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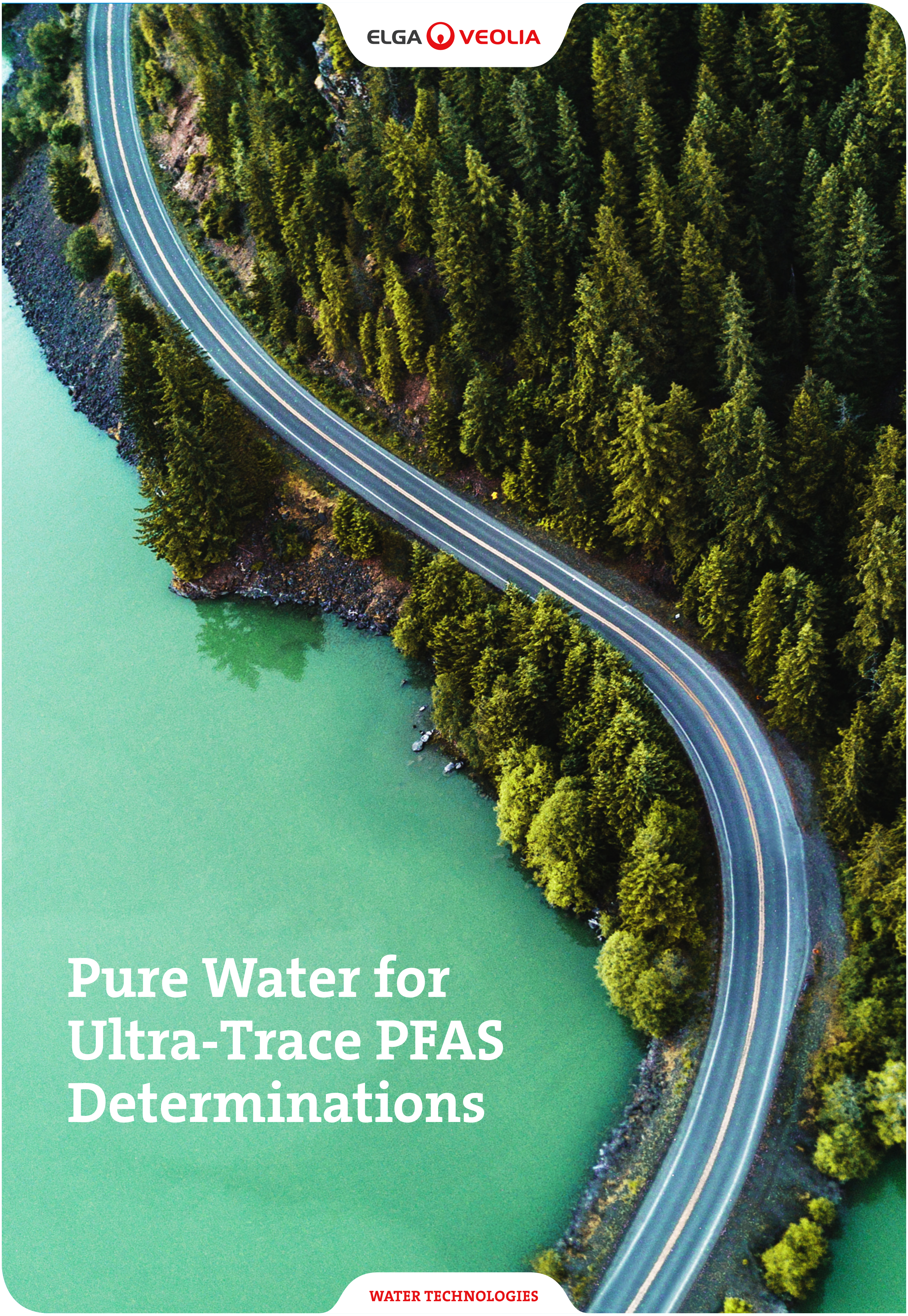


Pure Water for Ultra-Trace PFAS Determinations

WATER TECHNOLOGIES

Abstract

Increased awareness of the hazards associated with PFAS has led to an increased requirement for the analytical determination of PFAS at lower and lower levels. The usual approach for the analysis of individual PFAS is to use LC MS/MS or LC/HRMS; this requires large volumes of ultrapure water in many aspects of sample preparation and analysis, and any contamination within the water may easily affect the quality of data produced; this is particularly true of the ultra-trace environmental analysis of ubiquitous contaminants such as PFAS where a low background is critical, and the analytes sought may also be widely found in the components and reagents used. With the widespread occurrence of PFAS in drinking waters it is key to ensure ultrapure water generators utilise technologies that will efficiently remove them. The sensitivity possible with suitably purified water is illustrated with the measurement of sub-ng/l levels of perfluoro-octanoic acid (PFOA), perfluoro-octanesulphonic acid (PFOS) and Perfluorohexane sulfonate (PFHxS).

