WHITE PAPER

Determining Total Organic Fluorine in Wastewater and Process Water Samples

The new Profiler^F Total Fluorine Analyzer enables the determination of total organic fluorine in wastewater

Until now, analysis of targeted polyfluorinated substances (PFAS) has seemed sufficient to assessing the environmental impact of this large group of man-made, highly fluorinated substances. Consensus is forming among scientists that analysis of total organic fluorine (TOF) provides a better overall picture of PFAS impact and, as a result, an improved approach to this analysis is needed. The new Profiler^F Total Fluorine Analyzer enables the determination of TOF in wastewater and industrial process water samples with simultaneous total fluorine and free fluoride quantification.

Much effort is underway to understand the impact that perfluoroalkyl substances (PFAS) have on the environment. Due to the focus on adverse health effects of specific PFAS compounds, the first analysis methods used to quantify PFAS compounds were highly sensitive techniques such as liquid chromatography with tandem mass spectrometry (LC-MS) or triple-quadrupole mass spectrometry (LC-MS/MS). These targeted methods use sample preparation, isotopic standards and sensitive and selective detection to measure a handful of targeted chemicals and precursors.

Thousands of PFAS compounds have now been identified, and more attention has shifted to non-targeted analysis as it provides a better understanding of the total impact these PFAS compounds have on the environment.

Non-targeted techniques are of particular interest to the regulatory communities in Europe and the United States. While targeted techniques can measure a small subset of compounds with high sensitivity, the full scope of organofluorine compounds that are potentially detrimental to the environment is largely unknown.

Measuring free fluoride (FF) and total organic fluorine (TOF) in the high parts-per-billion (ppb) to parts-per-million (ppm) ranges is crucial for routine monitoring of discharged water near manufacturing sites and to track remediation efforts at contaminated sites. Most surface water and fluorinated drinking water contain FF ranging from 0.5 to 1 ppm in concentration, making it unnecessary to reach such ultra-low levels like those reported by existing targeted analyses.

Early non-targeted methods attempted to homogenize several PFAS compounds and precursors. One example of this approach is the Total Oxidizable Precursors (TOP) Assay. This qualitative or semi-quantitative method involves oxidation of PFAS precursors to perfluorocarboxylic acids (PFCA) that can be measured using commercially available LC-MS and LC-MS/MS methods. Overall TOP assay might not capture a complete picture of total PFAS as the number and type of precursors used is not standardized. Results can be difficult to repeat from laboratory to laboratory.

Other non-targeted methods such as the adsorption of PFAS compounds onto activated charcoal substrates followed by elution with alcohol and the use of sophisticated solid phase extraction methods in tandem with non-targeted detection are under development. An example method includes the measurement of adsorable organically bound halogens (AOX) by combustion ion chromatography (CIC). [1,2] Some laboratories have developed workflows to obtain an overall picture of total PFAS with tentative identification of unknowns by combining non-targeted and targeted techniques.[3] For example, Dubocq et al., utilized a combination of CIC, an ion selective electrode, LC-MS/MS and LC quadrupole time-of-flight mass spectrometry.

APPLICATION OVERVIEW

Traditional ion chromatography (IC) has been used extensively for monitoring FF, reaching low ppb detection limits. The addition of oxy-pyrohydrolysis techniques makes combustion ion chromatography capable of measuring total fluorine (TF) in various sample matrices down to high ppb levels. This white paper demonstrates the use of the new Profiler^{F} Total Fluorine Analyzer to measure TOF in wastewaters.

The system takes a single liquid sample and completes both a free fluoride analysis using direct IC and a total fluorine analysis incorporating new combustion technology. The analyzer automatically calculates and reports TOF by subtracting the free fluoride result from the total fluorine result. The analysis capability of the Profiler^{F} Wastewater is demonstrated by low-level measurement of water soluble TOF in the range of 250 ppb to 10 ppm.

Designed for non-targeted analysis, the Profiler^{F} Wastewater Analyzer is capable of measuring TF down to 200 ppb and FF levels down to 100 ppb, making it a valuable tool for fluoride characterization that compliments existing targeted analyses. Results obtained from the Profiler^{F} Wastewater Analyzer provide a broad assessment of fluorinated compounds in liquid samples, and are of particular interest for environmental monitoring of wastewater discharge and environmental remediation samples.

The Profiler^F Wastewater Analyzer combines two individual analysis methods into a single platform. For the FF analysis, an aliquot of sample is routed by an autosampler to an ion chromatograph where FF is determined using anion ion exchange chromatography with sequentially suppressed conductivity detection. Once data collection begins on the FF IC, a second aliquot of sample is routed to a combustion oven using automated liquid handling for the determination of TF.

