Cape Alliance for Pesticide Education
PO Box 631
West Barnstable, MA 02668
(508) 362-5927 info@greencape.org
Non-Toxic Strategies for a Sustainable Cape Cod

July 18, 2019

Elizabeth Callahan
MassDEP
One Winter Street
Boston, MA 02108

Re: Comments on Massachusetts Contingency Plan Changes for PFAS Chemical Regulations

Dear Director Callahan:

GreenCAPE is an advocacy and information organization founded in 1998 to increase public awareness of the risks of pollutants harmful to health and the vulnerable Cape Cod aquifer-our only drinking water supply. We thank your agency again for the earlier opportunity in May to provide preliminary comments in a local venue -the Town Hall in Hyannis. This was much appreciated as ours is a community impacted by PFAS from the use of AFFF at a nearby fire training facility and at a municipal airport. We also welcome inclusion in the process for establishing an MCP/MCL for PFAS as representatives of a PFAS-impacted community at the stakeholder's table.

These comments will only address aspects of the MCP that relate to the perfluorinated chemicals and concerns about these that have been brought to me in my capacity as director of the organization. There are many aspects I am unable to address, not being a chemist nor a regulator. We trust that this is only the first volley of regulatory effort on these persistent, bioaccumulative, and toxic perfluorinated chemicals and that DEP will keep tracking the rapid developments in PFAS research to reduce risk and exposure with regular updates to the MCP.

We are supportive of the addition of Reportable Concentrations (RC) and Method 1 standards for six perfluoroalkyl substances—Perfluoroheptanoic Acid (PFHpA), Perfluorohexanesulfonic Acid (PFHxS), Perfluorooctanoic Acid (PFOA), Perfluorooctane Sulfonate (PFOS), Perfluorononanoic Acid (PFNA) and Perfluorodecanoic Acid (PFDA) and the associated waste site cleanup standards. We also welcome the initiation of a process for establishing an MCL for PFAS. Together these may jump start desperately needed remediation activity in Hyannis and communities beyond.

Our unique condition on Cape Cod -living above a sandy EPA-designated sole-source aquifer with no access to any other source of drinking water, should be afforded a more protective designation in the new MCP as pollution in sandy soils demand urgent

attention and action for the welfare of the community and its water-dependent tourist economy. USGS reports provide ample evidence that groundwater can travel up to 3 feet a day in this sandy environment and many water bodies on Cape Cod are fed by groundwater. Communities dependent on aquifers for drinking water should be afforded a more protection by more frequent monitoring. At least 14 PFAS chemicals -so far-have been detected in Hyannis water due to the use of AFFF so it's concerning that only 6 PFAS have been addressed in this document. If the DEP would reconsider this and have the MCP be inclusive of the entire class of PFAS, contaminated sites would be remediated to a better standard, our water would be better protected and blood levels of PFAS would be lower. After PFOS and PFOA were phased out, blood levels in humans declined (NHANES) and this should be the goal with the remaining PFAS. Regulating PFAS as a class would temporarily impact some industries and agriculture but at the end of the process, the health of the people served by your agency must be the imperative. Tackling but a small number of the PFAS compounds fails to adequately punctuate the enormity and extreme burden those exposed to these forever poisons have and will continue to endure.

At one of two PFAS-contaminated sites in Hyannis, the Barnstable County Fire and Rescue Training Academy (BCFRTA), the soils are already so saturated with a variety of perfluorinated compounds, even rainwater drives multiple PFAS contaminants to the well heads of the public water supply system. PFAS rarely occur on contaminated sites as a single compound -another consideration for regulating them as a class. Fire training at the BCFRTA uses an average of over ½ million gallons per year (in some quarters as high as 378,000 gallons) which complicates tracking of plumes and municipal water treatment. There are excessively high levels of PFAS in Flint Rock Pond which abuts the BFCRTA and the sediments are now thought to be an independent contributor to ongoing groundwater contamination upgradient of the municipal wells. In this instance that pond water should be regulated as GW-1. The BCFRTA is a complex site and requires a higher level of remediation based on its location above a sole-source aquifer and the municipal public drinking water supply that is downgradient of it. The so-called soils are primarily sand which allow for quick percolation of these mobile compounds. While minimal cleanup has been done, (the site is in Phase II Comprehensive Site Assessment), potential excavation of impacted soils and/or pond sediments and implementation of more groundwater recovery and treatment systems should conform to the Proposed Method I Standards for PFAS once promulgated to insure the safety of the public drinking water supply for the next generations.

Our unique condition on Cape Cod -living above a sandy EPA-designated sole-source aquifer with no access to any other source of drinking water, should be provided a more protective designation in the new MCP as pollution in sandy soils demand urgent attention and action for the survival of the community and its water-dependent tourist economy. USGS reports provide ample evidence that groundwater can travel up to 3 feet a day in this sandy environment and many water bodies on Cape Cod used for swimming and fishing are fed by groundwater. Communities dependent on aquifers for drinking water should be afforded a more protective designation-e.g., groundwater and drinking water should be subject to identical safety standards. Groundwater is currently an important source of drinking water (and sometimes the only source) and will become

more significant as populations expand or migrate and climate change brings about more saltwater intrusion to older systems.

We would urge DEP to also move forward on monitoring PFAS in other problematic areas such as impaired areas under landfills which may not be lined or where there is reason to suspect the liner has been breached. Additional materials such as biosolids/sludge and effluent from wastewater treatment plants-noting the disastrous results on farms in AZ and ME- require investigation. Fish and shellfish monitoring should not be delayed, and wild game and birds should be monitored since there are a significant number of subsistence and sport fishermen and hunters on Cape Cod and western MA. Vegetables and fruits, especially where grown with water in PFAS impacted communities -all contribute to the dietary intake of individuals who may already have ingested PFAS via their drinking water so local produce should be analyzed with the goal of lowering the PFAS body burden in communities already exposed through drinking water for decades without benefit of filtration.

We continue to encourage the expansion of the MCP to include all PFAS based on recent research beyond our borders and the continued production of related compounds that quickly enter commerce without the requirement of demonstrated safety. As one example of this research: The European Chemicals Agency (ECHA) has recognized HPFO-DA – a fluorinated substance using the so-called GenX technology – as a substance of very high concern (SVHC) due to its probable serious effects on human health and the environment. This decision only adds urgency to scientific alarms about the long-term impacts of fluorinated substances and highlights the need to step up efforts to minimize their use and release. The decision to identify 2,3,3,3-tetrafluoro-2 (heptafluoropropoxy) propionic acid, its salts and its acyl halides (denoted as HFPO-DA) as SVHC was taken unanimously in the ECHA Member States Committee, which met recently in Helsinki. The Netherlands had proposed for HPFO-DA to be placed on the SVHC list, according to article 57(f) of REACH [3]. In recent years, HPFO-DA has increasingly been used as a replacement for PFOA in the production of high-performance fluoropolymers such as non-stick coatings or resins. According to the supporting dossier, exposure to HPFO-DA can be linked to toxicity for the liver, the kidney, the blood, and the immune system, and suspicions of carcinogenicity and endocrine disrupting effects for humans also exist. A group approach for PFAS will swiftly reduce exposures and avoid further regrettable substitutions with newer but still harmful products. We continue to encourage a class-based standard for PFAS as it is more appropriate for swiftly reducing human exposure to a group of related chemicals likely to harm multiple body organs and systems based on their similar chemical structure.

As Hyannis has a growing number of young families, there is concern about potential harm from drinking the water despite the considerable efforts of the Town of Barnstable to install GAC filtration and purchase water from nearby towns to bring the system in to compliance. Some studies that have been shared with me by concerned parents and grandparents -

Developmental Outcomes p.140 -Supporting Document for Epidemiological Studies for Perfluoroalkyls from ATSDR draft (https://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=1117&tid=237)

Prenatal exposure to perfluoroalkyl substances, immune-related outcomes, and lung function in children from a Spanish birth cohort study- https://www.sciencedirect.com/science/article/pii/S1438463918309246 - This longitudinal study suggests that different PFASs may affect the developing immune and respiratory systems differently.

Early life exposures to perfluoroalkyl substances in relation to adipokine hormone levels at birth and during childhood -Findings suggest adipokine hormone dysregulation in early life as a potential pathway underlying PFAS-related health outcomes, and underscore the need to further account for susceptibility windows and sex-dimorphic effects in future investigations. https://academic.oup.com/jcem/advance-article-abstract/doi/10.1210/jc.2019-00385/5520379?redirectedFrom=fulltext

PFOS, PFOA, estrogen homeostasis, and birth size in Chinese infants-- findings suggested that exposure to PFASs could affect estrogen homeostasis and fetal growth during pregnancy and that estrogens might mediate the association between exposure to PFASs and fetal growth.
https://www.sciencedirect.com/science/article/pii/S004565351930061X

Considering the above studies and regarding the question of Relative Source Contribution, could the assumption of 20% of a person's PFAS exposure from drinking water be sufficiently protective if an infant has been developing in vivo while exposed to a variety of PFAS since conception? While there are not yet any studies that demonstrate a conclusion either way at this time, there are MA communities where this pre-natal exposure has occurred and perhaps the 20% assumption might not be reliable in that circumstance. In communities of known PFAS water contamination, that assumption might need adjusting to offer protection to the most vulnerable.

Many from MA communities affected by PFAS attended the recent June PFAS Conference in Boston and heard Dr. Linda Birnbaum, noted scientist and director of the National Institute for Environmental Health Sciences, speak of new research and the implications for human health. Before she retires, members of DEP staff involved in the MCP and MCL process might contact her directly to learn the details of that NTP research which may bring more urgency to bear on PFAS decisions. Dr. Birnbaum's office phone number is: 919-541-3201; e-mail: birnbaumls@niehs.nih.gov. Dr. Birnbaum, shared research finding pancreatic cancer tumors in mice exposed to very low levels of PFAS implying that a health protective drinking water standard should be much lower. She cited .1ppt for PFOA alone- which is 700 times lower than the HA level set by the Environmental Protection Agency. While PFOA has already been tied to kidney and testicular cancer, among other diseases, recent research linking PFOA exposure to pancreatic cancer was the basis for the lower number she cited. The research was done by the National Toxicology Program- a division of the NIEHS. https://www.documentcloud.org/documents/6154935-PFOA-Chronic-Summary.html. A

technical report based on the research is in preparation and external peer review will take place later in 2019. Although the reports have yet to be released, some state regulators are already considering the NTP data as they set safety thresholds for PFAS. The Minnesota Department of Health cited the NTP tables in its April health-based guideline for PFHxS. And in March, California regulators set interim safety levels of 14 and 13 ppt for PFOA and PFOS, while citing "new cancer data recently released by the National Toxicology Program" and noting that safety levels and the health effects on which they are based may change. We urge you to take this new data into consideration for the MCL decision.

On a related note, preliminary research (not yet published, personal communication A. Timme-Laragy) conducted at the Clark Laboratory at UMASS/Amherst with the zebrafish embryo toxicity test (using OECD fish acute embryo toxicity test https://www.oecd-ilibrary.org/environment/test-no-236-fish-embryo-acute-toxicity-fet-test_9789264203709-en) which found that the AFFF in the application formula at 3% concentrate in water, (identified as legacy AFFF from the Joint Base Cape Cod and obtained via your agency) has over 300 different PFAS in it. In terms of toxicity, it is about 7-10x more toxic than PFOS alone. This finding accentuates the need for reconsidering the regulation of PFAS as a class as humans experience PFAS as mixtures, not single chemicals. This legacy foam contains at least 300-6 or 284 additional PFAS chemicals which are unidentified at this time and which MA residents could be drinking even if their water system is employing GAC filtration.

Dr. Birnbaum also shared that the health effects of the 4-carbon short chain PFAS called PFBS were similar to the 8-carbon long chain PFOS. This contradicts industry assumptions of the safety of the short chains- http://blogs.edf.org/health/2019/02/20/potential-biopersistence-short-chain-pfas/; **Internal exposure-based pharmacokinetic evaluation of potential for biopersistence of 6:2 fluorotelomer alcohol (FTOH) and its metabolites**- https://www.sciencedirect.com/science/article/pii/S0278691518300127?via%3Dihub. Also, of concern is that most of these shorter chain PFAS pass through GAC filtration and our community is unable to find out which PFAS are not being eliminated by the GAC filters.

Missing in regulatory action are the PFAS precursors -the identity of 50% of these precursors is still a mystery and they matter because they eventually become PFOS/PFOA. In addition, PFAS fluorotelomers transform into PFOA/S in the body, so these compounds should also be studied for possible inclusion into a subclass of PFAS variants. The fluorotelomers biotransform in only a few months and then stay as PFOA/S in the body for many years. Newer AFFF recipes contained more of these after the legacy PFOS/PFOA was removed but they have yet to be proven safer.

There was some discussion at the last meeting (post-meeting, actually) regarding the need for a reliable, affordable analytical method to quantify the aggregate of all forms of PFAS:

-The first two attachments explain an inexpensive assay that measures Total Organic Fluorine using Combustion Ion Chromatography (CIC). Use of this assay in Europe reveals that only 5%-50% of PFAS mass is measured by the more accurate Mass Spec methods. (The TOP assay is more limited and not as comprehensive as the CIC assay.) Since there are ~4000 + PFAS chemicals, it will become necessary to have the best analytical method to measure total PFAS. None of the Mass Spec methods will do this, and they are much more expensive. It doesn't appear there is a commercial laboratory that offers this testing in the United States presently but no doubt that will change to meet the demand. Sweden has been using Combustion Ion Chromatography (CIC) to test for total PFAS in samples for at least a decade.

-Bubble Nucleation- see article and paper on new test method (last two attachments).

It is unknown whether PFAS chemicals might expose sensitive populations via atmospheric transport. Some studies suggest that incineration of AFFF firefighting foams don't destroy the carbon/fluorine bond because the temperatures and time required are not well maintained or monitored at these facilities. Thus, we oppose MA DEP's practice of incinerating unused firefighting foams. The potential exists for the conversion of some of the PFAS into airborne contamination that unintentionally impacts other populations. Until newer technologies are discovered, it would be preferable to store the fluorine foam in a secure facility until methodologies are developed that can destroy it completely.

Regarding newer potential PFAS elimination technologies: "PFAS Pulverizer" The method is still in trial phase but is reported to be a destructive technology - https://www.woodtv.com/news/target-8/toxic-tap-water/msu-s-pfas-pulverizer-is-cleaning-water/1625352923?fbclid=IwAR3tjXiA1wgnw3wlCIAPZy6ZzNSkrjlfwAblHTM831-auITY6wKnNaUKXSg.

Once in the environment, water, and food supply, only the sound management of PFAS has any potential to reduce that risk to human health. Thank you for your action in updating the Massachusetts Contingency Plan to include perfluorinated chemicals and the opportunity for public comment.