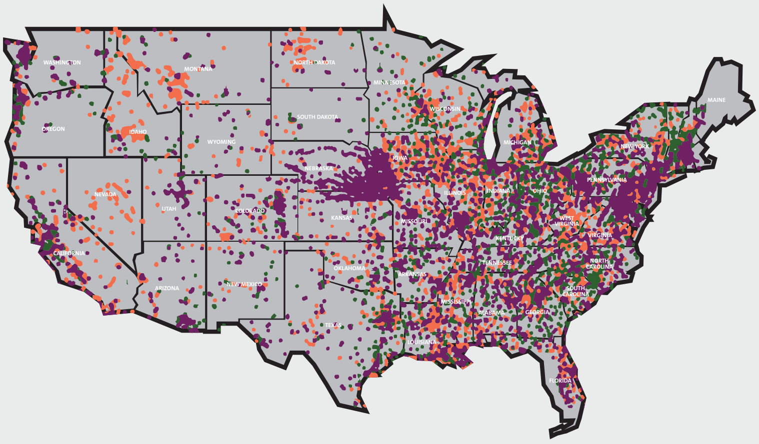
An introduction to PFAS

PFAS are the chemicals of the moment. They are the chemical arch-enemy No 1 and have moved from a useful aid to modern life to becoming a popular curse. (We are told in popular media that they are 'forever-chemicals', ubiquitously contaminating our world, and that defining and tackling the issue is ongoing for leading environmental agencies.)[1]

In reality, per- and polyfluorinated alkyl substances (PFAS) are man-made chemicals that have been widely used since the 1940s. They repel water and oils and have been incorporated in a great variety of consumer products, such as nonstick cookware, food containers, stain and water repellent fabrics and cleaning products. Other significant sources of PFAS environmental contamination are aqueous firefighting foams and industrial production facilities. PFAS are now a ubiquitous environmental pollutant, widely distributed across the globe through water and air movement and within plants and animals; they can be found in our drinking water and food.

Their tendency for Bioconcentration/Bioaccumulation, often results in significantly raised concentrations in living things relative to the local environment. Most people in the United States have PFAS in their blood[2]. A total of 9,252 PFAS (chemicals with at least a perfluorinated methyl group (–CF3) or a perfluorinated methylene group (–CF2–)) are listed in the EPA's most recent list of PFAS substances but only a handful of these, such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), which have the longest history of widespread use, have been widely monitored in the environment or have been thoroughly studied for their toxicological effects. Little is known regarding the safety of most PFAS, however some of those studied are proven to be hazardous; bio-accumulative, and suspected of harmful effects such as endocrine-disruptors and reprotoxic. The widespread contamination by PFAS is illustrated by Figure 1 which shows some of the potential sources of PFAS in the environment across the USA.

Map of USA - Potential Sources of PFAS Contamination[3]



The chemical bond between carbon (C) and fluorine (F) is extremely strong, and often labelled the strongest bond in organic chemistry. Increasing the number of fluorine atoms bonded to a carbon further increases the strength of these bonds. As a result PFAS chemicals are very stable; they can exist unchanged for an extremely long time and in some situations can take 1000s of years to degrade. The persistence of the PFAS chemicals mean that they can continue to exist long after their intended use is complete.[4]

The increasing concern over the environmental damage caused by PFAS has led to increased restrictions on their use. At the beginning of February 2023 ECHA published a proposal, which if adopted, would ban PFAS chemicals within the EU under REACH; it is possible that this could be implemented during 2025, and it is likely that other such organisations will also 'follow suit', subsequently.[5]

PFAS testing and major methodologies

The requirement to determine PFAS at lower and lower levels will inevitably increase substantially in the coming years, along with upcoming restrictions and regulations. Monitoring of food, the environmental and personal exposure will mean their determination within a vast array of matrices and the tendency for bioaccumulation ensures that extremely low detection limits will be critical. The US EPA proposes to introduce a legally-enforceable, national drinking-water standard for six PFAS. Under this PFOA and PFOS would each be limited to <4ng/L, and also limits for any mixture containing PFNA, PFHxS, PFBS, and GenX Chemicals, would be set.[6] Finalised rules regarding PFAS are expected during 2023. Contaminant-free reagents and analytical-equipment will be needed in order to achieve these extremely low detection limits.

