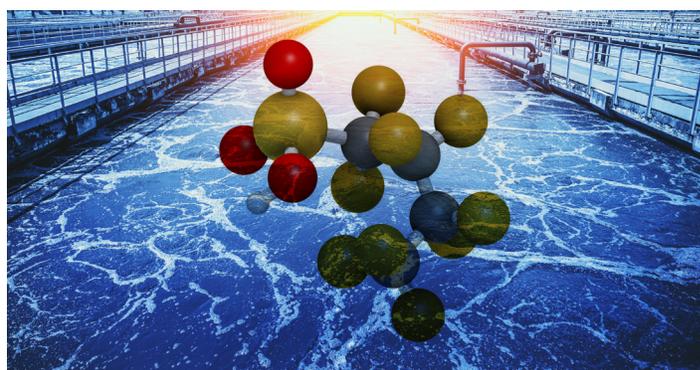


Detecting the elusive forever chemicals using combustion ion chromatography

Per- and polyfluorinated alkyl substances (PFAS) and their precursors are used in many human-made products, including non-stick cookware, food containers, polishes, and waxes. Their resistance to water, oil, and heat also makes them useful for many industrial processes and in firefighting foams, the byproducts of which can easily enter waterways. Although useful, PFAS are harmful environmental pollutants; the most widely researched PFAS chemicals, PFOA, and PFOS, have been linked with immunological problems, cancer, and developmental issues in animal studies, and there is evidence that they can lead to adverse health outcomes in humans.¹⁻³ PFAS bioaccumulate and once present in food chains, can be difficult to remove. This persistence and bioaccumulation have dubbed PFAS the ‘forever chemicals.’

Accurate measurement of environmental pollutants is key to detecting pollution and protecting waterways, particularly if they are used as a source for human consumption, but PFAS often elude detection. As the numbers of undetected PFAS and their precursors continue to rise,⁴⁻⁷ it is more important than ever that techniques are developed to screen for the presence of PFAS molecules, especially those that are not detected by targeted approaches.

Currently, the predominant method for the detection of PFAS is solid-phase extraction (SPE), followed by liquid chromatography with tandem mass spectrometry (LC-MS/MS) or gas chromatography with tandem mass spectrometry



(GC-MS/MS). Although powerful detection techniques, they rely on time-consuming, complex processes that can only identify a limited number of PFAS. As the number of untargeted PFAS molecules continue to rise, the tried and tested methods of the past no longer satisfy the needs of the future.

This paper summarizes a recent Thermo Fisher Scientific webinar: [Using combustion ion chromatography \(CIC\) to screen for extractable organic fluorine in PFAS, PFCA, FTOH, and FOSA in water monitoring](#), presented by Carl Fisher and Kirk Chassaniol. The webinar demonstrated that CIC provides an automated, precise method for the determination of adsorbable organic fluorine (AOF) in environmental water samples, making it an attractive complement to targeted methods to obtain a more accurate indication of PFAS contamination.

What is AOX by CIC and how does it work?

Ion chromatography (IC) cannot be used in isolation to analyze non-ionic PFAS. However, through first adsorbing these compounds followed by combustion and gas absorption (Figure 1), levels of adsorbable organic halides (AOX), which include AOF, can be determined using CIC.



Figure 1. A) CIC system including autosampler, combustion furnace, gas absorption unit and ion chromatograph, and B) adsorption module.

AOX by CIC analysis begins with the automated adsorption unit where the halogens present in water samples are retained on granular activated carbon. The inorganic halogens are washed out and the resulting samples are

introduced into a combustion tube where they are oxidized at high temperatures to produce sulfur dioxide, hydrogen halides and elemental halogens. These substances then pass into the gas absorption unit where sulfate and halide ions are absorbed into solution. The ions in this solution are readily detected using the IC system (Figure 2). By following this process of converting organic molecules to detectable ionic forms, organic halogens can be analyzed in the same way as their inorganic counterparts, allowing both groups of compounds to be detected by one IC unit.

Specific parameters ensure accurate detection of forever chemicals

Various parameters, made available by CIC, can be set to ensure effective detection of AOX, even in parts per billion amounts. This means that even previously undetected PFAS and precursors can now be potentially identified and characterized by subsequently screening samples using targeted techniques, providing the potential for a plethora of yet unknown discoveries.