Respectfully-

Sue Phelan, Director
GreenCAPE
West Barnstable, MA 02668
508.494.0276
www.GreenCAPE.org

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Determination of adsorbable organic fluorine from aqueous environmental samples by adsorption to polystyrene-divinylbenzene based activated carbon and combustion ion chromatography

Andrea Wagner[a], Brigitte Raue[a], Heinz-Jürgen Brauch[a], Eckhard Worch[b], Frank T. Lange[a,*]

[a] DVGW Water Technology Center (TZW), Karlsruher Str. 84, 76139 Karlsruhe, Germany
[b] Dresden University of Technology, Institute of Water Chemistry, 01062 Dresden, Germany

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ABSTRACT

A new method for the determination of trace levels of adsorbable organic fluorine (AOF) in water is presented. Even if the individual contributing target compounds are widely unknown, this surrogate parameter is suited to identify typical organofluorine contaminations, such as with polyfluorinated chemicals (PFCs), and represents a lower boundary of the organofluorine concentration in water bodies. It consists of the adsorption of organofluorine chemicals on a commercially available synthetic polystyrene-divinylbenzene based activated carbon (AC) followed by analysis of the loaded AC by hydropyrolysis combustion ion chromatography (CIC). Inorganic fluorine is displaced by excess nitrate during the extraction step and by washing the loaded activated carbon with an acidic sodium nitrate solution. Due to its high purity the synthetic AC had a very low and reproducible fluorine blank (0.3 μg/g) compared to natural ACs (up to approximately 9 μg/g). Using this AC, fluoride and the internal standard phosphate could be detected free of chromatographic interferences. With a sample volume of 100 mL and 2× 100 mg of AC packed into two extraction columns combined in series, a limit of quantification (LOQ), derived according to the German standard method DIN 32645, of 0.3 μg/L was achieved. The recoveries of six model PFCs were determined from tap water and a municipal wastewater treatment plant (WWTP) effluent. Except for the extremely polar perfluoroacetic acid (recovery of approximately 10%) the model substances showed fairly good (50% for perfluorobutanoic acid (PFBA)) to very good fluorine recoveries (100 ± 20% for perfluorooctanoic acid (PFOA), perfluorobutanesulfonate (PFBS), 6:2 fluorotelomersulfonate (6:2 FTS)), both from tap water and wastewater matrix. This new analytical protocol was exemplarily applied to several surface water and groundwater samples. The obtained AOF values were compared to the fluorine content of 19 target PFCs analyzed by high performance liquid chromatography–electrospray tandem mass spectrometry (HPLC–(−)ESI-MS/MS). In groundwater contaminated by PFC-containing aqueous film-forming foams (AFFFs) up to 50% of the AOF could be attributed to PFC target chemicals, while in diffuse contaminated samples only <5% of the AOF could be identified by PFC analysis.

1. Introduction

Many organohalogen compounds are xenobiotics of anthropogenic origin. Some of these halogenated chemicals, such as the so-called “dirty dozen” and further chemicals defined by the Stockholm convention on persistent organic pollutants (POPs) and its amendments [1,2], are so-called PBT chemicals (persistent, bioaccumulative and toxic). Compound classes, which are of environmental concern comprise chlorinated chemicals (e.g. polychlorinated biphenyls, chlorinated pesticides, dibenzodioxines and -furanes), brominated flame retardants [1], but also iodinated X-ray contrast media and their transformation products, which were detected in surface water, groundwater, bank filtrate and drinking water [3,4]. In the last two decades poly- and perfluorinated chemicals (PFC) became environmental chemicals of emerging concern because some long chain perfluoroalkyl compounds possess PBT properties [5–8].

The most prominent examples are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). PFOS was the first PFC added to the list of POPs in 2009 [9]. Polar PFC, such as PFOS, PFOA and their short chain homologues, can contaminate raw water resources for drinking water production and were detected in a number of tap waters [10–12]. The known raw and drinking

* Corresponding author at: DVGW Water Technology Center (TZW), Karlsruher Str. 84, 76139 Karlsruhe, Germany. Tel.: +49 721 9678 157; fax: +49 721 9678 104.
E-mail address: frankthomas.lange@tzw.de (F.T. Lange).

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water contaminations usually originate from local hot spots, such as application of fire-fighting foams, contaminated fertilizers or emissions from fluorochemical production sites [13]. Such hot spots need to be identified by chemical analysis. While target compound analysis comprises a limited number of chemicals, a large number of unknown fluorinated chemicals of other compound classes, unknown precursors, transformation products, homologues, and isomers might be present at certain sites as well.

Therefore, surrogate parameters should supplement target compound analyses and help (i) to identify contaminated sites which could be overlooked by target compound analysis, and (ii) to carry out mass balance considerations.

The best established surrogate parameter method for organohalogen determination in water is the standard method for adsorbable organic halogens (AOX), where X = Cl, Br, and I [14]. This water quality parameter measures the mass concentrations (calculated as Cl) of halogens bound to organic compounds, which can be adsorbed to activated carbon when applying a standardized protocol. However, organofluorine compounds cannot be assessed by the AOX protocol. Briefly, the AOX analysis consists of four principle steps: (i) extraction of organohalogens from water by activated carbon, (ii) washing with $NaNO_3$ solution to remove inorganic halides, (iii) mineralization (formation of HCl, HBr, and HI) by incineration of the wet activated carbon in a combustion furnace, and (iv) absorption of HCl, HBr, and HI and detection of Cl^-, Br^-, and I^- in a microcoulometric cell. This microcoulometric detection is based on the low aqueous solubilities of AgCl, AgBr, and AgI. Due to the good solubility of AgF (1.8 kg/L at 25 °C [15]) this sensitive method fails for the detection of organofluorine compounds. Another analytical challenge is to avoid the reaction of HF with SiO_2 from the quartz glass tube of the combustion furnace which can lead to a reduced fluoride recovery.

Therefore, other surrogate parameter approaches have been proposed for the determination of organofluorine compounds in water [16–21]. These approaches are based on oxidative [16–18] and reductive mineralization processes [19,20]. Also destruction-free detection of AOF by neutron activation analysis was reported [21].

All these surrogate parameters have in common that they are defined by operation. Of all organofluorine chemicals present in a water sample, only those compounds which are amenable to a certain protocol can be assessed. Besides PFC, other organic chemicals with a lower degree of fluorination, e.g. from pharmaceuticals or pesticides, might contribute to the organofluorine content of a sample.

Still no standardized surrogate parameter for organofluorine determination exists, but it is urgently needed as an indicator parameter to identify sources of organofluorine contamination in the aquatic environment and to obtain information on the amount of yet not identified organofluorine in different water bodies.

Because of higher concentrations of fluoride in natural waters (e.g. in surface waters generally 0.01–0.3 mg/L) [22] compared to the low estimated (sub-)μg/L levels of organofluorine in natural samples, the total fluorine concentration is nearly identical with the fluoride concentration. Due to the measurement uncertainties associated with organofluorine (OF) and total fluorine (TF) determination, OF cannot be reliably evaluated by subtraction of the fluoride concentration from total fluorine (TF). Therefore, an extraction step, which separates fluoride from organofluorine compounds, is necessary.

With regard to these requirements, there are two most promising surrogate parameter approaches for organofluorine determination, which are worth to be developed further: the draft German standard DIN 38409 H29 for the determination of the so-called AOF (a method similar to AOX, see above) [17] and the combustion ion chromatography after solid phase extraction (SPE-CIC) by Miyake et al. [16]. In 1996 the draft standard method DIN 38409 H29 for the determination of the AOF [17] was not approved due to non-satisfying validation data from round robin tests. Except for some extremely high contaminated sites, the working range of this method (50–500 μg/L) is much too high to measure the expected sub- to low μg/L organofluorine concentrations in municipal wastewaters, surface, ground-, and drinking waters.

The SPE-CIC method of Miyake et al. [16] has several advantages compared to the draft DIN 38409 H29. One major advantage is the significantly higher sensitivity of ion chromatography (IC) with large volume injection and conductivity detection compared to the potentiometric detection using a fluoride ion selective electrode in the DIN method. The second positive feature of this method is the possibility to determine the surrogate parameter extractable organic fluorine (EOF) and individual PFC or other fluorinated target compounds from the same extracts of an aqueous sample, which allows fluorine mass balance calculations for the produced extracts. However, the EOF determination affords a sequential elution procedure with organic solvents and a very elaborate washing step with a 0.01% NH_4OH solution. Thus, the analytical window for assessed organofluorine chemicals is more limited than in the AOF determination, where the nonselective activated carbon adsorbent, loaded with all adsorbable organofluorine compounds, is combusted. Unfortunately, while the validation of the draft DIN 38409 H29 obtained in round robin tests was considered insufficient [23], the paper on the SPE-CIC method [16] does not provide all necessary validation data, such as a documentation of LOQ determination and method reproducibility [24].

The aim of this study was to develop an improved and validated protocol for the determination of the surrogate parameter adsorbable organic fluorine (AOF) from aqueous environmental samples. For this purpose, we applied some advantageous features of both methods and introduced a new feature. We used a commercially available synthetic activated carbon with very low fluorine content for the extraction of organofluorine compounds from aqueous samples. This extraction procedure was combined with the sensitive hydropyrolysis CIC for mineralization of the adsorbed organofluorine compounds and detection of the formed fluoride. The aim was to develop a new analytical method which overcomes the major analytical problems (blanks, memory effects, insufficient or non existing validation data, low throughput) resulting from earlier work. In addition, this new method of analysis should be sensitive enough to measure the low expected organofluorine contents even in weakly contaminated samples, such as municipal wastewater treatment plant (WWTP) effluents, surface, ground-, and drinking waters.

2. Experimental

2.1. Chemicals and standards

Reagent grade water (18 MΩcm, <50 ng/L F^-) was prepared by a Millipore system (Billerica, MA). Methanol (ROTISOLV® HPLC, ≥99.9%) was obtained from Carl Roth (Karlsruhe, Deutschland). Isopropanol (2-propanol, EMSURE®, ≥99.8%) was purchased from Merck (Darmstadt, Germany). For tests with internal standards (ISs) oxalic acid dihydrate (analytical grade, >99.5%) and orthophosphate (aqueous solution of KH_2PO_4, CertiPUR®, 999 ± 2 mg/L) were both obtained from Merck (Darmstadt, Germany). β-glycerophosphate disodium salt pentahydrate (99.4%, Calbiochem, an affiliate of Merck, Darmstadt, Germany) was used as a model compound

for total phosphate. The fluoride standard (1000 ± 2 mg/L) for preparation of IC calibration solutions was obtained from Thermo Fisher Scientific (Idstein, Germany).

$NaNO_3$ (≥99.5%) and nitric acid (≥65%, analytical grade) were purchased from Merck (Darmstadt, Germany). Two sodium nitrate solutions were prepared according to DIN 9562 [14]. A $NaNO_3$ solution (0.2 mol/L) was prepared in reagent grade water and 2.5 mL nitric acid (65%) was added. From this solution a diluted $NaNO_3$ solution (0.012 mol/L) was prepared in reagent grade water.

For a description of the adsorbents used refer to Section 3.1.3.

The potassium salts of perfluorooctane sulfonate (K-PFOS, 98%) and 1H,1H,2H,2H-perfluorooctanesulfonic acid (synonym: 6:2 fluorotelomersulfonic acid, 6:2 FTS, 98%) were purchased from ABCR (Karlsruhe, Germany). The potassium salt of perfluorobutane sulfonate (K-PFBS, 98%) and perfluorooctanoic acid (PFOA, 96%) as well as perfluoroacetic acid (=trifluoroacetic acid, PFAA, ≥98%) were obtained from Sigma–Aldrich (Steinheim, Germany). Perfluorobutanoic acid (PFBA) (50 μg/mL) was purchased from Wellington (Ontario, Canada).

For recovery experiments a mixed standard solution at a total concentration of 3.7 μg/L F in methanol was used. The concentration of each single compound was 0.3 μg/L. This solution was prepared from a ready to use PFC mixture (≥98% of each compound, PFAC-MXA, Wellington, Ontario, Canada), which contained 5 μg/mL of PFBA, perfluoropentanoic acid (PFPA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), PFBS, perfluorohexanesulfonic acid (PFHxS), and PFOS in methanol. To this solution the following single standard substances were added: perfluoropropanoic acid (PFPrA, 97%, ABCR, Karlsruhe, Germany), perfluoroundecanoic acid (PFUnA, 96%, ABCR), perfluorododecanoic acid (PFDoA, 95%, Sigma–Aldrich, Germany), perfluorooctane sulfonamide (PFOSA, 97%, ABCR), 2H,2H-perfluorodecanoic acid (H_2PFDA, 97%, ABCR), 2H,2H,3H,3H-perfluoroundecanoic acid (H_4PFUnA, 97%, ABCR), 7H-dodecafluoroheptanoic acid (HPFHpA, 98%, ABCR), 6:2 FTS, and 1H,1H,2H,2H-perfluorohexanesulfonic acid (H_4PFHxS, ≥98%, Wellington, 50 μg/mL in methanol).

2.2. Adsorption of organofluorine compounds and removal of fluoride

For the adsorption of organofluorine compounds from 100 mL water samples 200 mg of the synthetic activated carbon (AC) adsorbent Ujotit AK-200-1200 (Dr. Felgenträger & Co. Öko.-chem. und Pharma GmbH, Dessau-Roßlau, Germany) was used. Due to the limited size of the available sample boats for the CIC instrument, it was necessary to divide the amount of 200 mg AC into two portions of 100 mg each filled between two polyethylene (PE) frits, (10 μm, Biotage, Uppsala, Sweden) in PE solid-phase extraction (SPE) cartridges (3 mL, Phenomenex, Torrance, CA). Two of these cartridges were connected with a Luer-Slip adapter for the analysis of each sample.

Prior to extraction 5 mL of the acidic $NaNO_3$ solution (0.2 mol/L) were added to 100 mL of the water sample. The sample was passed through the two cartridges at a flow rate of approximately 3 mL/min, followed by 50 mL of $NaNO_3$ washing solution (0.012 mol/L) at the same flow rate to remove adsorbed inorganic fluoride.

2.3. CIC analysis

Determination of adsorbable organic fluorine (AOF) was performed with a modified CIC system for ultra trace fluorine analysis (Fig. 1), consisting of an automated boat controller (ABC-100), an automatic quick furnace (AQF-100) with a water supply unit (WS-100) and a gas absorption unit (GA-100) (all from Mitsubishi Chemical Analytech Co., LTD, Kanagawa, Japan). The combustion unit was linked to an IC system (ICS-2100, Thermo Fisher Scientific, Idstein, Germany).

For analysis the adsorbent was transferred quantitatively in a ceramic sample boat (a1-envirosciences, Düsseldorf, Germany) with the help of a micro-spoon spatula and a dental scaler and was combusted in a furnace at 950–1000 °C while delivering 100 μL/min of reagent grade water by the solenoid pump of WS 100. Organically bound fluorine of the adsorbed organic substances was converted into hydrogen fluoride (HF). The addition of excess water into the combustion tube shifts the chemical equilibrium given in

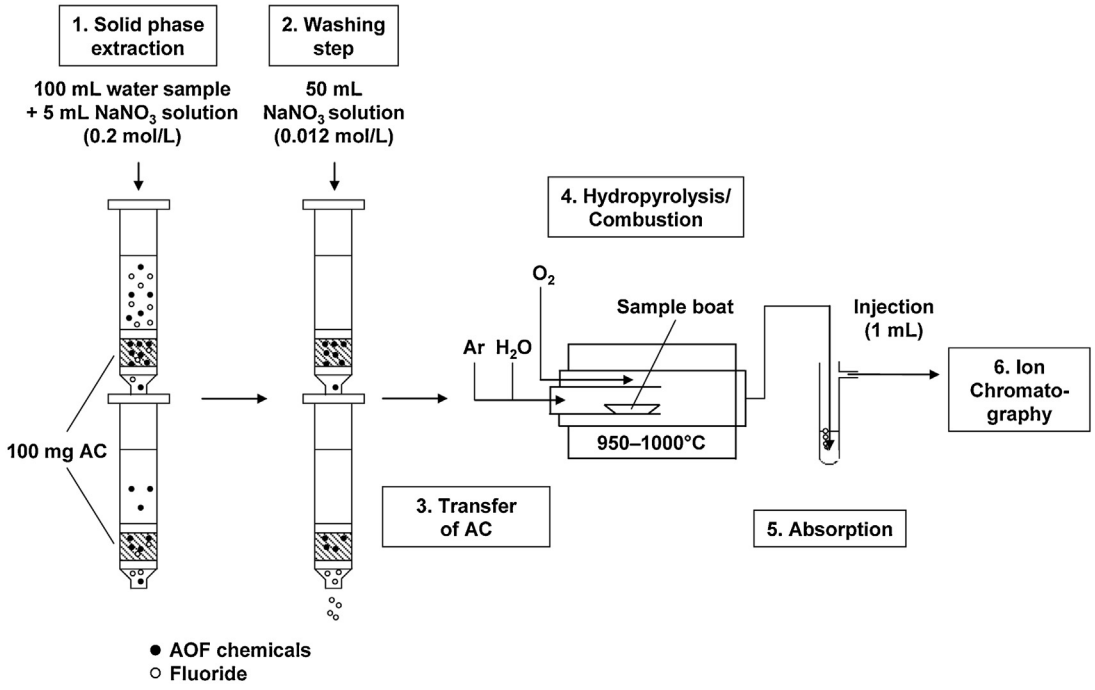

Fig. 1. Schematic representation of the sample extraction and CIC applied for AOF analysis.