A battery of highly sensitive methodologies have been developed to measure PFAS at ultra-trace levels. GC-MS, LC-HRMS and, increasingly, LC-MS/MS are the analytical technologies of choice for individual compounds. The chromatographic separation of PFAS compounds in currently validated methods typically involves a reverse phase mechanism using a C18 or Phenyl column in an acidic-methanol eluent. Due to the vast number of PFAS, screening methods will also be required, such as measuring the total organic fluorine present by techniques such as ion chromatography after adsorption and combustion. In most environmental samples preconcentration will be needed. Solid phase extraction (SPE) using adsorption on carbon or weak anion exchange (WAX) media are the most widely used techniques.

The table summarises the major "official" methodologies established.

Method	**EPA 537 & 537.1**	**EPA 533**	**EPA 8327**	**EPA 1633**	**EPA 1621 (draft)**	**AST D8421-22**	**AST D7968-19**	**ASTM D7979-19**
Sample Type	Drinking Water	Drinking Water	Ground/ Surface/ Wastewater	Aqueous, soil, biosolids, sediment, tissue	Aqueous	Municipal & industrial wastewater, leachate	Soil, sediment, sludge	Non-potable water
Sample Preperation	Solid Phase Extraction (polymetric sorbent)	Solid Phase Extraction (anionic sorbent)	Co-solvation + direct injection	Solid Phase Extraction (anionic sorbent) or solvent extraction + clean-up	Adsorption	Co-solvation + direct injection	Solid Phase Extraction + direct injection	Direct injection
Quantitation	Internal standard	Isotopic dilution	External calibration	Isotopic dilution	External calibration	External calibration	External calibration	Isotopic dilution
Measurement	LC-MS/MS	LC-MS/MS	LC-MS/MS	LC-MS/MS	Combustion IC	LC-MS/MS	LC-MS/MS	LC-MS/MS
Number of PFAS Measured	EPA 537 - 14 EPA 537.1 - 18	25	24	40	Total	44	21	21

When conducting analysis at trace levels it is critical that the equipment and reagents used do not contain the analyte to be determined or contribute to interference. Ultrapure water is a key reagent in PFAS analysis; It is used in the pre-treatment stages and as a mobile phase in LC, where, much more water can pass through the system with each analysis than the samples being analysed; it is also used in the preparation of samples, standards and blanks, and in instrument cleaning.

Contamination via any of these routes would degrade data and it is clear that high quality ultra-pure water is essential to achieve the detection limits needed.

Ultrapure water for a perfect PFAS-blank

Ultrapure water used for PFAS analysis is generated by purification of potable municipal water; This can contain PFAS at concentrations much higher than that which is required for testing levels as conventional treatments to generate potable water have limited effect on PFAS levels. For example, guidelines from UK Drinking Water Inspectorate (DWI) effectively allow PFOS and PFOA levels of up to 100 ppt (ng/l) without requiring remedial action; instances of measurements within ‘tier 2’ (10-100 ppt) continue to be reported. [7]UK Environment Agency (2021). It is, therefore, critical that the ultrapure water generation process can remove contamination before it is suitable for use in PFAS analysis.

Measurements of TOC (Total Organic Carbon) are typically used to indicate the level of organic compounds within ultrapure water, however, this is not suitable for ultra-trace PFAS monitoring as it is not sensitive enough (practical detection limits around 1 - 0.1 µg/l C), which is exacerbated by the high proportion, by mass, of fluorine within the compounds; For example PFOA (C8HF15O2) is only 23% Carbon and so a TOC limit of detection of 0.5µg/l actually equates to 2.2µg/l of PFOA. Considered process design for water purification equipment is essential for consistent performance regarding PFAS rejection.

