If PFOS is in the water, it binds to the cavities and blocks the signal from the ferrocenecarboxylic acid. The decrease in electrochemical response is proportional to the concentration of PFOS. The researchers claim that the method can detect PFOS levels down to about 20 parts per trillion.

In terms of selectivity for PFOS in the presence of other PFAS, the approach is "good but of course not 100%," Ugo says. One PFAS chemical in particular, perfluorobutanesulfonic acid (PFBS), interfered the most because like PFOS it has a sulfonate group, he says. The difference is that PFBS has four carbons, and PFOS has eight.

Jeffrey Dick, an electrochemist at Purdue University, and colleagues have adapted the approach for use in rivers and other natural waters, where ferrocenecarboxylic acid is not found in high concentrations.

"You're not going to find ferrocene out in the environment, and you probably

Purdue University researchers plan to test this electrochemical sensor for detecting per- and polyfluoroalkyl substances in the field.

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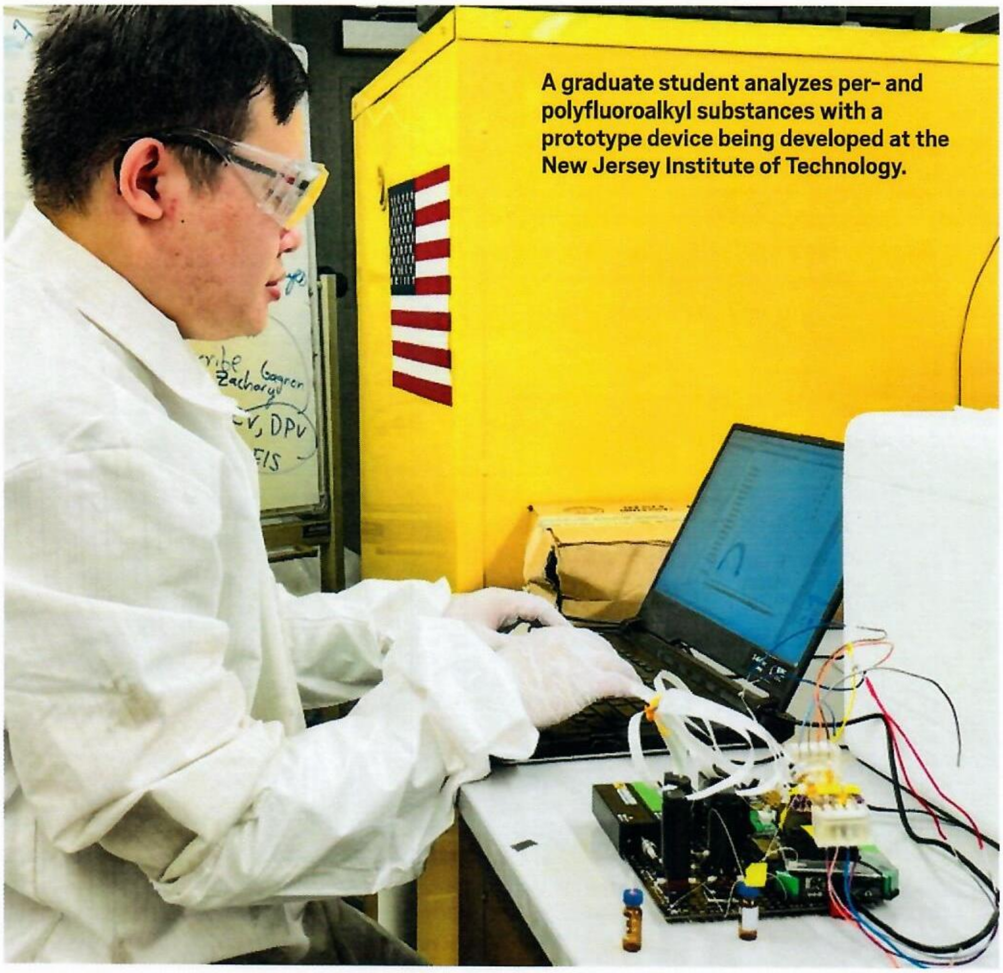


A graduate student analyzes per- and polyfluoroalkyl substances with a prototype device being developed at the New Jersey Institute of Technology.

don't want to introduce it into the environment," Dick says. "So we started brainstorming ways that we can take advantage of what's already in the environment for the sensing." The researchers settled on oxygen as the electrochemically active probe to generate a signal.