Table 1
Analytical conditions for the determination of AOF.

Combustion (AQF-100)		
Furnace temperature	950–1000 °C	
Gas for combustion	150 mL/min Ar/O_2 (during sample introduction into furnace) 300 mL/min O_2 (for final combustion)	
Water supply (WS-100)	100 μL/min reagent grade water	
Carrier gas (WS-100)	100 mL/min Ar	
Boat speed	10 mm/s	
Absorption time (additional transfer time for absorption of combustion gases after stop of combustion)	1 min	
Ion chromatography (ICS-2100)		
Pre-column	IonPac® AG20 (2 × 50 mm) (Thermo Fisher Scientific, Idstein, Germany)	
Column	IonPac® AS20 (2 × 250 mm) (Thermo Fisher Scientific, Idstein, Germany)	
Temperature	30 °C	
Injection volume	1 mL	
Flow rate	0.25 mL/min	
Eluent source	EGC II KOH cartridge	
Gradient elution	Time (in min)	KOH concentration (in mmol/L)
	0–5	2
	5–12	40
	12–16	40
	16–17	2
	17–25	2
Suppression	Anion Self-Regenerating Suppressor (ASRS® 300 2-mm), Auto Suppression® recycle mode	
Detection	Conductivity detection	
Software	Chromeleon 6.80 SR9	

Eq. (1) to the educt side and thus prevents the formation of silicon tetrafluoride.

$$SiO_2 + 4HF \leftrightarrows SiF_4 + 2H_2O \quad (1)$$

The HF formed was absorbed in 3.5 mL of an aqueous orthophosphate solution (500 μg/L) and measured as F^- by IC analysis, which enabled trace level determination of fluoride (limit of detection (LOD): 50 ng/L F^-, limit of quantification (LOQ): 150 ng/L F^-), using the IC conditions given in Table 1. The adsorbent of the second cartridge of the same sample was analyzed in the same way. Both results were corrected for the blank and added to give AOF.

For quantification of F^- by IC, calibration solutions were prepared from a sodium fluoride stock solution (1 g/L) and reagent grade water. To each calibration solution 500 μg/L orthophosphate was added as an IS. A 12 point calibration curve was established at 1, 2, 5, 8, 10, 12, 25, 50, 75, 100, 150, and 200 μg/L F^- (Figure S3).

2.4. Minimization of blanks and memory effects

To enable trace level determination of fluoride at (sub)μg/L levels, possible sources of contamination by fluorochemicals within the instrument were excluded by replacing those parts with fluorine-free materials like PEEK or ceramic. Ceramic sample boats were annealed in an oven (L3/11/C6, Nabertherm, Lilienthal, Germany) overnight at 900 °C. Before use, the extraction cartridges were cleaned with isopropanol and reagent grade water and closed with bottom luer caps and top caps (both from Biotage, Uppsala, Sweden). The adsorbent as well as the loaded cartridges were stored in a desiccator. For the minimization of memory effects, the gas transfer lines, and the absorption tube were automatically washed three times with reagent grade water before a sample was combusted.

Recoveries of fluorine from model substances were calculated as follows:

$$R_F = \frac{AOF_{spiked} - AOF_{native}}{AOF_{theoretical}} \times 100 \quad (2)$$

where R_F is the fluorine recovery in %, AOF_{spiked} and AOF_{native} are the measured AOF concentrations of the spiked and non-spiked sample matrix (tap water and WWTP effluent), respectively, in μg/L, and $AOF_{theoretical}$ is the theoretical AOF value calculated from the concentration of the spiked model compound (3 μg/L F for individual PFC and 3.7 μg/L F for a PFC mixture).

3. Results and discussion

3.1. Method development

3.1.1. Procedural blank of direct CIC analysis

Under the conditions described in Section 2.4 a reproducible procedural blank (sample treatment and two combustions) for the direct CIC analysis of reagent grade water was achieved (0.44 μg/L F, n = 10, RSD = 7%).

3.1.2. Selection of an internal standard

Because hydropyrolysis of samples led to a volume increase of the absorption solution, it was necessary to correct for this increase by adding an internal standard (IS) to this solution before the combustion started. Applicability of 20 μg/L oxalate, as well as 50 μg/L and 500 μg/L orthophosphate as an internal standard was tested (Fig. S1). At low concentration the peak area of the IS orthophosphate showed a large relative standard deviation (RSD) due to drifts. Working at a 50 μg/L phosphate level, RSD was 30% (n = 126). Therefore, we tested oxalate as an alternative IS. At 20 μg/L oxalate RSD was 49% (n = 62). These observed drifts, i.e. a decreasing trend in case of oxalate and the increase of peak area in case of 50 μg/L orthophosphate might be attributed to adsorption/desorption interactions with the glass surface [25–27]. In order to make such effects insignificant, we decided to work with orthophosphate and to increase its concentration to 500 μg/L. At this higher initial IS concentration peak area drifts were negligible and acceptable for consecutive method development (RSD = 4%, n = 170).

To assure, that the CIC analysis with phosphate IS would not be hampered by phosphorous containing samples we tested the influence of orthophosphate and β-glycerophosphate (a model substance for total phosphate). For this purpose the influence of model solutions at 1, 5 and 10 mg/L phosphate equivalents was

Table 2
Fluoride concentrations of different types of adsorbents (50 mg adsorbent, wetted with 100 μL of reagent grade water) measured by CIC analysis; A, activated carbon from natural or unknown origin; B, synthetic activated carbon made from polystyrene-divinylbenzene co-polymers; C, weak anion exchanger on the basis of a polystyrene-divinylbenzene co-polymer; concentrations in brackets were above the IC calibration range (0.2–15 μg/L F).

Adsorbent	Type of adsorbent	Average concentration ($n = 2$) ± standard deviation (in μg/g F)[a]
Activated carbon for AOX determination (LHG, Karlsruhe, Germany)	A	1.46 ± 0.06[b]
Activated carbon p.a. (Merck, Darmstadt, Germany)	A	9.22 ± 0.06
Hydraffin CC 8 × 30 (activated carbon made of coconut shell, Donau Carbon, Frankfurt am Main, Germany)	A	3.82 ± 0.04
Hydraffin XC 30 (mineral coal, Donau Carbon, Frankfurt am Main, Germany)	A	5.56 ± 0.38[b]
Activated carbon p.a. (powder, Roth, Karlsruhe, Germany)	A	6.18 ± 0.32[b]
Activated carbon made of glucose (in-house production, TZW) [29]	A	0.32 ± 0.02
Saratech 100562 (Blücher, Erkrath, Deutschland)	B	0.08 ± 0.02[b]
Saratech 10055 (Blücher, Erkrath, Deutschland)	B	0.08 ± 0.04[b]
Ujotit AC-200-1200 (Dr. Felgenträger & Co. Öko.-chem. and pharma GmbH, Dessau-Roßlau, Germany)	B	0.28 ± 0.02
Strata™-X-AW (Phenomenex, Aschaffenburg, Germany)	C	0.38 ± 0.10

[a] After system blank subtraction (ceramic boat + 100 μL of reagent grade water): 4.0 ± 1.5 ng F.
[b] Fluoride quantification with external calibration due to interference of phosphate with a huge sulphate peak.

investigated by analyzing 100 μL of these solutions by CIC. For the most concentrated (10 mg/L) orthophosphate as well as β-glycerophosphate solution an increase of IS peak area of 57% was expected under the assumption that phosphate was completely transferred into the absorption solution during the combustion process. However, the increase was below 3% and there was no correlation between tested phosphate concentration of the aqueous samples and the IS peak area increase. This small increase might be explained by the drifts also observed when analyzing only reagent grade water (see above). Therefore, no phosphate transfer from the ceramic boat to the absorption solution was observed, which would hamper the volume correction of the absorption solution, and, hence, the quantification of fluoride.

3.1.3. Selection of an adsorbent for the enrichment of organofluorine compounds

One of the most crucial issues for the development of an extraction method for organofluorine chemicals was the selection of an appropriate adsorbent. This adsorbent should meet several requirements:

(i) Low native fluorine concentration.
(ii) No interference of IC analysis due to by-products, which were formed during combustion of the adsorbent.
(iii) Commercial availability.
(iv) Sufficient adsorption capacity for important fluorochemicals, e.g. PFOA and PFOS.

For this purpose, three different groups of adsorbent materials were tested: activated carbons (AC) made of natural (A) or polymer (B) materials and one weakly basic anion exchanger (C). Table 2 gives a short description of all materials investigated together with their fluoride content measured by CIC analysis.

The activated carbons of natural (mineral coal, coal from coconut shells) or unknown origin (e.g. charcoal for AOX determination) had comparatively high fluorine contents between approximately 1.5 and 9 μg/g. Only the in-house produced sugar AC, synthesized from glucose according to Schnitzler [28] and used for the analysis of adsorbable organic sulfur (AOS) and halogens (AOX) [29], contained about one order of magnitude less fluorine (0.32 μg/g). However, this material is not commercially available. Therefore, it was excluded in further method development. A comparable low fluorine content of 0.38 μg/g was measured by CIC analysis of the weakly basic anion exchanger Strata™-X-AW, which is also used for the enrichment of PFC in target compound analysis by LC–MS/MS [30]. However, Strata™-X-AWwas not easy to handle, especially during the transfer to the sample boats. Therefore, Strata™-X-AW was also not used further.

The group of ACs made of synthetic polymers showed by far the lowest fluorine background, even below the values of sugar activated carbon or Strata X-AW. Among the three tested commercially available ACs made from polystyrene-divinylbenzene co-polymers the lowest fluoride contents were evaluated for the two Saratech ACs. However, the combustion products of these ACs lead to interferences in the IC analysis, see Fig. 2. Ujotit AC-200-1200 had the best performance. In contrast to the two other synthetic ACs the ion chromatogram of the absorption solution of this adsorbent showed an undisturbed fluoride peak. Also the phosphate peak (IS) was not interfered by the sulfate peak, like e.g. AOX AK from LHG (Fig. 2). Hence, Ujotit AC-200-1200 fulfilled all requirements and was used for further experiments. This finally selected adsorbent is further characterized by the following properties: particle size dsitribution: $d10$=237 μm, $d50$ = 333 μm, $d90$ = 466 μm, specific surface: 1156 m^2/g, loss on drying: 2.38%, residue on ignition: 0.6%. A photograph of the spherical particles of Ujotit AC-200-1200 is depicted in Fig. S4.

3.1.4. Removal of inorganic fluorine from the AC adsorbent by nitrate

Another challenge during the development of the AOF method was the separation of inorganic from organic fluorine species. Fluoride (above pH 5.5 the principal inorganic fluorine species in natural

Table 3
Residual fluoride ($n = 2$) on Ujotit AC-200-1200 after loading of 100 mL reagent grade water amended by 5 mL of a 0.2 mol/L nitrate solution and spiked at a level of 200 μg/L fluoride from NaF, followed by a cleanup with a 0.012 mol/L $NaNO_3$ solution.

Matrix	Amount of adsorbent (in mg)	Volume of 0.012 mol/L $NaNO_3$ solution (in mL)	F recovery ± standard deviation (in %)
Reagent grade water	2 × 50	10	0.20 ± 0.09
		25	0.10 ± 0.03
		50	0.08 ± 0.01
Tap water	2 × 100	50	0.03 ± 0.03
WWTP effluent	2 × 100	50	0.04 ± 0.02

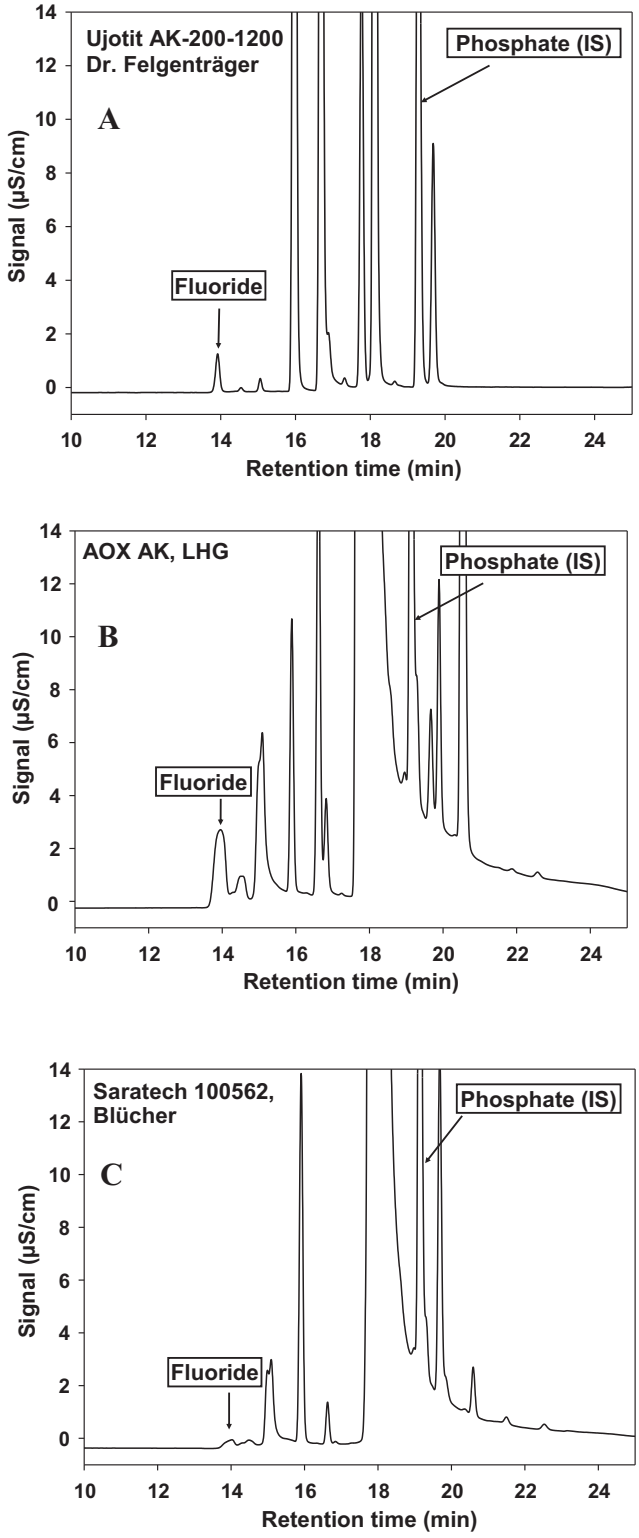

Fig. 2. Comparison of ion chromatograms of the absorption solution after combustion of 50 mg of Ujotit AC-200-1200, AOX AK LHG, and Saratech 100562 (Blücher); for comparison with the IC blank of pure water refer to Fig. S2.

waters [22]) occurs in many fresh waters in concentrations from 0.01 to 0.3 mg/L [31]. Hence, it would disturb the AOF measurement and has to be removed from the adsorbent. In AOX and AOS analysis similar problems were solved by displacement of halogenide ions and sulfate by nitrate ions [14,29].