Purification technologies for PFAS treatment

To achieve the very low levels of PFAS contaminants required the use of a multiple technology approach is essential, combining, as it does, the benefits of different purification technologies and the protection and recirculation of the water produced to maintain purity. The main relevant technologies are summarised below.

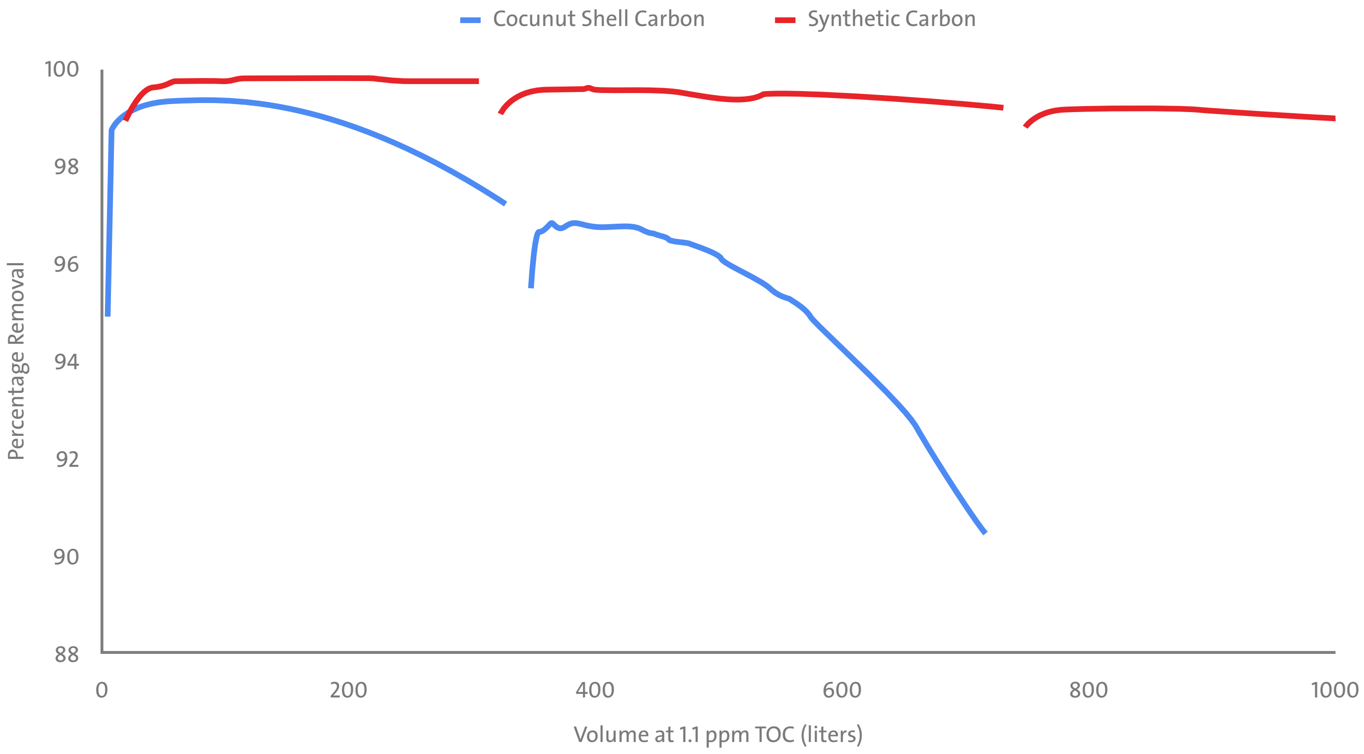
Technology	Mechanism	Species Treated
Activated Carbon (AC)	Adsorption onto surface	All types
Reverse Osmosis (RO)	Membrane filtration	>99% with molecular weight >100 Dalton
Ion Exchange (IE)	Replacement with hydroxide and hydrogen ions	Ionic and polar species
UV radiation (UV)	Photo-oxidation	All types

Reverse osmosis (RO) provides the most effective means to remove the great majority of the organic compounds present in solution or in colloidal form, including all types of PFAS. A proportion of very low molecular weight species may pass through the RO membrane but can be subsequently eliminated by adsorption onto activated carbon(AC), or ion-exchange (IE) resin following UV photo-oxidation.