Oxygen is typically found in natural waters, but not always. And fluctuating levels of oxygen are problematic for sensing. So Rebecca Clark, a graduate student in Dick's lab, investigated the hydrolysis of water to generate a constant stream of oxygen. Having a constant concentration of oxygen in the water ensures that "we're not seeing differences in signal just because there are different oxygen levels," Clark says.

The Purdue group has shown in the lab that its MIP-based sensor can detect PFOS in river water samples, which have high concentrations of humic acid and chloride (*ACS Sens.* 2020, DOI: 10.1021/acssensors.0c01894). The team has yet to test the sensor in the environment, but Clark intends to do so in the coming weeks. "We use a potentiostat to make the measurements," she says. "We can make a portable one for $50."

The approach is not great at differentiating between PFOS and smaller PFAS like GenX, a six-carbon replacement for PFOA, Dick says. But it is excellent at differentiating between fluorinated and nonfluorinated compounds, he says.

The researchers have also developed hardware for a multiplexed system that has 78 working electrodes (*Anal. Chem.* 2021, DOI: 10.1021/acs.analchem.0c05299), "so in theory you could measure 78 different analytes," Clark says. The multiplexed system could also be used with the same MIP on every electrode to get multiple measurements of the same analyte and improve the statistical power of the analysis, she says.

Qingwu Wang, president of the Massachusetts-based start-up 2Witech Solutions, is also developing electrochemical MIP-based sensors for PFOS and PFOA. Using differential pulse voltammetry, he claims to get a detection limit of 10 parts per trillion for each. His sensing device is portable and housed in a suitcase the size of a laptop computer.

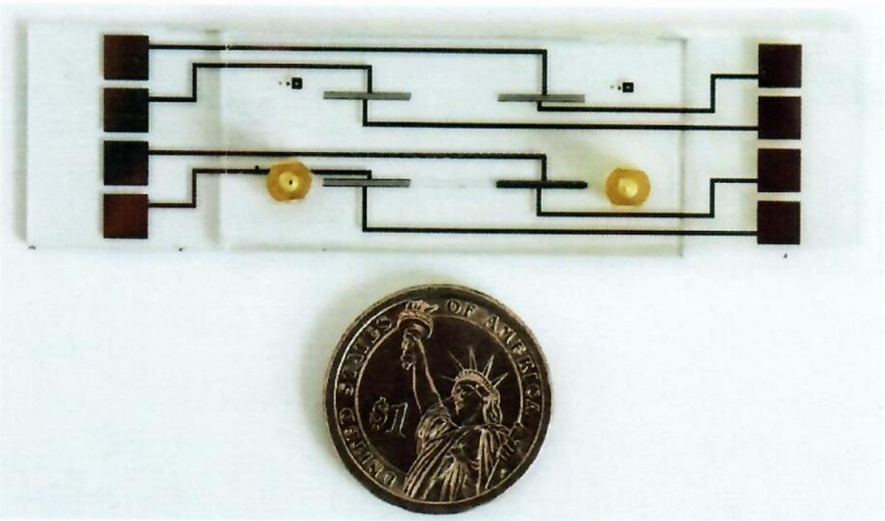
Wang expects to validate the device later this year on filtered water from potential customers. He is also working to modify the sensor to detect specific classes of PFAS or total PFAS by altering the MIP, but that work is just getting started, he says.

Wang declines to provide more details about his sensor, noting that he plans to file for a patent on it by July. But he says it would be ideal for investigating contaminated PFAS sites. "The sensor is a screening tool for field use. It is not for compliance use," he emphasizes.

MOFs meet microfluidics

MOFs, crystalline materials consisting of a metal ions joined by organic linkers, have also generated interest for PFAS sensing. MOFs have an extremely high surface area and pore volume, making them attractive for capturing PFAS.

Basuray and colleagues have shown that



A microfluidic chip for detecting per- and polyfluoroalkyl substances in water is being developed by Sagnik Basuray and colleagues at the New Jersey Institute of Technology.