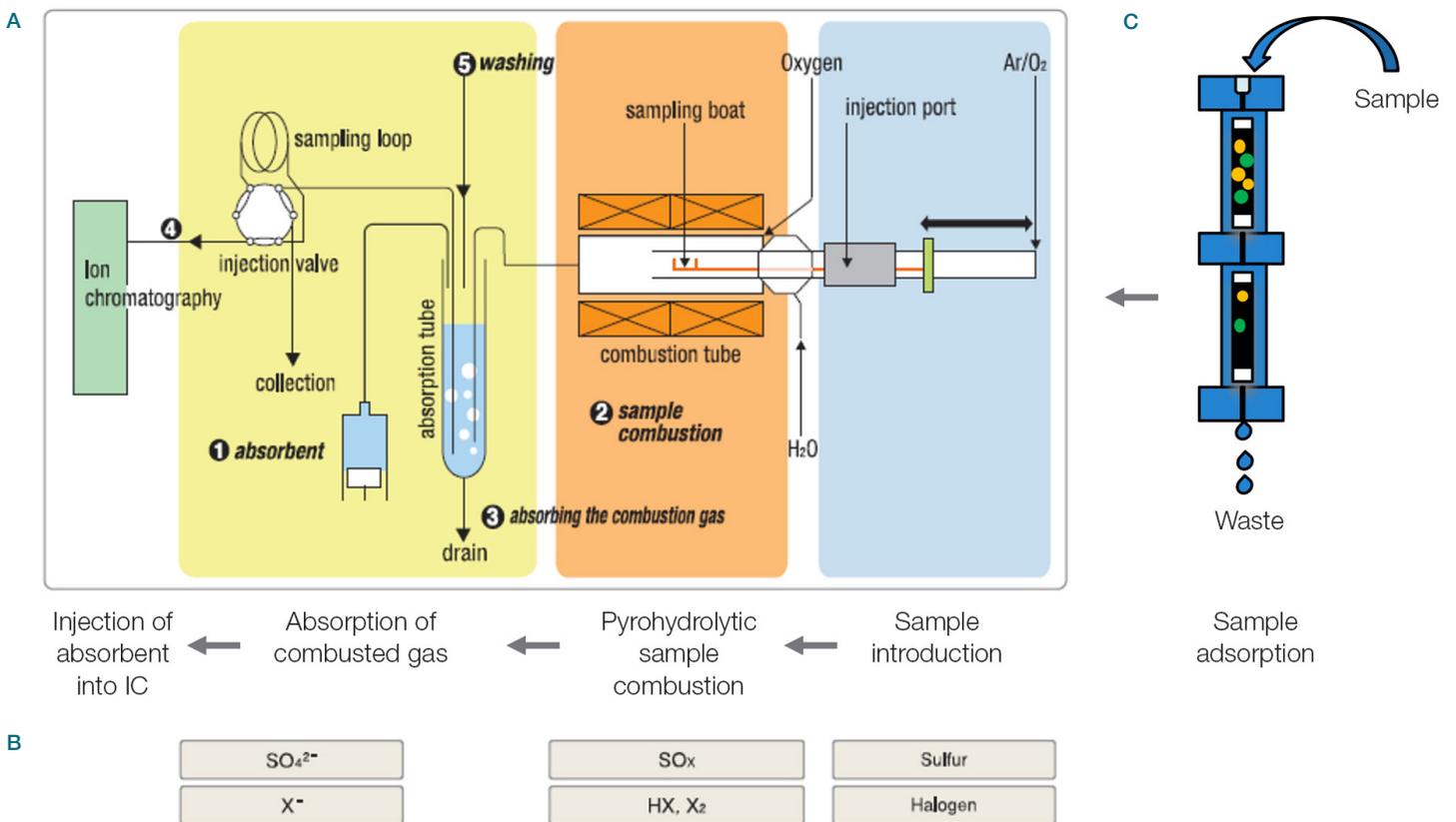


Figure 2. CIC process and resulting compounds. A) CIC process, B) Chemical forms present at each step, and C) Sample adsorption using granular activated carbon.

Accurate detection starts in the combustion chamber. By monitoring oxygen consumption, combustion is optimized, resulting in shorter and more consistent runs compared to results obtained using other technology, such as flame sensors. Moving into the detection stage, sample loops and preconcentration columns can be used to increase the amount of sample on the column and lower the detection limits. This stage is particularly important when working with trace amounts of AOX, as is often the case in water sampling.

The IC stage itself can also be enhanced to deliver more accurate detection, even at very low concentrations. By using a hydroxide eluent, water dips are minimized and, even without preconcentration, this enables larger sample sizes to be analyzed for the detection of trace elements. When automatic eluent generation is employed, it eliminates the need for technicians to handle strong bases and the potential error that can come with manual calculations and mixing.

Automation can then be taken one step further with the use of intelligent software. Overlaps can take place, allowing preparation and combustion stages to run on new samples while another is running through the IC stage. This reduces each sample run time by 10 minutes, a number that soon adds up to large time savings as the number of samples analyzed increases.