UV light at short wavelengths, such as that at a wavelength at 185nm, is sufficiently energetic to cleave bonds in organic compounds (including the very strong C-F bonds in PFAS), splitting larger molecules into smaller, often more polar, compounds.

The acids and carbon dioxide produced are removed on ion exchange resin. Effective photo-oxidation depends on optimising system efficiency through choice of lamp, reactor design and water flow-path.

Careful choice and thorough testing of components are essential for optimum performance. For example, a methyl ethyl ketone challenge of two different types of activated carbon is shown below. It enables differences in effectiveness and capacity to be assessed and, in this example, confirms the advantages of a synthetic carbon adsorbent over the widely used coconut carbon.



Example determination: Detection of Perfluoro-octanoic acid and Perfluoro-octanesulphonic acid in Ultrapure Water

Perfluoro-octanoic acid (PFOA) and perfluoro-octanesulphonic acid (PFOS) are found in the environment as a result of their widespread use in domestic and industrial products. Detection at ng/l concentrations is possible by LC-MS/MS but is dependent on using water which is sufficiently pure. Shimada, Kawaguchi, Iwamori and Kuroki have measured the PFOS and PFOA content of some samples of ultra-pure water.[8]

Ultra-pure water (PURELAB Ultra Analytic, ELGA LabWater) was used. This water had been purified initially by reverse osmosis and then by repeat recirculation within the water purification system through activated carbon, ion-exchange and 185nm ultraviolet photo-oxidation. The water was tested immediately after dispense to minimise environmental exposure.

Analytical Methodology

A 1 litre sample of the water was concentrated by solid-phase extraction (Presep-Agri, Wako Junyaku Co.). After elution with 10 ml of methanol, this was concentrated to 1 ml under a current of nitrogen to provide a sample for measurement.

Analytical Conditions

Apparatus	HPLC: Agilent 1100 MS: 3200QTRAP LC/MS/MS system
Column	TSKgel ODS-100V, 2.0 x 50 mm, 3 µm
Mobile Phases	A = 5mM Ammonium acetate, B = Acetonitrile

Gradient

	0 min.	3 min.	8 min.	8.1 min.	14 min.
A	90%	10%	10%	90%	90%
B	10%	90%	90%	10%	10%

Flow Rate	200 µl/min. Amount injected: 5 µl
Drier Temperature	400°C, Ionization Voltage: 4500 V, Ionization Method: ESI-Negative

Calibration

Standard solutions containing 0.1, 1 and 10 µg/l PFOS and PFOA were produced by diluting 10 µg/ml standards in acetonitrile (Wako Junyaku Co.) and analysed by this procedure. The calibration graphs are linear over this range and in both cases the 0.1 ng /l peak showed S/N >3. The best fit lines gave equations of 8599.3x + 438.9 and 7750.6x + 579.4 respectively.

Samples of water and a 1ng/l PFOS and PFOA standard were analysed. As set out in Table 1, recoveries for the standards were just over 100% and the water from the PURELAB Ultra showed the presence of less than 0.1 ng/l of both PFOS and PFOA.

	PFOS (ng/L)	PFOA (ng/L)
Water from PURELAB Ultra	<0.1	<0.1
Standard 1.0 ng/L solution	1.1	1.4

Example determination: Detection of Perfluoro-octanoic acid, Perfluoro-octanesulphonic acid and Perfluorohexane sulfonate in Ultrapure Water from a Chorus 1 Analytical Research.

The Environmental Analysis Division of AQUA PULSE CO.LTD, Japan has achieved extremely low detection limits of 0.02 ng/litre, in their analysis of PFOS PFOA and PFHxS. Water from the Chorus 1 Analytical Research used for these determinations, was concentrated 1000 fold, and gave results at less than the detection limit.

Yuko Iio, a researcher for Aqua Pulse, used a SCIEX Triple Quad™ 3500 LC-MS/MS System, in this study.[9]

Determinant	Concentration (ng/L): Chorus 1 Analytical Research Water
PFOS	<0.02
PFOA	<0.02
PFHxS	<0.02

Conclusion

Increased Regulation and associated trace determination of PFAS compounds is inevitable. Extremely pure water from a water purification system designed to remove PFAS is critical to allow reliable determination at the ultra-trace levels required for these environmental pollutants. The purity required can be achieved using a well-designed water purifier, containing carefully selected technologies, such as (RO, AC, UV and IE) and rigorously tested components.

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