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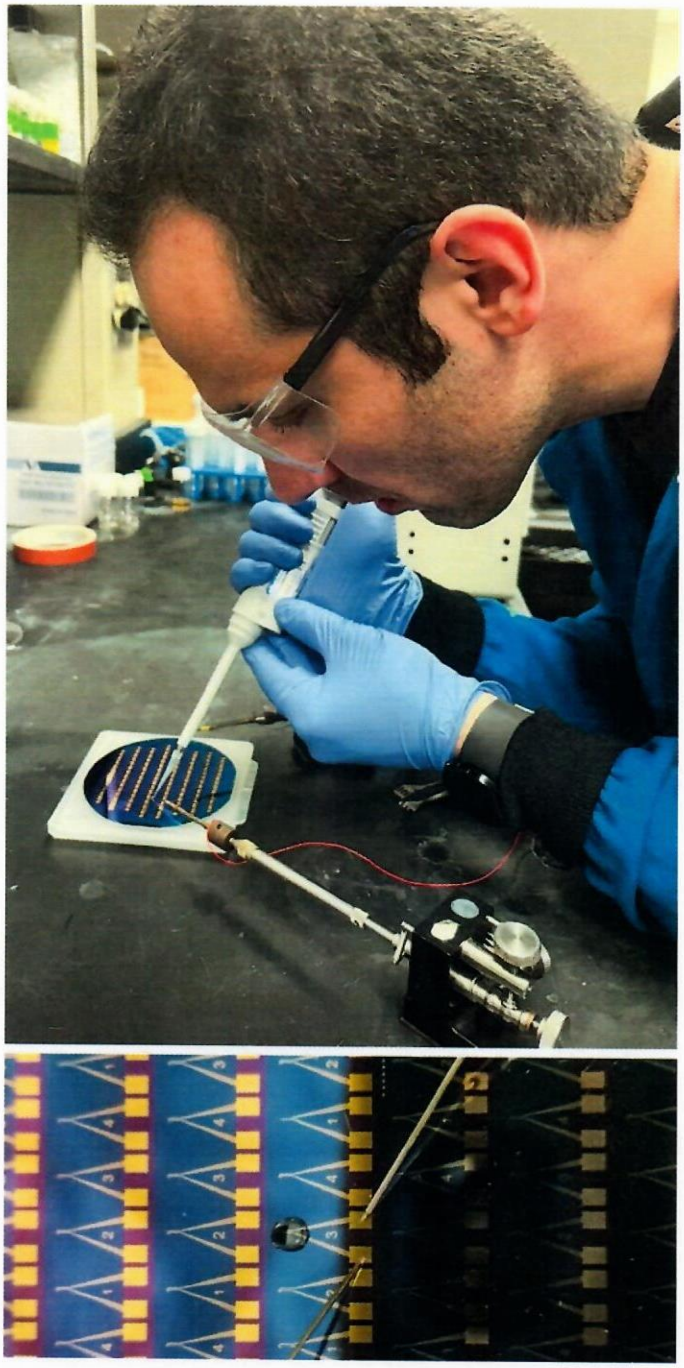


Researchers at Wayne State University are developing a sensor for detecting per- and polyfluoroalkyl substances in water using electrochemically generated bubbles and nanosize electrodes (top). Close-up of device (bottom).

CREDIT: ARMIN SEDIGHI AND BLAKE STRINGER/WAYNE STATE UNIVERSITY

a sensor platform containing a chromium-based MOF, Cr-MIL-101, can be used to detect PFOS in water at levels down to 10 parts per trillion (ppt) (*ACS Appl. Mater. Interfaces* 2020, DOI: 10.1021/acsami.9b22445). But with optimization of the device architecture, "we believe we can lower that an order of magnitude, to 1 ppt," Basuray says.

The platform contains MOF capture probes embedded in a microfluidic channel, which is sandwiched between two microelectrodes. The background potential of MOFs is easily measured with impedance, Basuray says. When the MOF adsorbs PFOS, the potential changes, resulting in an increase in impedance that is proportional to the concentration of PFOS.

But just like with MIPs, MOFs can capture more than one type of PFAS chemical, so selectivity is an issue. "Cr-MIL-101 also has an affinity for PFOA," Basuray says.