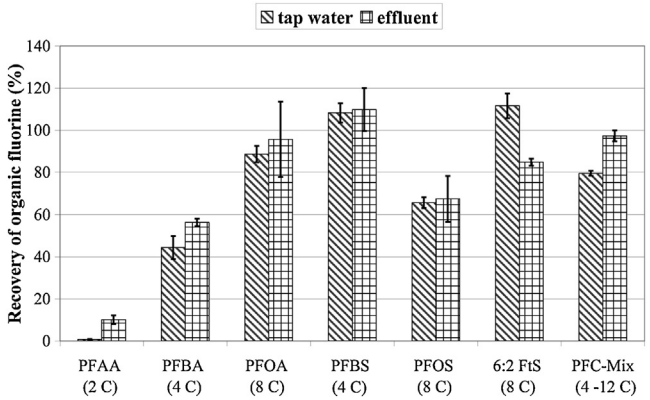

Fig. 3. Organofluorine recovery ($n = 3$) from selected PFC model substances during AOF analysis of tap water and WWTP effluent, spiked at a concentration of 3 µg/L F (single analyte spiking) and 3.7 µg/L F (spiking with a mixture of 19 PFC); The whiskers on the bars indicate the standard deviations of a recovery experiments ($n = 3$) in %.

Therefore, we examined the exchange efficiency of nitrate for fluoride by breakthrough experiments with spiked reagent grade water, tap water, and a WWTP effluent (spike concentration 200 µg/L F) on Ujotit AC-200-1200 filled cartridges. The extraction conditions were as given in Section 2.2, except for preliminary experiments with reagent grade water when the cartridges were filled with 50 mg AC instead of 100 mg. The percentage of residual spiked fluoride was determined after subtraction of the native level of the respective water matrix. Experiments were carried out in duplicate. The results are shown in Table 3.

The preliminary experiments with reagent grade water showed that the residual fluoride decreased with increasing volume of the $NaNO_3$ washing solution. The maximum tested volume was maintained in the experiments with tap water and a wastewater effluent. Under these conditions a virtually quantitative removal of fluoride ions from the activated carbon was observed.

In spite of the higher adsorption capacity the residual fluoride from spiked tap water and wastewater was even less than with reagent grade water. This might be explained by competitive adsorption of other compounds, such as natural organic matter and dissolved salts, which lead to an earlier breakthrough of fluoride.

3.2. Method validation

3.2.1. Determination of LOD and LOQ

LOD and LOQ for the entire AOF protocol (SPE-CIC) were calculated according to the blank value method of DIN 32645 [32] ($n = 10$) with LOD $= 3 \times SD/s \times F_D$ and LOQ $= 10 \times SD/s \times F_D$, where SD is the standard deviation of the overall blank (CIC system, nitrate solutions, 2 × 100 mg AC, and 100 mL reagent grade water), s the slope of the calibration function in the low concentration range (detection of fluoride by IC with conductivity detection), and F_D the dilution factor. LOD and LOQ were 0.1 µg/L and 0.3 µg/L, respectively.

3.2.2. Recoveries of model PFC from tap water and WWTP effluent

In order to check the assessment of environmentally relevant organofluorine compounds the recovery of fluorine from some PFC model substances in AOF analysis was determined (Fig. 3). For this purpose, Karlsruhe tap water and a municipal WWTP effluent of the WWTP Karlsruhe-Neureut were spiked with individual model substances (PFAA, PFBA, PFOA, PFBS, PFOS, 6:2 FTS) at a level of 3 µg/L *F*. In addition, both matrices were spiked at 3.7 µg/L *F* with a mixture of 19 PFCs (for composition, see Section 2.1). The native AOF background of these matrices were 0.45 ± 0.09 µg/L F ($n = 3$) for tap water (inorganic fluoride (IF) measured by IC according to

Table 4
Concentration of fluoride measured by IC and AOF (average ± standard deviation (n = 2)) and concentrations and F contribution of identified PFCs to AOF; SW, surface water; GW, groundwater.

Sample	Fluoride in μg/L F	AOF in μg/L F	F of identified PFCs in μg/L F	F Concentrations of individual PFC measured by HPLC–ESI-MS/MS in ng/L									
				PFBA	PFPA	PFHxA	PFHpA	PFOA	PFDoA	PFBS	PFHxS	PFOS	6:2 FTS
SW 1	145 ± 2	1.01*	0.04[a]	6	2	3	1	3	–	15	2	8	1
SW 2	134 ± 1	0.93*	0.02[a]	3	1	2	1	3	1	5	1	6	1
GW 1	162 ± 1	1.31 ± 0.07	0.55 ± 0.01	11	19	36	9	19	–	23	142	287	7
GW 2	159 ± 1	1.91 ± 0.15	0.87 ± 0.01	12	21	48	11	29	–	30	225	473	17
GW 3	157 ± 1	2.46 ± 0.06	1.24 ± 0.02	12	30	73	16	40	–	37	315	682	33

[a] Single measurement due to limited sample volume.

[33] was 50 μg/L) and 2.02 ± 0.05 μg/L (n = 3) for the WWTP effluent (IF = 116 μg/L). Therefore, the spiked concentrations were of a realistic order of magnitude. It should be taken into account that subtraction of the native AOF values from the results of the spiked sample had only little influence on the tap water results, but might have led to somewhat higher errors for the WWTP effluent matrix.

With only one exception (6:2 FTS), organofluorine recovery from all tested PFCs and also from the PFC mixture were somewhat higher in the WWTP effluent than in tap water. However, these differences were rather small and for PFOA, PFBS, and PFOS even within the standard deviation (n = 3).

In previous experiments aqueous samples (100 μL), spiked with different fluorinated model compounds including some C4 to C8 PFC (PFOA, PFBS, and PFOS; spiking level: 300 μg/L), were given into a sample boat and directly analyzed by CIC. By this means the recoveries of mineralization throughout the combustion process were evaluated. The F recoveries from WWTP effluent (n = 5) were 99 ± 5% for PFOA, 97 ± 3% for PFBS, and 73 ± 4% for PFOS. Therefore, the similar recoveries of these PFCs in direct CIC and CIC after sample extraction (Fig. 3) demonstrate that the extraction procedure was quantitative for these chemicals.

The lower recoveries of PFOS compared to PFBS and PFOA, both in direct CIC of an aqueous solution and after extraction on AC, are very likely rather due to adsorption to the labware prior to extraction (sample bottles, syringes, extraction device) than due to incomplete combustion. Such losses due to adsorption of PFOS, e.g. to sample bottles and vials for extracts, were also observed by the working group which developed the German standard method for PFC target compound analysis. Therefore, in the standard method an addition of at least 40% of methanol in the sample extracts is mandatory and the addition of 5% of methanol to aqueous samples is recommended, if such adsorption effects are observed or suspected [30]. However, while in [30] PFC are extracted by a weak anion exchanger, where a few percent of methanol can be tolerated, the addition of methanol to the samples was avoided for AOF analysis to prevent breakthrough of organofluorine chemicals during adsorption to AC.

As expected, in both water matrices the F recoveries of perfluoroalkyl carboxylates (PFCAs) increased with increasing chain length. PFAA, the shortest homologue of PFCAs, was only recovered by ≤10% by AOX measurement while the recovery increased to approximately 50% for PFBA with a C4 chain. This can be explained by a partial breakthrough of the short chained PFCAs on the Ujotit AC-200-1200 cartridges. Such a breakthrough behavior is well known from breakthrough of PFCAs in technical AC filters in waterworks [13].

Although the PFC mixture contained 19 different poly- and perfluorinated chemicals with carbon chain lengths between C4 and C12, a good overall F recovery (80 ± 1% from tap water and 97 ± 2% from WWTP effluent) was achieved.

In these recovery experiments about 70% of the adsorbed organofluorine was adsorbed on the first cartridge and about 30% on the second cartridge. This partition between the cartridges was almost independent of the model compound tested. We therefore concluded that the partition of the adsorbed chemicals between first and second cartridge is the result of a non-equilibrium adsorption which is determined by the adsorption kinetics.

3.3. Application of AOF analysis to field samples

The first samples, which were analyzed with the new AOF protocol, were Karlsruhe tap water from the TZW laboratory and the effluent of the WWTP Karlsruhe-Neureut (see Section 3.2.2). The tap water AOF concentration of 0.45 μg/L F and the effluent concentration of 2.0 μg/L F were 1.5 and approximately 7 times higher than the LOQ. This demonstrates that the method is sensitive enough to be applied to low contaminated waters.

In addition, surface water (SW) samples of the Rhine river and groundwater (GW) samples were analyzed for AOF (Table 4). The groundwater samples were taken downstream from a site, which was contaminated by PFC based aqueous film-forming foams from fire-fighting activities.

While surface water samples of the Rhine showed low concentrations of individual PFCs (sum of PFC concentration of SW 1 was 66 ng/L and of SW 2 was 38 ng/L, measured by HPLC–ESI-MS/MS [30]), the determination of PFC in groundwater samples revealed a significant contamination (Σ(PFC) = 870–1946 ng/L). At the contaminated site PFHxS, PFOS, PFHxA and 6:2 FTS were the predominant PFCs. This pattern is typical for contamination of water samples with AFFFs [34]. Individual contributions of PFCs to AOF depend on their degree of fluorination and are shown in Table 4.

Concentrations of AOF were around 1 μg/L for diffuse contaminated surface water samples and between 1.3 and 2.5 for groundwater samples from an AFFF contaminated site (Table 4). Whereas 42–50% of AOF of the tested groundwater samples could be explained through individual PFCs, more than 95% of AOF of diffuse contaminated surface water samples remained unidentified. This suggests that other unidentified organofluorine containing compounds, besides unknown PFC e.g. fluorinated pharmaceuticals and pesticides, must be responsible for this gap. The results are consistent with the results from analyses of organofluorine in seawater by the so-called EOF method [16]. In this study at a reference site without known contamination only 1–3% of organofluorine was identified by target PFC analysis, while at a site with known contamination by AFFFs 34–36% could be explained by single substance analysis of PFCs.

4. Conclusion

The new developed AOF method is two orders of magnitude more sensitive than a former German draft standard. This protocol is currently used as the basis for future work to establish a standard method within the German Institute for Normalization (DIN, working group DIN NA 119-01-03-01-12 “ion chromatography”).

As an element specific parameter the selectivity of this method lies between non specific AOX and highly compound specific target compound analysis, e.g. by HPLC–MS/MS and allows for a distinction of highly polluted vs. diffuse polluted sites. First application to aqueous environmental samples proved the suitability of the protocol to analyze even low contaminated samples. In case of known contaminations with a certain class of organofluorine chemicals, here PFC from AFFF application, about 40–50% of the AOF could be explained by the fluorine bound in the target chemicals. In low and diffuse polluted surface waters only less than 5% of the AOF could be attributed to the selection of the investigated PFC.

Similar to other surrogate parameters, which are defined by operation, such as the group parameter AOX, also AOF comprises chemicals of a certain analytical window, particularly of certain polarities and thus recoveries. Therefore, an AOF value obtained by application of the presented protocol does not represent a hypothetical and not yet measurable total organic fluorine (TOF) concentration, but a lower boundary of organofluorine concentration in water instead, as defined by the analytical protocol.

Further research is needed to estimate the impact of other important classes of fluorinated chemicals, especially in the field of fluorinated pesticides and pharmaceuticals.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2013.04.051.

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Trace analysis of total fluorine in human blood using combustion ion chromatography for fluorine: A mass balance approach for the determination of known and unknown organofluorine compounds

Yuichi Miyake [a], Nobuyoshi Yamashita [a,*], Man Ka So [a,b], Pawel Rostkowski [a,c], Sachi Taniyasu [a], Paul K.S. Lam [b], Kurunthachalam Kannan [d,e,**]

[a] *National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan*
[b] *Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China*
[c] *Department of Environmental Chemistry & Ecotoxicology, University of Gdańsk, 18 Sobieskiego Str., PL 80-952 Gdańsk, Poland*
[d] *Wadsworth Center, New York State Department of Health, Empire State Plaza, P.O. Box 509, Albany, NY 12201-0509, USA*
[e] *Department of Environmental Health Sciences, School of Public Health, State University of New York at Albany, Empire State Plaza, P.O. Box 509, Albany, NY 12201-0509, USA*

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Abstract

The number of perfluorochemicals (PFCs) that have been found in biological and environmental matrices is increasing as analytical standards and methods evolve. Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) constitute only a fraction of the total suite of PFCs found in environmental and biological matrices. A robust method and approach is needed to evaluate the mass of fluorinated compounds in biological matrices. In this study, we developed a method to measure total fluorine (TF) and organic fluorine (TOF) in human blood matrices using combustion ion chromatography (CIC). Blood matrices (whole blood, serum, and plasma) were analyzed in bulk to determine TF. An aliquot of the blood was also extracted with organic solvents such as methyl-tert-butyl ether (MTBE) and hexane, and organic and aqueous extracts were separated, to fractionate organofluorines from inorganic fluorine. The organic layer was analyzed for TF by CIC, and for known PFCs by high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). PFCs measured by HPLC-MS/MS accounted for >80% of the TF in the organic fraction. The aqueous fraction contained inorganic fluorine and other non-extractable organofluorines. However, in the bulk sample, fluoride and non-extractable organofluorines accounted for >70% of the TF in blood samples from the general population. In occupationally exposed individuals, known organofluorines accounted for a major proportion of the TF. These results suggest the existence of yet uncharacterized fluorine fraction in human blood. Further studies are needed to characterize the aqueous fraction that contains inorganic fluorine and non-extractable forms of fluorine.

Keywords: Fluoride; Perfluorochemicals; PFOS; PFOA; Ion chromatography; Human blood

1. Introduction

In 1966, Taves reported the occurrence, in human sera, of fluoride, which was thought to be originating from fluoridated drinking water [1]. Later studies found organic fluorine in human blood, in addition to the inorganic fluoride normally present [2,3]. However, due to the lack of adequate analytical capabilities at that time, no specific identification of organic fluorine was possible. Later, in the 1990s, with advances in analytical techniques, specific organic forms of fluorine, particularly perfluorinated chemicals (PFCs) such as perfluorooctanesulfonate (PFOS) and

* Corresponding author at: National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan. Tel.: +81 29 861 8335; fax:+81 29 861 8335.
** Corresponding author at: Wadsworth Center, New York State Department of Health, and Department of Environmental Health Sciences, School of Public Health, State University of New York at Albany, Empire State Plaza, PO Box 509, Albany, New York 12201-0509, USA. Tel.: +1 518 474 0015; fax: +1 518 473 2895.
E-mail addresses: nob.yamashita@aist.go.jp (N. Yamashita), kkannan@wadsworth.org (K. Kannan).

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perfluorooctanoate (PFOA), were identified in human sera [4]. Although the earlier studies focused on measurement of PFOS and PFOA, the two predominant forms of PFCs in biota, the number of organofluorines detected in environmental and biological matrices has increased to >15 in the last few years [5–8]. Nevertheless, it is still not known whether all of the organic forms of fluorine have been identified, and accounted for, in biological and environmental matrices. Some precursor compounds, such as *N*-ethyl perfluorooctanesulfonamidoethanol, are metabolized in the body, and their metabolic intermediates (e.g., perfluorooctanesulfonamidoacetate) can be present in tissues [9]. It is not known whether metabolic intermediates of other PFCs can similarly concentrate in tissues. Analytical standards and methods are not available to measure the residue levels of all of the degradation intermediates.