Detecting the elusive PFAS with AOF by CIC

Recently, a Thermo Fisher Scientific team ran a series of experiments to demonstrate the ability of CIC to detect AOX in environmental water samples. Using a Thermo Scientific™ Dionex™ Integriion™ HPIC™ system for detection, wastewater and spiked wastewater samples were analyzed using CIC with an isocratic 30 millimolar potassium hydroxide eluent for the chromatographic step. Short run times and excellent recovery of organic halogens, as well as accurate resolution of each of the halogens, were obtained (Figure 3 and Table 1).

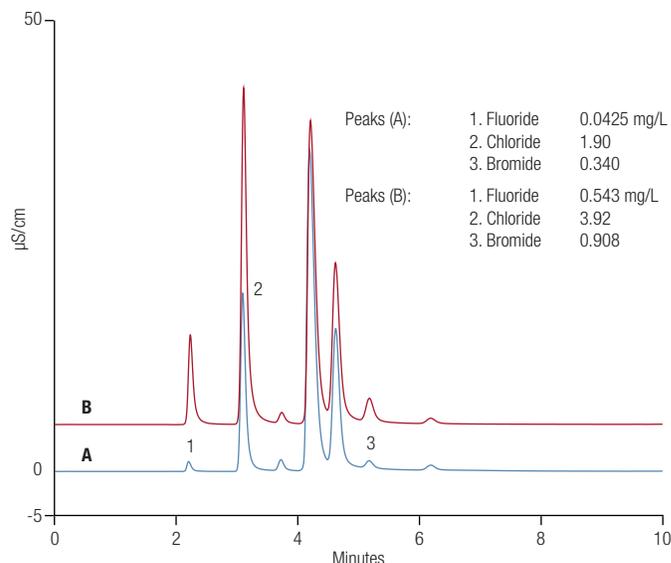


Figure 3. Ion chromatograph showing peaks for each of the halogens in both the wastewater (A) and spiked wastewater (B) samples.

Table 1. Recovery of each halide in the spiked wastewater sample (n=3).

Analyte	Amount spiked (μg/L)	Average (μg/L)	RSD	Recovery (%)
Fluoride	50.0	53.7	4.75	107
	80.1	86.6	1.31	108
	160	173.7	1.33	109
	250	275	4.19	110
Chloride	50.0	43.8	4.70	87.6
	80.0	76.7	2.95	95.9
	160	147.4	1.41	92.1
	320	291	4.54	90.8
Bromide	115	118	5.08	103
	184	198	2.95	108
	367	402.7	2.96	110
	574	656	3.38	114

A similar technique was used to determine AOF in four water sample types. Again, potassium hydroxide was used as the eluent, supplied by an eluent generator cartridge. Surface water, municipal wastewater, industrial wastewater, and groundwater samples were analyzed, with perfluorobutanesulfonic acid (PFBS) and 4-fluorobenzoic acid (4-FBA) added to a final concentration of 10 µg/L to determine the recoveries of representative organic fluorinated compounds in environmental samples.

The wastewater matrix showed recoveries from 85% to 102% for PFBS and 82% and 127% for 4-FBA, confirming the ability of AOF by CIC to determine the presence of PFAS compounds and supporting its use as a prescreening tool to detect compounds that are not included in targeted methods.

Table 2. Recovery data for PFBS and 4-FBA

Surface water		Wastewater		
Sample	PFBS recovery (%)	Sample	PFBS recovery (%)	4-FBA recovery (%)
1	94	1	102	90
2	105	2	91	83
3	99	3	86	82
4	92	4	89	n.d.
5	109	5	93	n.d.
6	98	6	85	83
7	98	7	94	127
8	99			