Basuray says it is easier to design a sensor to detect total PFAS. "You could have a MOF that attracts every one of those fluorinated molecules," he says. "But one MOF by itself might not be enough to ascertain whether a certain molecule, like PFOA or PFOS, is there."

To overcome the selectivity problem, Basuray is collaborating with an expert in artificial intelligence to develop an algorithm that can help tease apart signals from multiple MOFs, each with its own binding affinity to various PFAS. "As it's learning more and more MOFs with the different PFAS, it becomes more robust in giving values for each of them," he says.

To target the six PFAS subject to the EPA's proposed limits for drinking water, the sensor would need about 10 MOFs, Basuray says.

The researchers are developing two versions of the microfluidic chip, one for use in the field and one that can be integrated into wastewater treatment systems, Basuray says. For use in the field, a sampler can be added in front of the chip to help remove interferents like carbon, pharmaceuticals, and heavy metals, he adds. The approach is unique in that liquid continuously flows through the channel. This property facilitates integration into wastewater monitoring, he says.

Basuray hopes to commercialize the sensor in the next 2 years. He founded the start-up company Essence Diagnostics to integrate the chips and other technology into a prototype system.

So far, the company has focused on PFOS and PFOA, but the sensor has the potential for multiplexing, says Charmi Chande, who is leading the commercialization efforts. "We want to expand it to 1,4-dioxane and other contaminants in the future," she says.

PFAS-induced bubbles

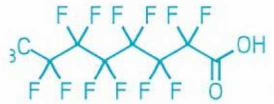
Long Luo, an electrochemist at Wayne State University, and colleagues are developing a much different electrochemical approach for detecting PFAS. The team applies voltage to tiny electrodes in water. The energy splits the water, forming hydrogen gas bubbles. In the presence of PFAS, which are good surfactants, it takes a lot less current to form the bubbles. In fact, the amount of current needed to generate the bubbles is inversely proportional to the concentration of PFAS in the water (*Anal. Chem.* 2019, DOI: 10.1021/acs.analchem.9b01060).

The method can distinguish between long- and short-chain PFAS, but it can't differentiate between PFOA and PFOS, which both contain eight carbons. Long-chain PFAS have good surface activities, which affect the surface tension and stability of bubbles, Luo says. The sensor does not respond to PFAS with fewer than six carbons, because the surface activity of those molecules is not enough to be detected, he says.

Other surfactants in water can also interfere with bubble formation, but Luo does not see that as a big problem. Those surfactants are destroyed by water treatment processes, such as using ultraviolet and ozone, so "we rarely have other surfactants in drinking water," Luo says. "The method is a screening technique to tell you if your water is of concern or not."

The method's detection limit is about 40 parts per trillion for PFOS and PFOA, Luo says. And that is after a preconcentration step involving electrochemical aerosol formation, which improves the sensitivity by 1,000 times (*Anal. Chem.* 2019, DOI: 10.1021/acs.analchem.9b02758). Detecting PFOS and PFOA at the EPA's proposed limit of 4 parts per trillion is still a challenge with the bubble generation approach, Luo says.

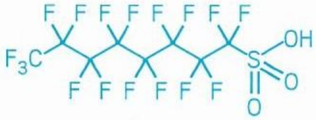
“We are working with the US Army, which is interested in the technology because we don’t need any reagents,” Luo says. “We just need an electrode and water.” The next step toward a commercialized product is to combine the preconcentration step and detection in a single device and address interferences from other hydrocarbon surfactants, Luo says. “At the end of 2 years, we hope to have a prototype.”


PFOA

Novel sensing materials

At the EPA’s Office of Research and Development in Cincinnati, Ateia’s work focuses on ways to treat PFAS contamination. But he thinks some of the techniques used to concentrate PFAS before they are destroyed could be combined with sensing.

“The novel adsorbents that we see showing promise are much better than activated carbon or conventional ion-exchange resin because they’re kinetically much faster,” Ateia says. Using these materials in a concentration step before detection could improve the sensitivity and selectivity of PFAS sensors, and it would add no more than an hour to the process, he adds.


PFOS

The EPA’s Small Business Innovation Research program has funded several start-up companies, including Wang’s 2Witech Solutions, that are developing ways to detect and treat PFAS in the environment. The latest round of funding went to projects focused on developing novel adsorbents, Ateia says.