In general, it is known that PFOS and PFOA constitute only a portion of the PFCs found in environmental and biological matrices; other fluorochemicals such as fluorotelomer alcohols and long-chain perfluorocarboxylates (PFCAs) have become increasingly important components of monitoring surveys and risk evaluation. Several PFCs, including PFOS and PFCAs, have been nominated as candidate persistent organic pollutants in 2005, for further scrutiny and investigations [10]. If we are to make a comprehensive assessment of sources and risks of PFCs, it is important that we identify and quantify all of the forms of PFCs, and determine their environmental dynamics, fates, and toxicities. This is particularly important for those PFCs that are yet to be identified. Because the production methods and usage patterns of PFCs are complex, PFCs are released into the environment in multiple forms (e.g., polymers, precursors, degradation intermediates, metabolites). In view of the lack of appropriate analytical standards and methods for all of the potential PFCs that can occur in the environment, we developed a novel approach that involves extraction and fractionation of the sample matrix for individual measurements of total fluorine (TF), inorganic fluorine (IF), and total organic fluorine (TOF), by combustion ion chromatography (CIC).

Measurements of TF, IF, and TOF will allow us to elucidate the presence of other, unidentified inorganic or organic forms of fluorine in the sample matrix. It is a challenging task, because of the difficulties associated with analysis of fluorine at trace levels. The currently available techniques to measure TF, using combustion methods, ion-selective electrodes, or ion chromatography, can detect fluoride only at sub-parts-per-million or parts-per-billion levels [11–18]. However, several PFCAs are typically present at parts-per-trillion to sub parts-per-billion levels in aqueous matrices, including blood [5,9,19,20]. Thus, there is a need to improve the analytical method, to be able to determine TF at lower parts-per-billion or parts-per-trillion levels. One of the reasons for the current high quantitation limit is the high background levels or contamination arising from instrumental or procedural blanks. Recent improvements in the analysis of TF using CIC enabled the determination of TF in environmental matrices such as fly ash [15]. We developed the new CIC for organic fluorine that is applicable to part per billion level analysis in water sample [21]. In this study, we applied the CIC method with some additional modifications and improvements, for the trace level analysis of fluorine in human blood. This method is capable of detecting TF at parts-per-billion (μg F/L) levels in blood. Sample matrices were extracted and fractionated by systematic, multiple extraction schemes, to provide polar and non-polar fractions, and organic and inorganic fluorine fractions (Fig. 1). Contributions of known PFCs to TF, and the percentage of unknown organofluorines in TF, were determined. Several human blood samples were analyzed using this method for validation, and a mass balance analysis was performed to compare known and unknown proportions of fluorinated compounds in the blood.

2. Experimental

2.1. Sample collection

Blood samples were collected from adult male volunteers ($n = 3$; age 28–38) from Tsukuba, Japan, in 2003 and from two occupationally exposed ($n = 2$; age 43 and 51) employees at a fluoropolymer manufacturing facility in Japan in 2004. Both whole blood and serum were analyzed for occupationally exposed individuals. Similarly, samples of plasma ($n = 4$; age 20–60) were collected from adult male volunteer donors from New York State, USA, in 2001. Sampling containers, syringes, and needles used for blood collection were tested for target fluorochemicals prior to use. This was important, because serum tubes with fluoropolymer sealing can contribute to contamination of samples. Our studies found that the maximum amounts of residual PFCAs and fluorotelomer carboxylates (FTCAs) in serum tubes were 2200 pg and 3400 pg, respectively [22].

2.2. Extraction and fractionation

Known PFCs including PFOS, perfluorohexanesulfonate (PFHxS), perfluorobutanesulfonate (PFBS), perfluorooctanesulfonamide (PFOSA), perfluorooctadecanoate (PFOcDA), perfluorohexadecanoate (PFHxDA), perfluorotetradecanoate (PFTeDA), perfluorododecanoate (PFDoDA), perfluoroundecanoate (PFUnDA), perfluorodecanoate (PFDA), perfluorononanoate (PFNA), PFOA, perfluoroheptanoate (PFHpA), perfluorohexanoate (PFHxA), perfluoropentanoate (PFPeA), N – EtFOSA (n-ethyl perfluorooctanesulfonamide), N – EtFOSAA (n-ethyl perfluorooctanesulfonamidoacetate), 8:2 FTCA (fluorotelomer carboxylate), and 8:2 FTUCA (fluorotelomer unsaturated carboxylate) in human blood were determined by ion-pair extraction followed by HPLC-MS/MS quantification. Details of the ion-pair extraction method have been described elsewhere [4,5]. Briefly, a HP1100 liquid chromatograph (Agilent Technologies, Palo Alto, CA) interfaced with a Micromass (Beverly, MA) Quatro Ultima Pt mass spectrometer was used in the electrospray negative ionization mode. A 10 μL aliquot of the sample extract was injected onto a guard column (Zorbax XDB-C8, 2.1 mm i.d. × 12.5 mm, 5 μm; Agilent Technologies) connected sequentially to a Betasil C18 column (2.1 mm i.d. × 50 mm length, 5 μm; Thermo Hypersil-Keystone, Bellefonte, PA) with 2 mM ammonium acetate aqueous solution (solvent A) and methanol (solvent B) as mobile phases, start-

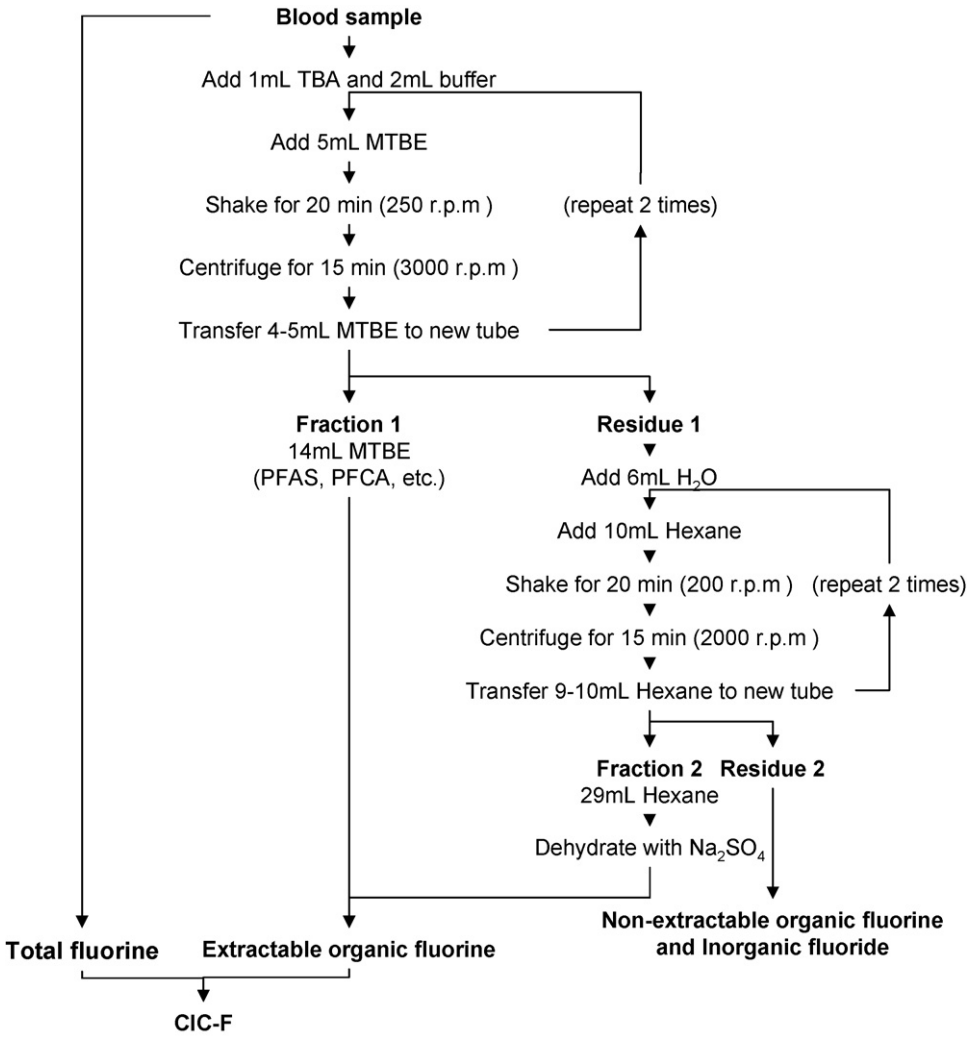

Fig. 1. Schematic outline of the multiple extraction scheme for total fluorine, organic fluorine, and inorganic fluoride in human blood, using combustion ion chromatography (CIC).

ing at 10% methanol and increasing linearly. At a flow rate of 300 μL/min, the gradient was increased to 30% methanol at 0.1 min, 75% methanol at 7 min, and 100% methanol at 10 min, and was kept at that level until 12 min before reversion to original conditions, at the 20-min time point. The capillary was held at 1 kV. Cone-gas and desolvation-gas flows were kept at 60 and 740 L/h, respectively. Source and desolvation temperatures were kept at 120 and 400 °C, respectively. MS/MS was operated under multiple reaction monitoring (MRM) mode, and the parameters were optimized for transmission of the $[M-K]^-$ or $[M-H]^-$ ions of target chemicals.

An aliquot of each blood sample was subjected to fractionation steps, as illustrated in Fig. 1, for the analysis of TF, IF, and TOF [5,15]. Blood samples were extracted by an ion-pair extraction procedure using methyl-tert-butyl ether (MTBE), and the extracts were collected (Fraction 1). The residue from this procedure was further extracted with hexane (Fraction 2) and combined with MTBE extracts for the analysis of organic fluorine (TOF) (Fig. 1). The final residue after hexane extraction is expected to contain inorganic fluorine (IF) and any non-extractable forms of fluorine. TF was determined by taking an aliquot of the blood on a silica boat and placing it directly into the CIC.

2.3. Instrumental analysis and quantification

Concentrations of TF and TOF were determined using combustion ion chromatography (CIC; Table 1) [21]. This method involves modifications to the traditional combustion ion chromatography (CIC), by the combination of an automated combustion unit (AQF-100 type AIST; Dia Instruments Co., Ltd.) and an ion chromatography system (ICS-3000 type AIST; Dionex Corp., Sunnyvale, CA). In this study, we removed possible sources of fluorochemical contamination in blanks by replacing certain parts of the instrument with non-fluorinated materials; the customized instrument, combustion ion chromatograph for fluorine (CIC-F), as described in detail elsewhere [21], was used for our studies. A schematic diagram of the CIC-F instrument is shown in Fig. 2. The sample extract or the blood sample was set on a silica boat and placed into a furnace at 900–1000 °C. Combustion of the sample in the furnace converted organofluorines and inorganic fluoride into hydrogen

Table 1
Analytical conditions for total fluorine and extractable organic fluorine determination in blood using combustion ion chromatography

Combustion	
Instrument	AQF-100 (type AIST); Dia Instruments Co. Ltd.
Furnace temperature (inlet)	950 °C
(outlet)	1000 °C
Carrier gas	150 mL/min (Argon) → inlet boat (3.5 min hold) → switch over to Oxygen gas (3 min hold)
Water supply gas (Argon)[a]	150 mL/min
Combustion gas (Oxygen)	300 mL/min
Injection volume of blood	100 μL
Ion chromatograph	
Instrument	ICS-3000 (type AIST); Dionex Co. Ltd.
Detector	Conductivity detector
Column	IonPac AS20 (2 mm i.d.)
Mobile phase	Potassium hydroxide solution 2 mM (2 min hold) → 5.4 mM/min (7 min) → 40 mM (4 min hold) → 2 mM (8 min hold)
Flow rate	0.25 mL/min
Column oven temperature	35 °C
Injection volume of absorbent	1500 μL

[a] Water (0.2 to 0.3 mL/min) is supplied with argon gas in the furnace for complete hydride generation and to improve the recovery of total fluorine.

fluoride (HF) completely, using a special type of furnace with water supply. Water supply of 0.2 to 0.3 mL per minute was applied with argon gas in the furnace during combustion. The HF was absorbed into sodium hydroxide solution (0.2 mmol/L). The concentration of F^- in the solution was analyzed using ion chromatography. The IC mobile phase (0.25 mL/min) was initially 2 mM (2 min hold) of potassium hydroxide and then was increased to 40 mM at a rate of 5.4 mM/min (4 min hold). The column was returned to 2 mM KOH (8 min hold) prior to the next injection. Sodium fluoride (99% purity; Wako Pure Chemical Industries, Tokyo, Japan) was used as a standard for quantification. Five calibration points prepared routinely at 0.2, 1, 5, 25, and 100 μg/L, and injected at 1.5 mL, to check for linearity of the instrument. The calibration curve exhibited excellent linearity with R^2 of >0.99. Quantification was based on the response of the external standards that bracketed the concentrations found in the samples. The detailed analytical conditions of CIC-F were reported elsewhere [21]. All solutions were prepared in Milli-Q water (18 MΩ cm), and the fluoride concentration in the Milli-Q water was <0.025 μg/L. The total time for analysis was approximately 20 min per sample. Quality assurance and quality control measures, including the validation of the fractionation procedure, recoveries of target compounds, and interferences, are discussed below. Concentrations of TF and TOF are reported as corresponding fluoride ion (ng or μg F^-/mL).

Table 2
Concentrations of inorganic fluoride in fractions 1 and 2 by multiple extraction methods (mg F/L)

Concentration of NaF spiked (μg F/mL)	Ion-pair MTBE extraction	Hexane extraction
	Fraction 1	Fraction 2
1	<0.006	<0.006
10	<0.006	<0.006
100	<0.006	<0.006

3. Results and discussion

3.1. Separation of inorganic fluoride in extracts

Separation of inorganic fluoride from the organofluorines is crucial for mass balance analysis. The separation of inorganic fluorine from organic forms was examined by spiking known concentrations of sodium fluoride (1,10,and 100 mg F/L) into blood matrices and extracting first by ion-pair extraction (Fraction 1) and then by hexane (Fraction 2) as shown in Table 2. Concentrations of fluoride in each of the fractions were analyzed by CIC-F. It was found that the organic extracts from the ion-pair procedure (i.e., MTBE and hexane extracts) did not contain (<0.006 mg F/L) spiked sodium fluoride (1, 10, 100 μg F/mL) and suggested negligible residue of inorganic fluoride after this procedure. The MTBE and hexane extractions have been known to extract organic forms of fluorine such as perfluoroalkyl acids [4]. The recoveries of acidic PFCs, including perfluoroalkyl-

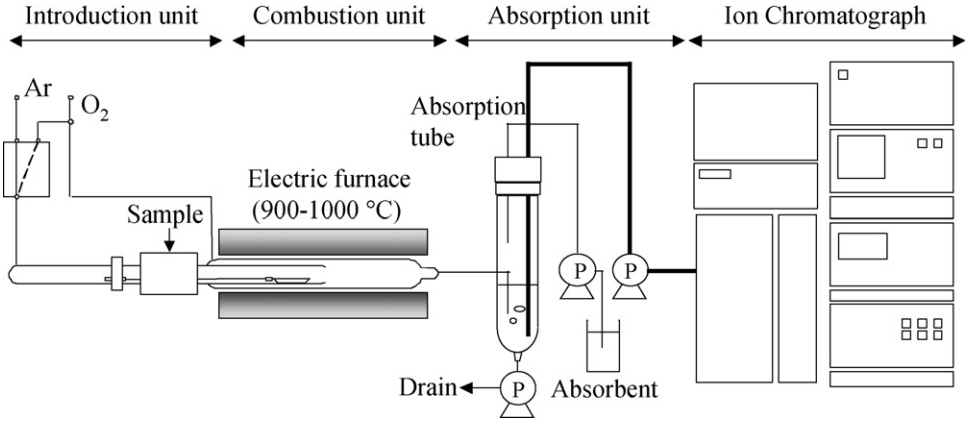

Fig. 2. Schematic illustration of combustion ion chromatograph for fluorine (CIC-F).