Through automated liquid handling, a sample is delivered through a pyrotube specifically designed for handling aqueous samples. The sample is combusted in the pyrotube using a combination of high temperature, oxygen and steam to liberate the organically bound fluorine ion. A carrier gas transfers the fluoride products of combustion through a condenser and into an absorption tube containing water. The liberated fluoride is captured in the water in the absorption tube. This fluoride-containing sample is delivered to a second ion chromatograph where total fluorine is determined using anion ion exchange chromatography with sequentially suppressed conductivity detection. Organic fluorine is determined by taking the difference of the concentration of TF and FF.

A Metrosep A Supp 7 - 150/4.0 mm column, which utilizes a carbonate/bicarbonate eluent, is used for both IC analyses. Additionally, both systems utilize sequential suppression through a Metrohm Suppressor Module (MSM) for chemical suppression followed by carbonate suppression using a Metrohm CO_2 Suppressor (MCS). Sequential suppression improves the analytical performance of the conductivity detector and lowers the detection limits.[4,5]

Calibration standards were prepared using a certified, free-fluoride standard containing 100 ppm F^- (from sodium fluoride, NaF, CAS# 7681-49-4) combined with potassium nonafluoro-1-butanesulfonate (C4F9SO3K, CAS# 29420-49-3) as a source of organic fluorine.

TABLE 1. CALIBRATION STANDARDS

Std ID	Free F (mg/L)	Org F (mg/L)	Total F* (mg/L)
#1	0.25	0.24	0.49
#2	0.49	0.49	0.98
#3	0.98	0.99	1.96
#4	2.01	2.02	4.03
#5	2.99	3.02	6.01
#6	4.01	4.01	8.02
#7	4.95	4.93	9.88
#8	9.85	9.78	19.62

*Total Fluorine was calculated from the sum of Free Fluoride and Organic Fluorine.

For data collection of both FF and TF, peak areas were determined using automatic integration with MagIC Net 3.3 software. A single, custom result for Total Organic Fluoride (TOF), in units of mg/L, was calculated using the formula below:

TOF (MG/L)=TF-FF

Eight (8) calibration standards, each containing free fluoride and organic fluorine from 0.25 to 10 mg/L, were analyzed. Chromatograms for each standard level are overlaid for comparison.

FREE FLUORIDE

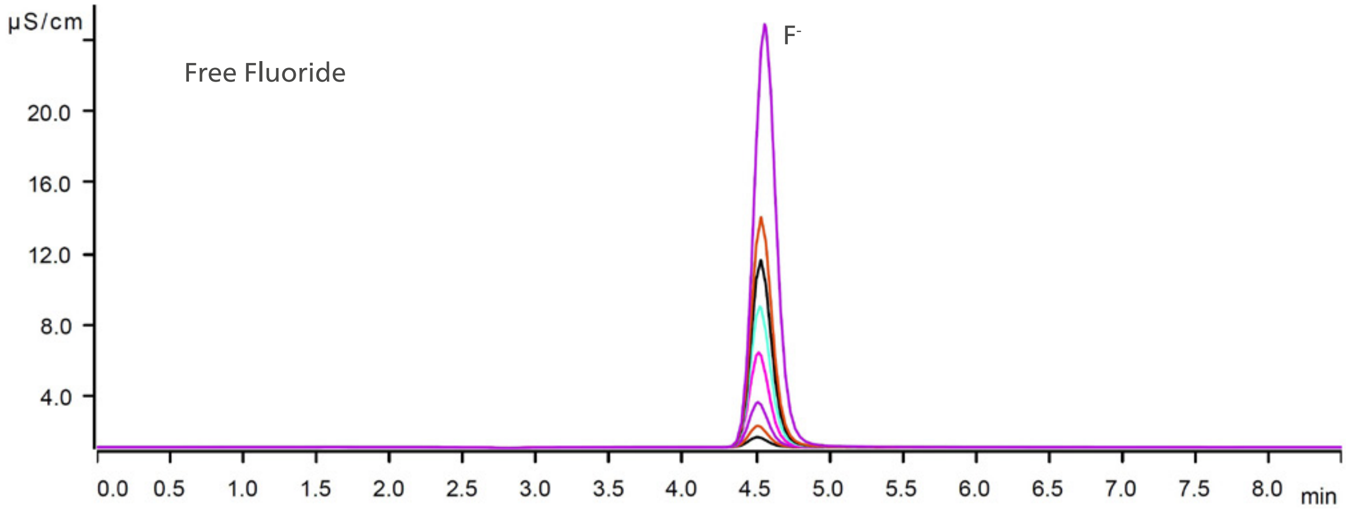


Figure 1.