Ateia is also collaborating with researchers at Argonne National Laboratory to develop electronic PFAS sensors. Junhong Chen, lead water strategist at Argonne and a molecular engineering professor at the University of Chicago, is the lead on that project.

The sensors integrate 2D nanomaterials, such as thermally reduced graphene oxide, into a field-effect transistor. “These materials give us really high sensitivity in terms of detection because they are very sensitive to the electronic perturbations in the surrounding environment,” Chen says. Different molecular probes target different analytes. “The art is in the design of the probes,” he says.


GenX

The sensors rely on interactions between PFAS and sensing materials that produce electronic signals measured as charge, Chen says. He declines to provide additional information, saying the work has yet to be published.

Differentiating between PFAS remains a challenge, Chen says. But the first step is to develop sensors that can detect total PFAS at low part-per-trillion levels, he says. Differentiation is the second step. “We are working on both” and using machine learning to help us get to that goal, he says.

Stability is also important, Chen says. “When you put a sensor into the field to monitor a water body, over time your sensor shifts or changes, and your signal will be inaccurate.”

From lab to portable product

As researchers work to improve the sensitivity, selectivity, and stability of field-portable PFAS sensors, other teams are trying to make highly sensitive lab-based methods more portable.

Silvana Andreescu, the Egon Matijević Endowed Chair of Chemistry and chair of the Department of Chemistry and Biomolecular Science at Clarkson University, is working with colleagues to integrate a silver nanoparticle-based method of detecting PFAS onto a robust platform that can be used outside the laboratory.

The researchers measure the exchange of electrons between silver nanoparticles and a microelectrode one particle at a time using single-particle collision electrochemistry (*Angew. Chem., Int. Ed.* 2022, DOI: 10.1002/anie.202209164). In the presence of PFAS, citrate molecules from the surface of the nanoparticles are exchanged with PFAS. Through F-F interactions, the silver nanoparticles become agglomerated, which results in a decrease in the particle collision frequency. “The reason we thought of using this method is the extremely low detection limits for PFAS,” Andreescu says.

The citrate ligands allow the researchers to selectively measure long-chain PFAS, such as PFOS, that contain a sulfonate group. The method can detect PFOS down to 10 parts per trillion, but

“The novel adsorbents that we see showing promise are much better than activated carbon or conventional ion-exchange resin because they’re kinetically much faster.”

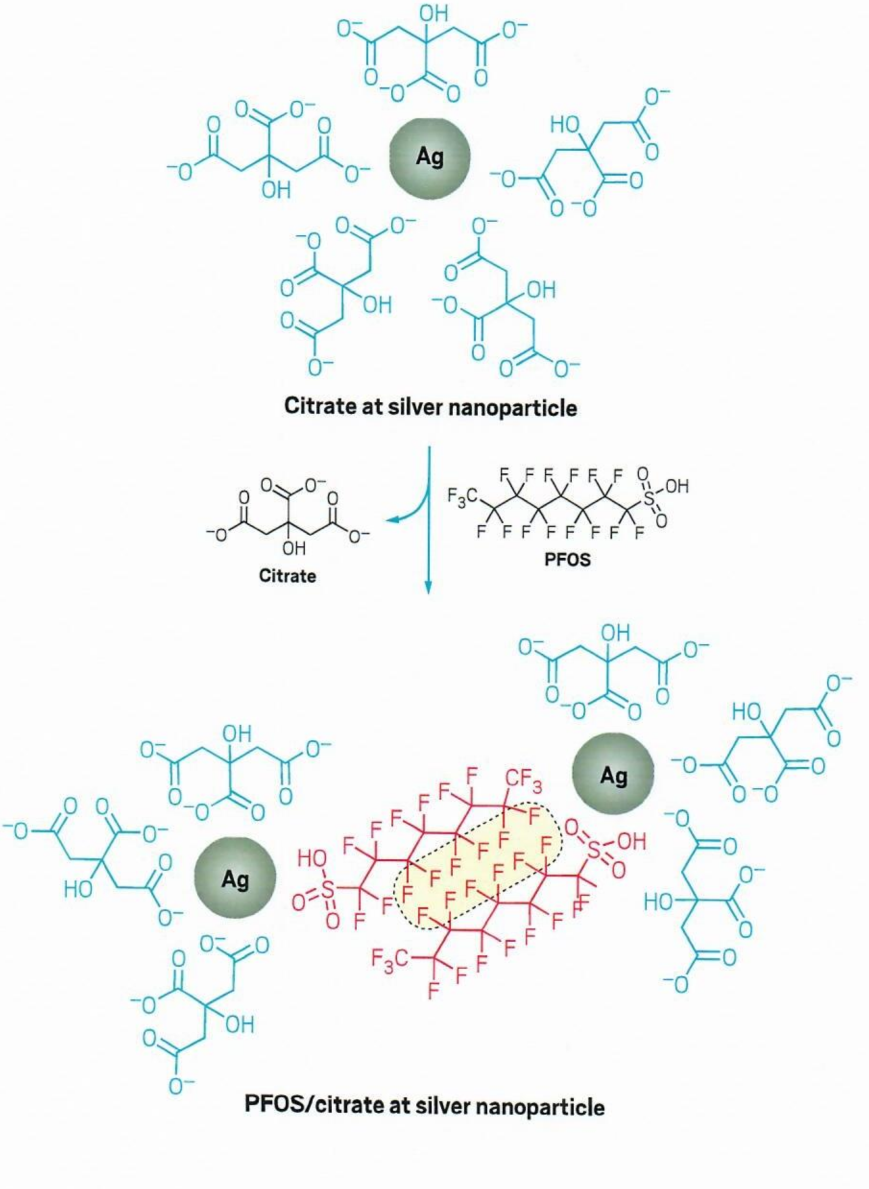
—Mohamed Ateia Ibrahim, environmental engineer, Office of Research and Development, US Environmental Protection Agency