Table 3
Recoveries and standard deviations (SD) of individual PFCs determined by multiple extraction and HPLC-MS/MS ($n = 5$)

Group	Compound	Average (%)	SD (%)
PFASs	PFOS	81.2	1.4
	PFHxS	85.0	6.0
	PFBS	84.3	2.9
	PFPrS	93.2	5.6
	PFEtS	78.4	4.3
PFCAs	PFOcDA	80.5	3.3
	PFHxDA	70.6	4.1
	PFTeDA	85.4	4.5
	PFDoDA	92.0	2.7
	PFUnDA	103.0	3.6
	PFDA	94.0	3.4
	PFNA	74.4	3.0
	PFOA	87.2	1.7
	PFHpA	88.0	1.6
	PFHxA	90.1	2.1
	PFPeA	105.9	5.8
	PFBA	129.1	8.7
FTCAs	8:2 FTCA	88.7	5.5
	8:2 FTUCA	99.8	2.1
FOSAs	N-EtFOSAA	109.3	4.9
	PFOSA	68.3	1.9
	N-EtFOSA	52.0	1.0

sulfonates (PFASs – carbon numbers ranging from C2 to C8), perfluoroalkylcarboxylates (PFCAs – carbon numbers ranging from C5 to C18), and some fluorotelomer carboxylates through ion-pair and hexane extracts were between 71% and 109%, except for PFBA and N-EtFOSA (Table 3). Because of the high water solubility of inorganic F^- (e.g., the water solubility of sodium fluoride is 18,000 mg/L), this anion is expected to partition into the aqueous phase rather than the organic phase.

3.2. Co-elution of fluoride and organic acids

One of the issues with the analysis of F^- using CIC is the co-elution of certain low-molecular-weight organic acids (such as formic acid, lactic acid, and acetic acid) with fluoride, resulting in potential interferences in measurements of TF [23,24]. The separation of fluoride from the interfering organic acids was examined with two types of chromatographic columns having different ion-exchange properties. The same mobile phase conditions as described in Section 2.3 were used for the two columns. We tested an anion exchange column, IonPac AS17 (Dionex Corp., Sunnyvale, CA; 2 mm i.d. × 250 mm length, 10.5 μm), which is routinely used for the determination of inorganic anions. However, this column did not resolve fluoride from the organic acids (Fig. 3). In contrast, fluoride and organic acid peaks were fully resolved when IonPac AS20 (77.5 μeq/column; 2 mm i.d. × 250 mm length, 7.5 μm), which has a 10-fold greater ion-exchange capacity than IonPac AS17 (7.5 μeq/column); this column was used under identical operating conditions.

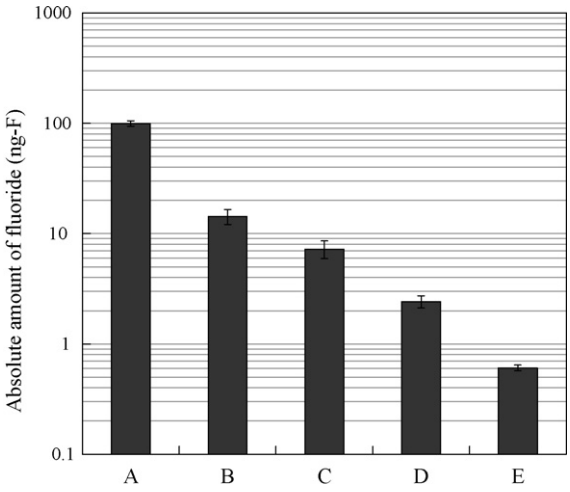

Fig. 4. Absolute amount of fluoride in CIC instrumental blanks ($n = 4$). (A) With use of standard gases and equipment; (B) after changing from standard gases to high purity gases; (C) after removal of fluoropolymer parts in ion chromatograph, gas lines, valves, and regulators; (D) after addition of activated carbon to trap impurities from the gases; and (E) after changing from syringe pump made up of fluoropolymer to ceramic syringe pump.

3.3. Instrumental and reagent blanks

Several experiments were conducted to check for the sources of contamination of organofluorines and inorganic fluoride in instrumental blanks (Fig. 4). Prior to the application of the analytical technique to measure TF in blood samples, the background level of fluoride from the analytical procedure was found to be approximately 100 ng. Therefore, efforts were made to remove/reduce fluoride contamination originating from the ana-

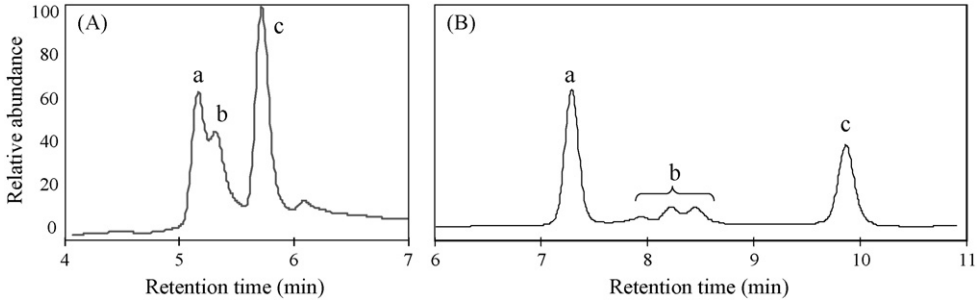

Fig. 3. Chromatograms of fluoride and organic acids obtained with (A) IonPac AS17 column and (B) IonPac AS20 column. Peak 'a' corresponds to fluoride ion; Peaks 'b' and 'c' are unknown low-molecular weight organic acids.

lytical procedure. Fluoride was detected in the sodium hydroxide solution that is used to absorb HF generated from combustion of samples containing fluorinated compounds. This suggested that the source of contamination is present within the CIC instrument or the gases. Gases were then replaced with high- purity gases (Ar: 99.9999%, O_2: 99.9995%). Ion chromatograph tubing, gas lines, valves, and regulator, which contained materials or parts that are made up of polytetrafluoroethylene (PTFE), were replaced with either stainless steel, polyetheretherketone, or polyethylene tubing. Furthermore, a gas purifier containing activated carbon was placed in the gas line, to remove trace levels of fluorine from the gases. Following these modifications, backgrounds levels of fluorine in instrumental and reagent blanks decreased by more than 100 to 1000-fold, compared to the level found in a traditional CIC (Fig. 4).

The limit of detection (LOD) of organofluorine was evaluated for each sample, based on the maximum blank concentration, the concentration factors, and the injection volume of the sample. The LOD for blood samples was 3 μg F/L (ppb) when 1 mL of blood sample was used for analysis, in a final volume of 0.5 mL. The LODs can be decreased by increasing the volume of sample taken for analysis or by further reducing the background levels. Thus, CIC-F with low background contamination and improved sensitivity for fluoride by >2–3 orders of magnitude, compared to that of a traditional CIC, was attained.

3.4. Mass balance analysis of perfluorochemicals in blood

Four samples of human plasma from New York (USA), and three samples of whole blood from the general population in Japan and from two occupationally exposed individuals in that country were subjected to CIC-F analysis. Concentrations of known PFCs, extractable organic fluorine and total fluorine in these samples are shown in Table 4. Reproducibility of the results was tested by analyzing the samples three times and the coefficient of variation among the three analyses ranged from 4% to 10%. Concentrations of TF in plasma of individuals from the United States ranged from 140 to 189 ng F/mL, whereas TF concentrations in whole blood of Japanese individuals (non-occupationally exposed) ranged from 181 to 262 ng F/mL. With the caveat that the method and the matrix used by Taves and other workers during the 1960s to 1980s [1,3,16] were different from those used in our study, we found total fluoride concentrations in plasma to be 5- to 10-fold higher than concentrations reported during the 1960s–1980s. A recent study found that the mean concentration of F^- in plasma of 127 subjects from the United States who had 5.03 mg/L in their drinking water was 106 ± 76 μg/L [25]. Based on the limited number of samples analyzed in this study, a temporal increase in F^- concentrations in the blood of the individuals from the United States can be suggested. Nevertheless, the concentrations of F^- in plasma are known to vary depending on the concentrations in drinking water and diet [26]. In particular, water and water-based beverages are the chief sources of dietary fluoride intake in the United States [27]. Fluoride intake has increased in the United States since 1930 [28].

Table 4
Concentrations of known PFCs (ng/mL), extractable organic fluorine (ng F/mL) and total fluorine (ng-F/mL) in human blood[a]

Type		Sample ID	PFASs			PFCAs								FOSAA	FOSA	Sum PFCs (ng F/mL)	EOF in Fr1 (ng F/mL)	EOF in Fr2 (ng F/mL)	TF (ng F/mL)	Sum PFCs/EOF in Fr1 ratio (%)
			PFOS	PFHxS	PFBS	PFDoDA	PFUnDA	PFDA	PFNA	PFOA	PFHpA	PFHxA	PFPeA	N-Et FOSAA	PFOSA					
Control																				
Japan	Whole blood	JW1	7.2	0.34	<0.02	0.045	0.65	0.28	0.68	1.1	<0.02	<0.02	<0.02	0.17	0.90	7.51	8.89	<6	208	84
	Whole blood	JW2	0.84	0.060	<0.02	0.024	0.12	<0.02	0.14	0.14	<0.02	0.027	<0.02	0.12	0.41	1.21	<6	<6	262	–
	Whole blood	JW3	1.1	0.058	<0.02	0.022	0.10	<0.02	0.13	0.17	<0.02	<0.02	<0.02	<0.02	0.77	1.55	<6	11.9	181	–
USA	Plasma	UP1	8.3	9.3	<0.01	0.027	0.11	0.17	0.56	3.7	0.20	0.088	0.13	0.93	0.015	15.1	17.8	9.74	140	85
	Plasma	UP2	47	5.8	<0.02	0.074	0.68	0.60	2.1	5.4	0.094	0.19	0.15	0.38	0.0097	40.7	45.1	15.6	149	90
	Plasma	UP3	63	13	<0.02	0.053	0.38	0.41	2.1	12	0.26	0.60	0.52	1.7	0.029	60.8	59.0	<6	181	103
	Plasma	UP4	51	5.1	<0.02	0.037	0.21	0.24	1.2	7.2	0.047	0.20	0.061	0.76	0.024	42.9	45.3	<6	189	95
Occupational exposure																				
Japan	Whole blood	OW1	38	16	<1	<1	1.5	<1	0.86	570	<1	<1	<1	<1	5.5	436	424	<30	605	103
	Whole blood	OW2	110	8.2	2.5	<1	1.4	<1	1.9	530	1.2	<1	<1	<1	69	488	505	<30	624	97
Japan	Serum	OS1	150	47	<1	<1	7.6	1.8	5.6	1400	<1	0.84	<1	<1	1.3	1110	1070	<30	1300	104
	Serum	OS2	330	19	5.4	<1	4.3	0.98	4.9	1200	2.3	<1	<1	<1	11	1070	1020	<30	1160	105

[a] PFOcDA, PFHxA, PFTeA, 8:2FTCA, 8:2FTUCA, and N-EtFOSA was analyzed in human blood, but the concentrations were below LOD.

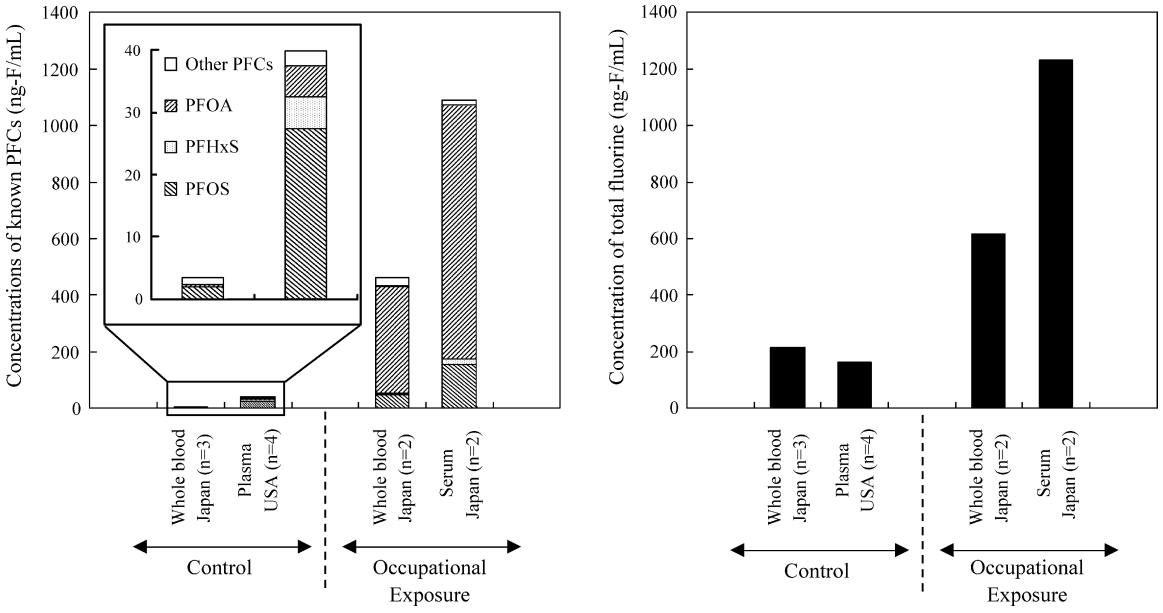

Fig. 5. Concentration of individual PFCs and TF in human blood.

Concentrations of individual PFCs measured using HPLC-MS/MS, and TF measured using CIC-F in blood and plasma samples from Japan and the United States are shown in Fig. 5. Approximately 30% of the TF in the US blood samples is contributed by known PFCs, with the remaining portion composed of inorganic fluorine and non-extractable forms of organofluorines (Fig. 6). Similarly, >80% of the TF in blood samples from Japan was inorganic fluorine and non-extractable organofluorine compounds. Whole blood samples from occupationally exposed individuals in Japan showed a strong contribution by PFOS and PFOA to TF. In a study of rats exposed to PFOA in the laboratory, PFOA was the major contributor to TF in the blood [29].

Concentrations of total PFCs in plasma samples from the United States ranged from 15 to 61 ng F/mL, and those in blood samples from Japan ranged from 1.2 to 7.5 ng F/mL (Table 4). This includes 13 PFCs representing PFASs and PFACs. Concentrations of PFCs in the blood of occupationally exposed Japanese individuals (436–488 ng F/mL) were two to three orders of magnitude higher than those in the samples from the non-occupationally exposed individuals in that country [30]. Concentrations of total PFCs measured using HPLC-MS/MS accounted for >80% of the TOF measured in Fractions 1 and 2 using CIC-F. These results suggest that most of the organic forms of fluorine were accounted for by the ion-pair extraction procedure. However, the aqueous fraction containing inorganic F^- still contained a major portion (>70%) of the TF in blood samples of the non-occupationally exposed individuals from the United States and Japan (Fig. 5). In occupationally exposed individuals, 80–90% of the TF was found as PFOA and PFOS. The differences in the distribution of known and unknown fluorinated compounds between the environmentally exposed individuals and occupationally exposed individuals suggest that inorganic fluoride levels are comparable among populations, whereas the organofluorine concentrations vary depending on the exposure levels of individuals. These results further suggest that the unknown fraction still accounts for a major proportion to TF and may contain several unidentified/non-extractable organic forms of fluorine.