TOTAL FLUORINE

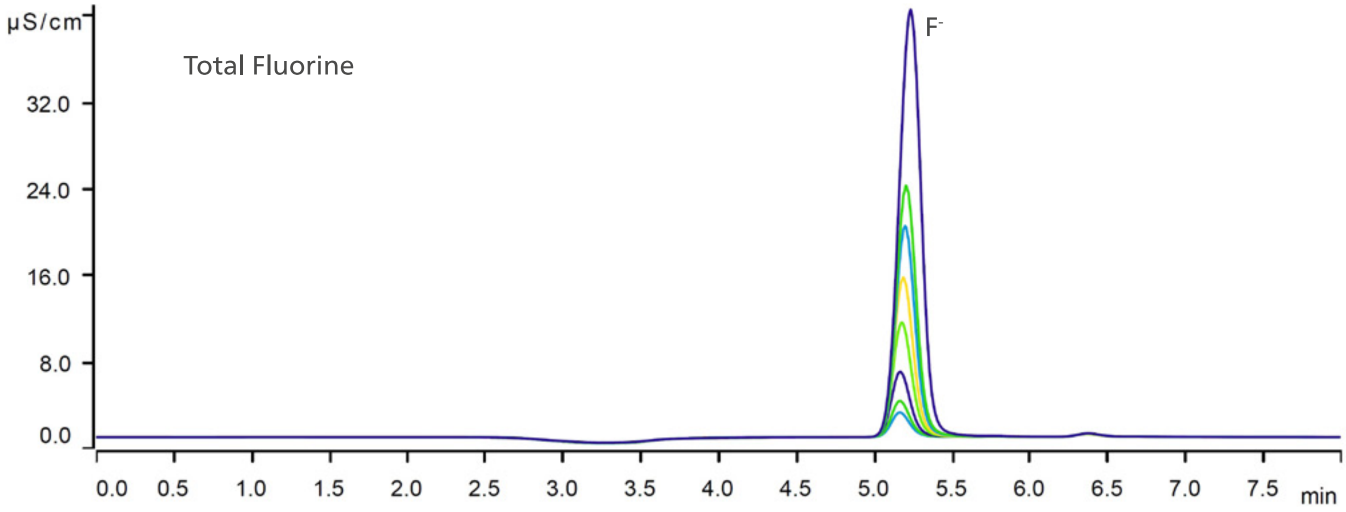
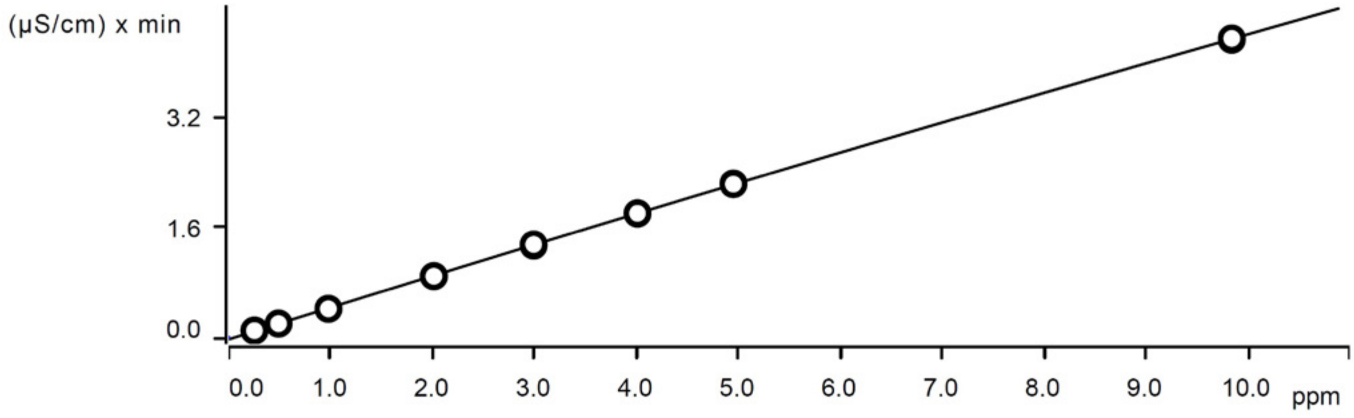


Figure 2.

Three replicates from each calibration standard were averaged to generate a calibration plot for free fluoride (Figure 3).