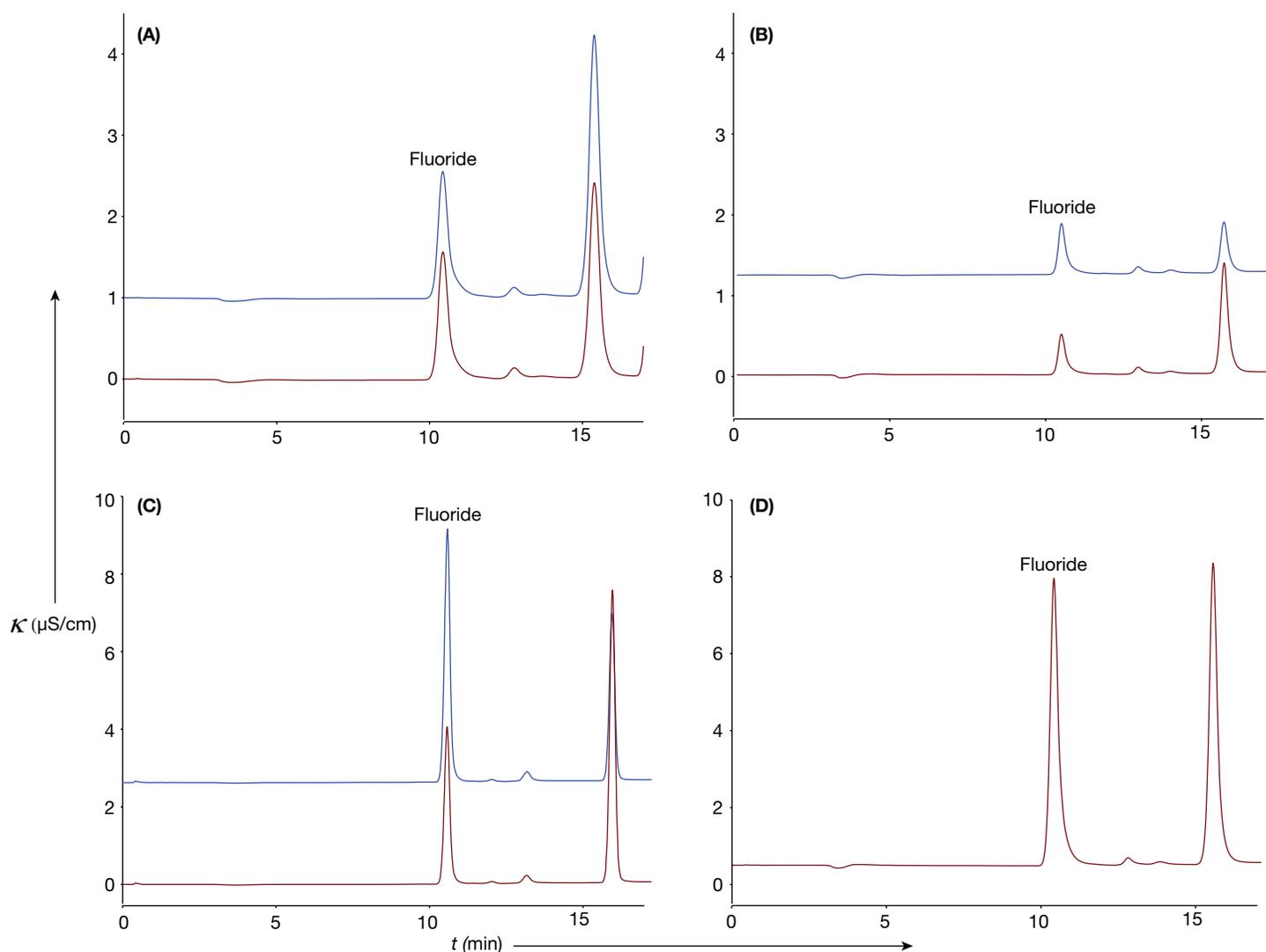


Figure 4. Ion chromatographs obtained after adsorption on activated carbon and combustion of four different water sample types. (A) municipal wastewaters, (B) groundwaters, (C) surface waters, (D) industrial wastewater (diluted 1 to 10).

Precise and accurate determination of AOX and AOF in environmental water analysis

What these results tell us is that CIC can be used as a single technique to determine AOX and AOF in environmental water samples. Importantly, this technique can be used not only for total levels but also to provide determinations for individual halogens.

AOX and AOF by CIC provide a fast, precise, and more accurate alternative to existing standardized techniques, by delivering greater automation and increased speed. These benefits deliver reduced error rates, time savings, and more accurate determinations. Moreover, along with being a replacement technology for combustion sample preparation and analytical titrations, CIC can be used as a complementary technique. Because CIC provides a simpler and more cost-effective method, it is an ideal pre-screening tool to identify suspicious samples which may contain additional PFAS compounds that were not included in the targeted LC-MS/MS method. The suspicious samples can then undergo an unknown screen using high-resolution accurate mass (HRAM) mass spectrometry. CIC helps make this process more cost-effective and saves time because it identifies which samples should be screened using HRAM, avoiding the need to screen all samples.

Although standards organizations globally are focusing their methods on the detection of PFAS compounds with SPE and LC-MS/MS or GS-MS/MS, it is widely known that the majority of PFAS and precursors continue to go undetected with this technique. It is hoped that this work, and others like it, will fuel a deeper and wider consideration of CIC to enable the uncovering of a greater number of previously undetected perfluorinated compounds.

For more detailed information on AOX and AOF by CIC and the results of these studies, watch the [webinar](#) or read the application notes for [AOX by CIC](#) and [AOF by CIC](#).

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