In summary, determination of contribution of individual PFCs to total fluorine, using the mass balance approach, is important to reveal the occurrence of unidentified fluorinated compounds in environmental and biological matrices. Such analysis will help in elucidating bioaccumulation of yet-unidentified fluorinated chemicals. In this study, the CIC with multiple extractions and fractionation has proven to be a valuable technique for the determination of trace levels of TF in human blood.

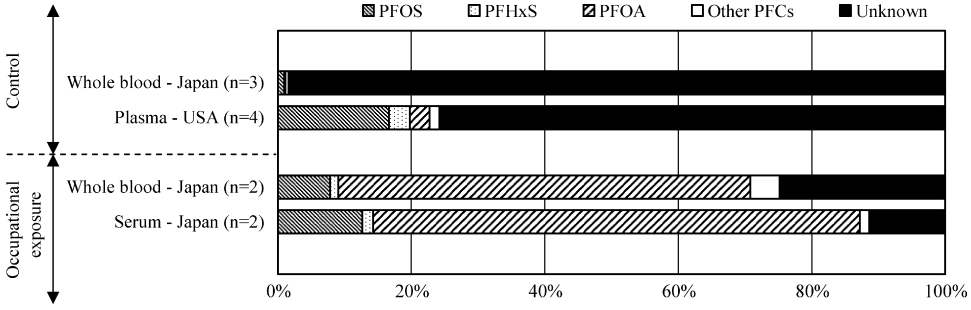

Fig. 6. Contributions of individual PFCs to TF in human blood.

We found known organofluorines to account for only <30% of the fluoride in the blood of individuals. Inorganic fluorine and other non-extractable organofluorine compounds account for a major portion of F^- in human blood. Further studies are needed to characterize the unknown fractions. Application of the mass balance approach to source materials (e.g, industrial products), and to environmental and biological samples, will provide valuable information on the extent of contamination by other unidentified fluorochemicals in the environment.

Acknowledgments

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Bubble-Nucleation-Based Method for the Selective and Sensitive Electrochemical Detection of Surfactants

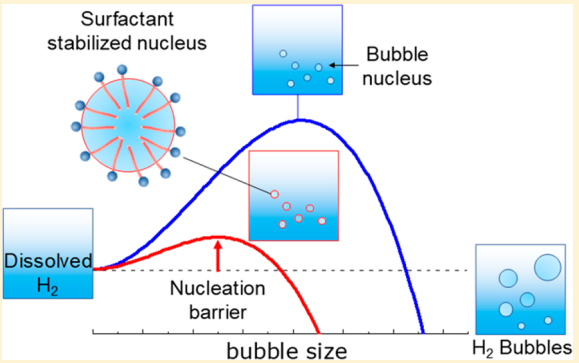
Ruchiranga Ranaweera,[†] Carina Ghafari,[‡] and Long Luo*[,†]

[†]Department of Chemistry, Wayne State University, Detroit, Michigan 48202, United States

[‡]Chemistry Department, Kalamazoo College, Kalamazoo, Michigan 49006, United States

Supporting Information

ABSTRACT: We present the first bubble-nucleation-based electrochemical method for the selective and sensitive detection of surfactants. Our method takes advantage of the high surface activity of surfactant analyte to affect the electrochemical bubble nucleation and then transduces the change in nucleation condition to electrochemical signal for determining the surfactant concentration. Using this method, we demonstrate the quantitation of perfluorinated surfactants in water, a group of emerging environmental contaminants, with a remarkable limit of detection (LOD) down to 30 μg/L and a linear dynamic range of over 3 orders of magnitude. With the addition of a preconcentration step, we have achieved the LOD: 70 ng/L, the health advisory for perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) in drinking water established by the U.S. Environmental Protection Agency. The experimental results are in quantitative agreement with our theoretical model derived from classical nucleation theory. Our method also exhibits an exceptional specificity for the surfactant analytes even in the presence of 1000-fold excess of nonsurfactant interference. This method has the potential to be further developed into a universal electrochemical detector for surfactant analysis because of its simplicity and the surface-activity-based detection mechanism.



Surfactants are widely used as dispersants, emulsifiers, detergents, fabric softeners, and wetting agents in many household items and industrial products and processes.[1] Because of the environmental impact and toxicity of various surfactants, current legislation requires that the amount of surfactants released into the sewer system is minimized and that the concentrations in rivers and lakes are maintained at low levels.[2] For example, perfluorinated surfactants (PS) has been widely used in coating and surfactant applications since the 1950s (e.g., nonstick coating and fire-fighting foam) because of the chemical and thermal stability of a perfluoroalkyl moiety and its distinctive hydrophobic and lipophobic nature.[3,4] As a result of the extensive use of PS and their emission, a broad range of these compounds have been detected in the environment, wildlife, and humans. Recent biomedical studies have revealed the positive associations between PS exposure and disease parameters in the general population.[5] As a result, the U.S. Environmental Protection Agency identified addressing the problem of fluorinated substances as one of the national priorities in 2018.[6] Many well-known methodologies for surfactant determination require either expensive and complicated instruments (for example, liquid and gas chromatographs) or the use of relatively large amounts of organic solvents (such as chloroform in the spectroscopic "methylene blue" method),[7] making them unsuitable for in situ detection applications.[8] Therefore, there is a critical need to develop new and improved methods for surfactant detection.

The formation and evolution of vapor and gas bubbles in a liquid body is a phenomenon of vast fundamental and applicative interest, for example, in commercial electrolytic processes,[9,10] in cavitation,[11−13] in biomedical applications,[14−16] and in functional material fabrication.[17−20] Here, we present a new application of gas bubbles for surfactant detection. Our method is based on the interactions between gas nuclei and surfactant molecules during electrochemical gas bubble nucleation. According to classical nucleation theory (CNT),[21] nucleation of a gas bubble requires a supersaturation of dissolved gas because of the energy barrier of establishing a new gas−liquid interface (Scheme 1). In the presence of surfactant molecules, gas nuclei can be stabilized because of the reduced surface tension of the gas−liquid interface, leading to a decrease of the supersaturation level required for bubble nucleation. In our method, we take advantage of the high surface activity of surfactant analyte to affect the bubble nucleation, and transduce the change in the supersaturation level required for bubble nucleation to electrochemical signal for highly sensitive and specific detection of surfactant analytes.

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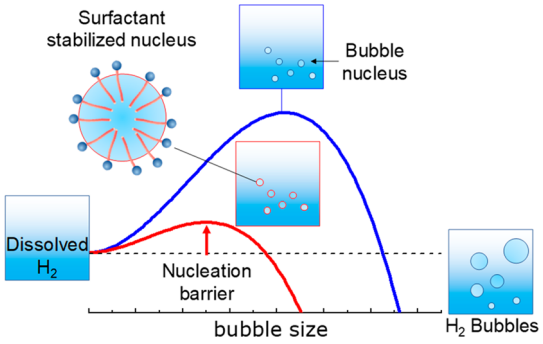
Scheme 1. Bubble-Nucleation-Based Electrochemical Method for Surfactant Detection[a]



[a]Because of the high surface activity of surfactant molecules, they stabilize H_2 bubble nuclei, leading to a reduced nucleation barrier.

EXPERIMENTAL SECTION

Chemicals and Materials. Perchloric acid ($HClO_4$, 70%), sodium perchlorate ($NaClO_4$, 98%), tridecafluorohexane-1-sulfonic acid, nonafluorobutane-1-sulfonic acid, perfluorooctanoic acid, perfluoroheptanoic acid, undecafluorohexanoic acid, heptafluorobutyric acid, poly(ethylene glycol) (400 g/mol), TWEEN 20, lysozyme from chicken egg white, and humic acid were purchased from Sigma-Aldrich. Potassium perfluorooctanesulfonate was purchased from Matrix Scientific. Perfluoroheptanesulfonic acid was purchased from Synquest Laboratories. Glass capillary (outside diameter/inside diameter, 1.65/1.10 mm, soft temperature, 712 °C) was received from Dagan Corporation. Platinum (Pt wire, 25 μm diameter, 99.95%) wires were purchased from Surepure Chemetals. Silver conductive epoxy was purchased from MG Chemicals. A Visiprep SPE Vacuum manifold (Supelco Inc., Bellefonte, PA, USA) was used for solid-phase extraction. BondElut LMS polymer 500 mg SPE cartridges were purchased from Agilent. Surface tension measurements were conducted using the pendant drop method on a Kruss DSA100 goniometer. All aqueous solutions were prepared from deionized (DI) water (PURELAB, 18.2 MΩ cm, total organic carbon < 3 ppb).

Electrochemical Measurements. All experiments were carried out using a CHI 760E potentiostat and inside a grounded Faraday cage. An Ag/AgCl electrode in a saturated KCl solution was used as the counter/reference electrode during the measurements with nanoelectrodes. A mixture of 0.10 M $NaClO_4$ and 1.0 M $HClO_4$ was used as the supporting electrolyte for all the experiments. A serial dilution of perfluorinated surfactants was made in 1.0 M $HClO_4$/0.10 M $NaClO_4$ solution. Cyclic voltammograms of nanoelectrodes were run to obtain the peak current for each compound with different concentrations. The scan rate was fixed at 100 mV/s.

Nanoelectrode Fabrication Method. Pt nanoelectrodes were fabricated according to a previously reported method with some modifications.[22] A 1.5 cm long Pt wire was attached to a tungsten rod using Ag conductive epoxy. The end of the Pt wire was electrochemically etched to make a sharp point in 15 wt % $CaCl_2$ solution. With use of a function generator, 110 Hz sinusoidal wave with an amplitude of 4.3 V was applied to the Pt wire for 60 s. Sharpened wire was washed with deionized water and was then inserted into a glass capillary and thermally sealed using a H_2−O_2 flame. The sealing was inspected against possible gas bubbles using an optical microscope during the sealing process. Then the sealed tip was polished successively using silicon carbide polishing sandpapers (Buehler with grid size 600 and 1200) until a Pt nanodisk was exposed, which was monitored by an electronic feedback circuit. The radii of nanodisk electrodes, r, were determined by the diffusion-limited current for proton reduction (i_{lim}) in 0.10 M $HClO_4$ solution containing 0.10 M $NaClO_4$. The migration effects are suppressed by adding 0.10 M $NaClO_4$ as the supporting electrolyte. The radii were calculated using the following equation: $i_{lim} = 4nFDCr$, where D is the diffusion coefficient of H^+ and C is the concentration of $HClO_4$, respectively. A literature value of $D = 7.8 \times 10^{-5}$ cm^2/s was used.[23] The radii estimated using this method are within 10% difference from the ones determined from the conventional ferrocene oxidation method.

Preconcentration Method. Sample preconcentration was carried out using solid-phase extraction following U.S. EPA Method 537.[4] Briefly, the solid-phase extraction cartridge cleanup and conditioning was done with 15 mL of methanol followed by 18 mL of DI water. One liter of sample was passed through the cartridge at an approximate rate of 10−15 mL/min with the help of a vacuum manifold. Then the analyte was eluted from the cartridge with 15 mL of methanol. The eluate was collected and completely dried under a gentle stream of N_2 in a heated water bath (60−65 °C). Finally, 1.0 mL of 1.0 M $HClO_4$/0.10 M $NaClO_4$ solution was added to solvate the dried sample for electrochemical bubble-nucleation experiments.

RESULTS AND DISCUSSION

To electrochemically probe the bubble-nucleation condition, we adopted a nanoelectrode-based approach developed by Luo and White.[24] In this approach, a sub-50-nm Pt nanoelectrode is used to perform hydrogen evolution reaction (HER) in acid solutions. As the nanoelectrode potential is scanned negatively, the HER current increases exponentially until it reaches a peak value (i_{peak}). Past i_{peak}, the HER current immediately drops to a minimal value, which corresponds to the nucleation and formation of a gas bubble at the nanoelectrode, blocking the electrode surface.[24−26] The supersaturation level of dissolved H_2 gas required for H_2 bubble nucleation is proportional to the i_{peak} value.[24]

We chose perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) as the model analytes because they have been found at the highest frequency and concentration in the environment and humans among all PS. The PS pattern in global river waters reveals that PFOS and PFOA account for ∼60% of the total mass concentration of PS.[27−33] This percentage is up to >80% in biological samples such as human milk and serum because of the bioaccumulation of PFOA and PFOS.[34] Figure 1a shows the cyclic voltammograms of an 11 nm radius Pt nanoelectrode in PFOS-containing $HClO_4$ solutions. All voltammograms at various concentrations of PFOS (C_{PFOS}) exhibited a cathodic peak at ca. −0.3 V, corresponding to the H_2 bubble nucleation and formation at the nanoelectrode surface. The C_{PFOS} was varied from 10^{-4} to 10^{-1} g/L. As C_{PFOS} increases, i_{peak} decreases. When i_{peak} is plotted against log(C_{PFOS}), there is a good linear relationship between them ($R^2 = 0.92$) with a slope of −0.82 nA/dec (Figure 1b). The LOD based on 3 times the standard deviation of the blank (i.e., in the absence of PFOS) is calculated to be 80 μg/L. The reduced i_{peak} in response to the increasing PFOS concentration is consistent with the detection mechanism that PFOS stabilizes bubble nuclei and, therefore, lowers the supersaturation requirement for bubble nucleation.

The same linear response has also been observed for PFOA, the other dominant PS contaminant, and the carboxylic acid

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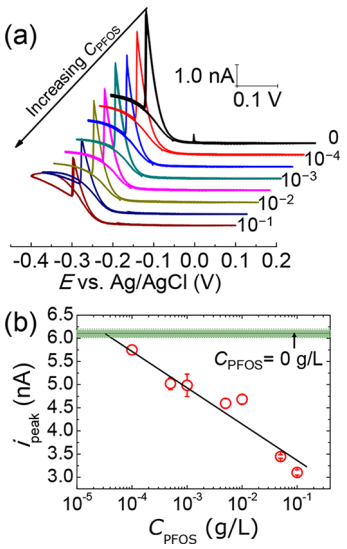

Figure 1. (a) Cyclic voltammograms for an 11 nm radius Pt nanoelectrode in 1.0 M $HClO_4$ containing 0.1 M $NaClO_4$ and various PFOS concentrations (g/L): 0, 10^{-4}, 5×10^{-4}, 10^{-3}, 5×10^{-3}, 10^{-2}, 5×10^{-2}, and 10^{-1}. Scan rate = 100 mV/s. (b) Plot of i_{peak} vs C_{PFOS}. Error bars are the standard deviations at each C_{PFOS} from at least three measurements. The best fit of the data points is plotted with $R^2 = 0.92$, which has a slope of −0.82 nA/dec. The horizontal black line shows the mean value of i_{peak} in the absence of PFOS and the corresponding standard deviation is highlighted in green. The LOD based on 3 times the standard deviation of the blank is calculated to be 80 μg/L.

counterpart of PFOS, in the same concentration range (Figure S1, Supporting Information). The obtained LOD for PFOA is 30 μg/L, which is slightly better than that for PFOS. It should be caused by the higher surface activity of PFOA than PFOS (their corresponding surface tension minima in water are 15.2 and 34.5 dyn/cm, respectively).[35] The LODs of our detection method for PFOA and PFOS are ~2 orders of magnitude better than those of suppressed conductivity detection (~2 mg/L)[36] and slightly worse than those of tandem mass spectrometry detection (~0.5 μg/L),[4] the two most common detection methods for surfactant analysis used in high-performance liquid chromatography.