FREE FLUORIDE

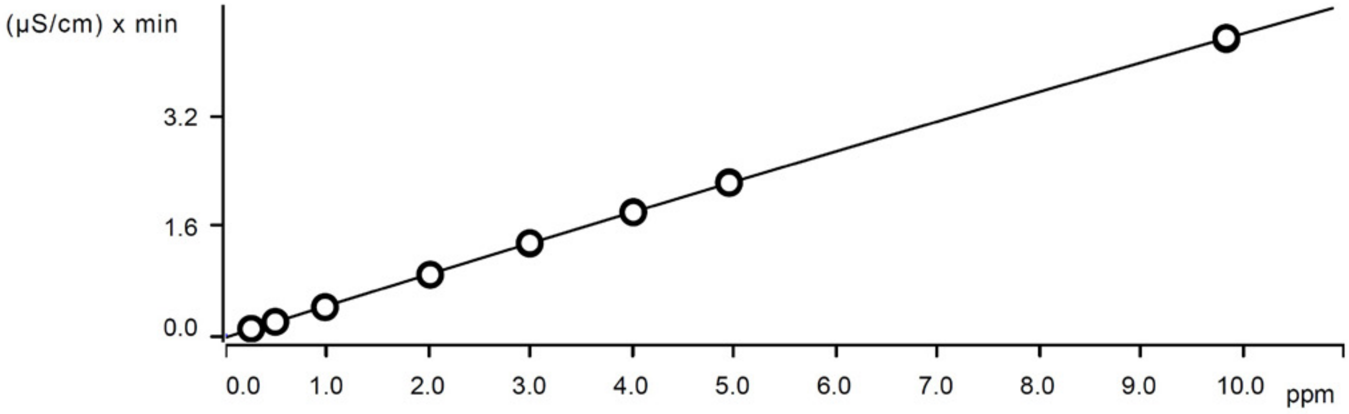


Function:	$A = -0.0323164 + 0.0231782 \times Q - 5.48409E\text{-}6 \times Q^2$
Relative standard deviation	0.648153 %
Correlation coefficient	0.999985

Figure 3.

Three replicates from each calibration standard were averaged to generate a calibration plot for total fluorine (Figure 4).

TOTAL FLUORINE



Function:	$A = -0.0324471 + 0.0231981 \times Q - 5.58547E\text{-}6 \times Q^2$
Relative standard deviation	0.660985 %
Correlation coefficient	0.999984

Figure 4.

The following Continuing Calibration Verification (CCV) standards were prepared in a manner similar to the calibration standards:

TABLE 2.

CCV Std ID	Free F (mg/L)	Org F (mg/L)	Total F (mg/L)
#1	0.98	0.99	1.96
#2	2.01	2.02	4.03
#3	2.99	3.02	6.01

RESULTS

Replicate measurements of CCV standards containing 1, 2, and 3 ppm each of free fluoride and organic fluorine were measured and recovery was determined. Recovery data is presented in Tables 3, 4 and 5.

TABLE 3.

1 ppm CCV	Free F (mg/L)	Org F (mg/L)	Total F (mg/L)
#1	0.96	0.99	1.95
#2	0.96	0.83	1.79
#3	0.94	0.93	1.87
Average	0.95	0.92	1.87
RSD (%)	1.2	8.8	4.3
Expected	0.98	0.99	1.96
Recovery (%)	97.3	92.6	95.4

TABLE 4.

2 ppm CCV	Free F (mg/L)	Org F (mg/L)	Total F (mg/L)
#1	1.98	1.96	3.93
#2	1.98	2.00	3.98
#3	1.98	1.97	3.96
#4	1.99	1.98	3.97
#5	1.98	1.91	3.89
#6	2.03	1.91	3.94
Average	1.99	1.96	3.95
RSD (%)	1.0	1.9	0.83
Expected	2.01	2.02	4.03
Recovery (%)	99.0	96.8	97.9

TABLE 5.

3 ppm CCV	Free F (mg/L)	Org F (mg/L)	Total F (mg/L)
#1	2.99	3.21	6.20
#2	2.99	2.92	5.91
#3	2.98	2.91	5.89
#4	2.98	2.98	5.96
#5	3.03	2.97	6.00
#6	2.98	2.93	5.91
Average	2.99	2.99	5.98
RSD (%)	0.65	3.8	1.9
Expected	2.99	3.02	6.01
Recovery (%)	100.1	98.9	99.5

The Profiler^F Wastewater analyzer is a hyphenated system; multiple instrumental results (FF and TF measurements) are interdependent and the error associated with each final result is compounded. Typical error for each analysis is expected to be 5 – 10%, which would yield the expected error of the compounded result to be 10 – 20%. However, despite the compounded error, the Relative Standard Deviation of the results was half the expected value ranging from of 1 – 8%. This excellent precision, driven by the new technology of this analyzer, allows for experimental certainty and meaningful results from the analysis even when analyzing a single sample only once.

CONCLUSIONS

Using a single standard for both free fluoride and organic fluorine, we have demonstrated the analysis range and recoveries of the Profiler^F Wastewater analyzer. In addition, carryover studies showed that concentrations of FF and TF were below the lowest calibration level. This indicates that there is no significant carryover of the F for the concentrations analyzed in this work.

This white paper demonstrates the superior analytical capability of the Profiler^F for the analysis of industrial process water and waste streams, providing a non-targeted screen of samples for further analysis by LC-MS and LC-MS/MS. Current studies in place with the US EPA are examining the utilization of non-targeted methods for permitting purposes.

References

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