it’s not quite ready for use in the field.

“The electrode itself is tiny,” Andreescu says. “But the instruments that we use are laboratory based. We measure current like picoamps. We can’t really do portable measurements with this technique in the current setup.”

Andreescu and colleagues are now looking for ways to integrate the detection capability with a low-cost, portable platform such as screen-printed electrodes. The electrodes are “similar to the ones that are used for glucose sensing,” Andreescu says.

Proposed mechanism for the interaction between perfluorooctanesulfonic acid and silver nanoparticles



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A lot of effort is underway to develop field-deployable PFAS sensors, but it will likely be a few more years before any of them are ready to hit the market. Many researchers are eager to commercialize a product; some, like Basuray, see the effort as more than just a business opportunity.

Luo, the bubble-generating electrochemist at Wayne State University, in Detroit, learned about PFAS in the summer of 2018, when Michigan declared a state of emergency because of high levels of the chemicals in the city of Parchment’s drinking water. For years, Luo had been developing measurement approaches that rely on interactions between an analyte and electrochemically generated gas bubbles. When he heard the news about PFAS in his state, he got the idea to adapt the approach to detect the chemicals.

Similarly, Ugo, the researcher who laid the groundwork for MIPs-based electrochemical detection of PFAS, began his work on detecting PFAS because of contaminated drinking water in the Veneto region of Italy. First discovered in 2013, the contamination had been going on for decades because of pollution by a plant owned by Miteni, which declared bankruptcy and shut down in 2018.

Dick likewise started his work on PFAS sensors because of contaminated drinking water. At the time he was a professor at the University of North Carolina at Chapel Hill and the Chemistry Department’s liaison to federal affairs at the university. “I was really lucky to be able to go up with them to Capitol Hill and talk with lawmakers on both sides of the aisle about the problem of PFAS in North Carolina” and globally, he says.

Wilmington, North Carolina, has been grappling with PFAS-contaminated drinking water for many years. The city is downstream from a Chemours plant in Fayetteville that makes PFAS, including GenX chemicals.

Last year Dick moved his entire research group to Purdue, with hopes of commercializing a PFAS sensor in the coming years. “The technology-transfer culture here at Purdue is incredibly exceptional,” he says, adding that it “did contribute to my decision to move here.”

Clark expects to defend her PhD dissertation later this year. The most rewarding aspect of the project, she says, is “being able to make something that has practical applicability to people.” She hopes to continue researching PFAS in the future. “I’m really interested in getting things off of a benchtop and into the setting where they’re useful, whether that’s clinical medicine or sensors or anything that gets things from the benchtop to the public.” ■