We further tested PS compounds with different fluoroalkyl chain lengths using our method. Figure 2 shows the plot of the

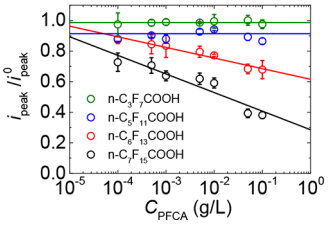

Figure 2. Plots of the normalized peak current (i_{peak}/i^0_{peak}) vs the concentration of perfluorinated carboxylic acids (C_{PFCA}) with different alkyl chain lengths. i^0_{peak} is the peak current at $C_{PFCA} = 0$.

peak current against the concentration of perfluorinated carboxylic acids (PFCA) with fluoroalkyl chain length, n = 3, 5, 6, and 7. The peak currents are normalized with respect to the peak current in the absence of PFCA to account for the nanoelectrode size effect as larger electrodes require larger currents to nucleate a bubble.[23,26,37] The corresponding unnormalized data are provided in Figure S2. As n decreases from 7 to 3, the slope is reduced from −0.12 dec^{-1} at n = 7 to −0.07 dec^{-1} at n = 6 and becomes close to 0 when n = 5 and 3. The trend of sensitivity change is consistent with the order of surface activity: n-C_7F_{15}COOH > n-C_6F_{13}COOH > n-C_5F_{11}COOH > n-C_3F_7COOH (Figure S3), further confirming our mechanism in Scheme 1. A similar trend has also been observed for perfluoroalkyl sulfonate compounds (Figure S4).

To quantitatively understand the detector response, we derived the expression of i_{peak} as a function of C_{PFOS}. According to CNT, the formation free energy of a gas bubble in solution, ΔG_{bubble}, is the sum of the energy cost of creating a new gas/liquid interface and the energy gain through the liberation of dissolved gas into the bubble volume, as expressed by eq 1.[38]

$$\Delta G_{bubble} = 4\pi\gamma r_{bubble}^{\ 2} + \frac{4\pi}{3}\Delta G_V r_{bubble}^{\ 3} \quad (1)$$

where γ is the surface tension of the gas/liquid interface and ΔG_V is the energy difference between the dissolved and gaseous state of the molecule in that volume. ΔG_{bubble} initially increases as a function of r_{bubble} before reaching a peak value, $E_{nuc} = \frac{16\pi\gamma^3}{3(\Delta G_V)^2}$, which is the nucleation energy barrier depicted in Scheme 1. Bubbles that overcome this energy barrier are energetically favored to continue to grow; otherwise, they are inclined to shrink and return to the dissolved form. Because bubbles of the critical size necessarily arise from the growth of subcritical nuclei, their formation relies upon relatively improbable fluctuations along the free energy barrier. The rate of critical nuclei formation or nucleation rate, J, is thus governed by the Arrhenius equation:

$$J = Z\exp\left(-\frac{E_{nuc}}{kT}\right) = Z\exp\left(-\frac{16\pi\gamma^3}{3\Delta G_V^{\ 2}kT}\right) \quad (2)$$

In the experiment, we scanned the potential of a nanoelectrode negatively at a constant scan rate (that is, a fixed duration time at each potential) to nucleate a H_2 gas bubble, and then we recorded the i_{peak}. Because the time required to nucleate a bubble defines the nucleation rate (J), when the duration time is fixed, we are setting a threshold value for J and seeking for the minimum current to reach this value. Hence, eq 2 can be rearranged and simplified to be

$$\Delta G_{V,nuc} = A\gamma^{3/2} \quad (3)$$

where A is a constant $\left(=\left(\frac{16\pi}{3kT\ln(Z/J)}\right)^{1/2}\right)$ and $\Delta G_{V,nuc}$ is the volume energy difference of the gas molecules when a bubble nucleates.

On the left side of eq 3, $\Delta G_{V,nuc}$ can be expressed as a function of i_{peak}.[39,40]

$$\Delta G_{V,nuc} = \frac{i_{peak}}{K_H 4nFD_{H_2}r} - P_{ambient} \quad (4)$$

where K_H is Henry's law constant for H_2 gas, D_{H_2} is the diffusion coefficient of H_2, n is the number of electrons transferred per H_2 (=2), F is Faraday's constant, r is the nanoelectrode radius, and $P_{ambient}$ is the ambient pressure.

On the right side of eq 3, γ is a nonlinear function of C_{PFOS} governed by the Gibbs equation.[41] We measured γ of the PFOS-containing solutions by the pendant drop method (Figure S5). The plot of γ versus $\log(C_{PFOS})$ in Figure 3a reveals an excellent linear relationship at the concentration range from 10^{-4} to 10 g/

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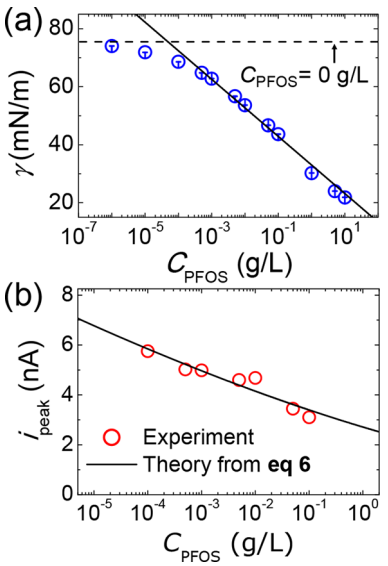

Figure 3. (a) Surface tension of PFOS-containing $HClO_4$ solutions measured by the pendant drop method. The best fit of the data points for $C_{PFOS} = 10^{-4}$ to 10 g/L is represented by the solid black line with $R^2 = 0.99$ and a slope of −9.8 mN/m·dec. (b) Comparison of experimental data and theoretical fit in the form of eq 6.

L. Outside this range, the data starts deviating from the linearity. Accordingly, γ can be numerically expressed by

$$\gamma = a \log(C_{PFOS}) + b \quad (5)$$

with $a = -9.8$ and $b = 33$ for $C_{PFOS} = 10^{-4}$ to 10 g/L. The linear function intercepts with the γ value of the blank ($C_{PFOS} = 0$) at $C_{PFOS} = \sim 50$ μg/L, which is consistent with the experimental LOD of ~80 μg/L for PFOS. Substituting eq 4 and eq 5 into eq 3, we obtain the following expression of i_{peak}.

$$i_{peak} = K_H 4nFD_{H_2} r[A(a \log(C_{PFOS}) + b)^{3/2} + P_{ambient}] \quad (6)$$

The experimental data agree very well with the theoretical fit in the form of eq 6 (Figure 3b), which again confirms our proposed bubble-nucleation-based detection mechanism. From the above derivation, we can conclude the nearly linear relationship between i_{peak} and $\log(C_{PFOS})$ originates from the linear dependence of the γ on $\log(C_{PFOS})$. Therefore, the sensitivity of this detection method is determined by the surface activity of analytes. Additionally, eq 6 also predicts that the electrode size (r) and properties of electrogenerated gas (D_{H_2}, K_H, and n) will contribute to the sensitivity of this method.

The native LOD of our detection method is around 30 and 80 μg/L for PFOA and PFOS, which are limited by the surface activity of these two compounds. These values are ~3 orders of magnitude higher than the desired LOD: 70 ng/L, which is the health advisory for PFOS and PFOA in drinking water established by the U.S. EPA.[6] This challenge can be overcome by adding a preconcentration step using solid-phase extraction which is currently used in the standard U.S. EPA method for PS analysis.[4] Figure 4 shows the LOD for PFOS was improved to ~40 ng/L after a 1000-fold preconcentration step using solid-phase extraction. The corresponding CVs are provided in Figure S6.

We further tested the specificity of this method for detecting surfactant analytes by adding an excess of nonsurfactant interference, poly(ethylene glycol) (PEG, 400 g/mol), which has a similar molecular weight as PFOS. Figure 5a shows the cyclic voltammograms of a Pt nanoelectrode in the presence of 1 mg/L PFOS and a 10-, 100-, and 1000-fold excess of PEG. The addition of PEG leads to a negative shift of the HER onset potential as compared to the PFOS-only sample, but the i_{peak} does not show any notable difference (Figure 5b). Apart from that, we have also tested different concentrations of humic acid and lysozyme. We observed no trend in the peak current compared to that of the blank (Figure S7). These results show the exceptional specificity of our method for surfactant analytes. However, we would like to point out that we did not observe the peak current change for a neutral surfactant, Tween-20 (Figure S7). The reason for this unusual behavior is currently under investigation.

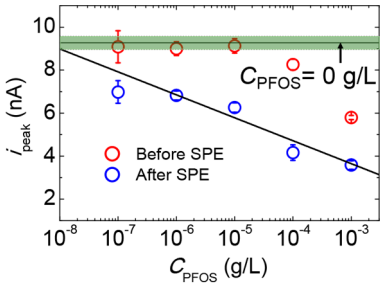

Figure 4. Plot of i_{peak} vs C_{PFOS} for PFOS samples before and after preconcentration using solid-phase extraction (SPE). The data after SPE is linearly fitted with $R^2 = 0.92$ and a slope of −1.1 nA/dec. The horizontal black line shows the mean value of i_{peak} in the absence of PFOS. The corresponding standard deviation is highlighted in green. The LOD based on 3 times the standard deviation of the blank is calculated to be 40 ng/L.

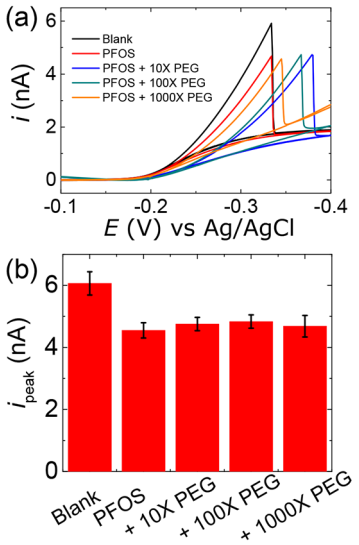

Figure 5. (a) Cyclic voltammograms and (b) the corresponding average i_{peak} for a 7 nm radius Pt nanoelectrode in 1.0 M $HClO_4$ containing 0.1 M $NaClO_4$, 1.0 mg/L PFOS, and a 10- to 1000-fold excess of poly(ethylene glycol) (PEG, 400 g/mol). Scan rate = 100 mV/s.

CONCLUSIONS

In conclusion, we have presented a bubble-nucleation-based electrochemical detection method for surfactant analysis for the

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first time. This method has a high specificity for surfactant analytes, a broad linear dynamic range of over 3 orders of magnitude, and a remarkable LOD of ~30 μg/L (~2 orders of magnitude better than suppressed conductivity detection, a conventional detection method for surfactant analysis). With a preconcentration step, we have demonstrated the improvement of the LOD for PFOS to the target LOD. We have also established the theory for this new method. This method has the potential to be developed into a universal electrochemical detector for surfactant analysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.9b01060.

Plot of i_{peak} vs C_{PFOA}; plots of i_{peak} vs PS concentrations of different perfluoroalkylcarboxylic acids; photographs showing pendant drop shapes with different alkyl chain lengths; plots of i_{peak} vs PS concentrations of different perfluoroalkyl sulfonates; photographs showing pendant drop shapes with different PFOS concentrations; cyclic voltammograms of nanoelectrodes for PFOS samples with and without SPE preconcentration; plots of the normalized peak current (i_{peak}/i^0_{peak}) vs the concentration of humic acid, lysozyme, and Tween-20 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: long.luo@wayne.edu.

ORCID

Long Luo: 0000-0001-5771-6892

Notes

The authors declare no competing financial interest.

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PERSISTENT POLLUTANTS

New electrochemical method detects PFOS and PFOA

Bubble nucleation is the basis for rapid and cost-effective analysis

by ***Emma Hiolski, special to C&EN***

MAY 13, 2019

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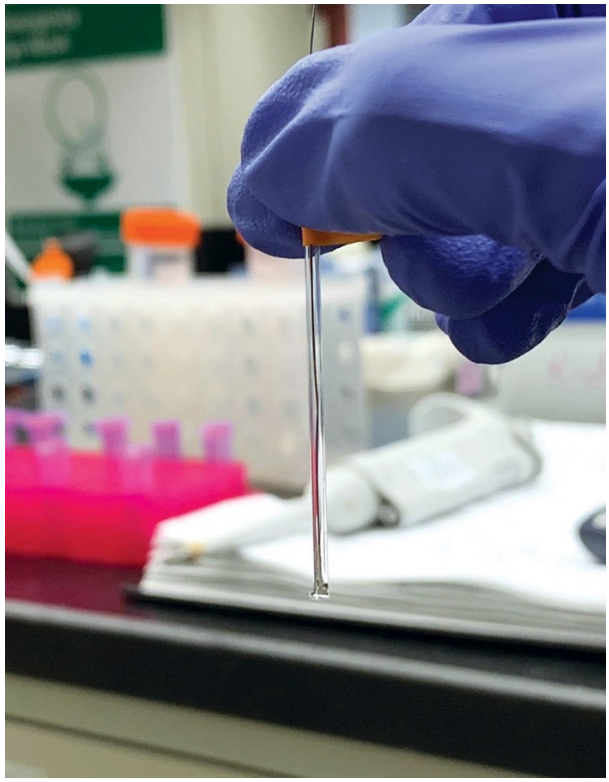
Bubbles and tiny electrodes may hold the key to faster, more cost-effective detection of perfluorinated surfactants that can contaminate drinking water. Researchers have developed an electrochemistry-based method to detect surfactants, specifically perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), with high sensitivity and specificity (*Anal. Chem.* 2019, DOI: **10.1021/acs.analchem.9b01060**).



Credit: Courtesy of Long Luo

Nanoelectrodes (<100 nm diameter) are used to detect and quantify perfluorinated surfactants in solution through bubble nucleation at the electrode surface.

Perfluorinated surfactants are highly stable due to perfluoroalkyl moieties, and are common in products like nonstick coatings and fire-fighting foam. Chronic exposure to two such perfluoroalkyl substances, PFOS and PFOA, has been linked to health issues in humans. Though these **two chemicals are no longer used in industry**, they persist in the environment and can contaminate drinking water.

Long Luo, an analytical chemist at Wayne State University, began his search for a novel way to detect these harmful chemicals after one such **PFOS/PFOA contamination event in a Michigan town** during the summer of 2018. The most commonly used detection method uses high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS), which requires complex instrumentation and can cost up to $300 per sample, Luo says. Hoping to develop a simpler, less expensive method, the team turned to electrochemistry.

Their method is based on a phenomenon known as electrochemical bubble nucleation. Applying electric potential to an electrode in an aqueous solution splits water into hydrogen gas and oxygen. Ramping up the current increases gas concentration near the electrode until a bubble forms, blocking the electrode surface and causing the current to drop. Surfactants reduce surface tension and make it easier for such bubbles to form, meaning the amount of current required to form those bubbles is inversely related to surfactant concentration.

To test their method, Luo and his collaborators fabricated tiny platinum electrodes less than 100 nm in diameter (smaller electrodes are more sensitive). The team could detect PFOS and PFOA concentrations as low as 80 µg/L and 30 µg/L, respectively. Preconcentrating samples using solid-phase extraction moved the limit of detection below 70 ng/L—the health advisory level for drinking water **set by the U.S. Environmental Protection Agency**. The method also remained sensitive and selective for surfactant detection even in the presence of a 1,000-fold greater concentration of poly(ethylene glycol), a nonsurfactant molecule with a molecular weight similar to that of PFOS.

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