Pyrohydrolytic Sample Preparation for AOF Determination in Water Samples According to EPA 1621

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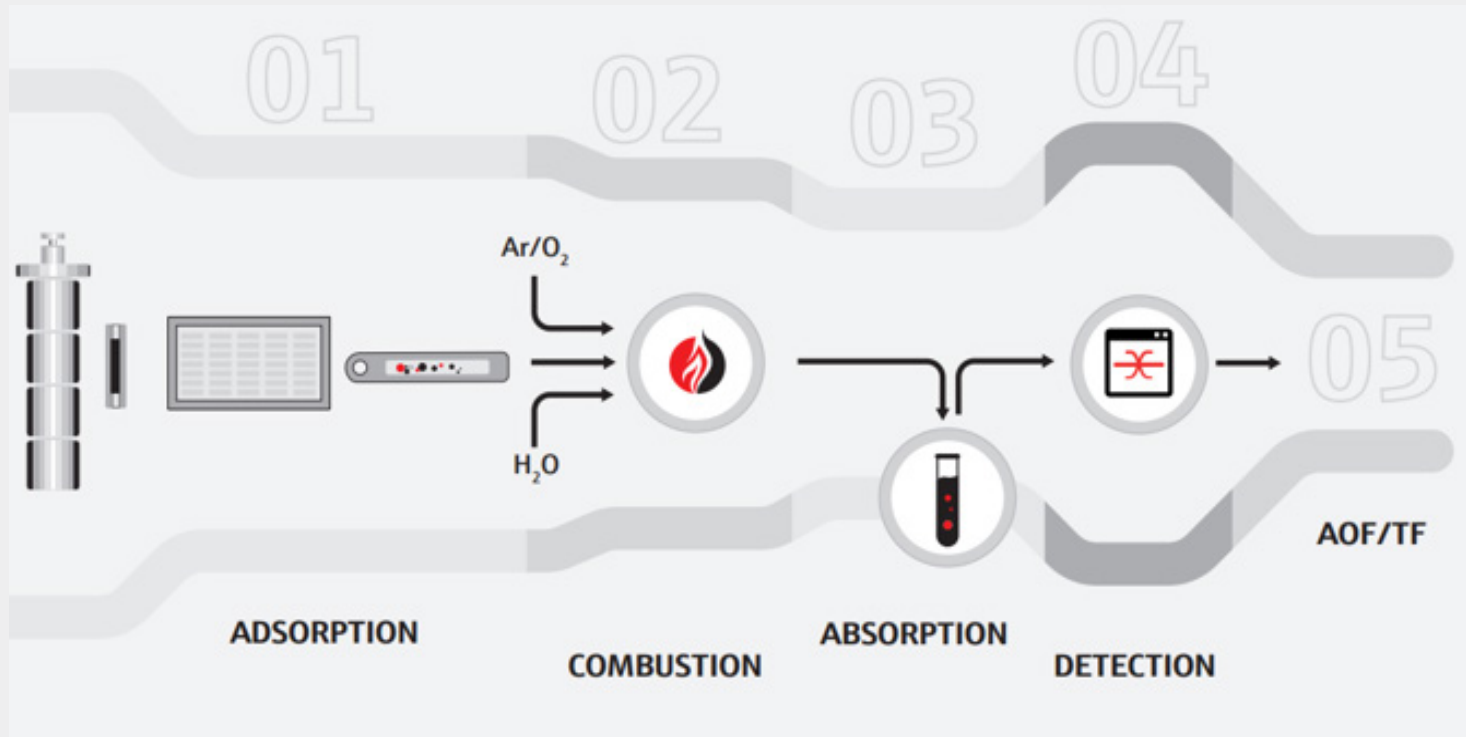
BACKGROUND

The determination of AOF is now described in various standard methods, including EPA 1621. The analysis is based on the enrichment of organic fluorine compounds on activated carbon columns as the first step, followed by combustion of the loaded columns at ≥ 1000 °C in a pure oxygen or oxygen-argon atmosphere with the addition of water (pyrohydrolysis) and adsorption of the formed HF gas in aqueous solution. In the last step, the fluorine content of this solution is detected using ion chromatography. Table 1 outlines the typical measurement parameters utilized for EPA 1621 and criteria for success.

Figure 1 | Schematic of preparation, pyrohydrolytic combustion, and detection of AOF columns

Parameter	Specification
Method blank	Below 4 µg/L for column 1 and 2, duplicates
Standard(25 µg/L)	Initial performance and recovery test (IPR) Recovery: 80-120% RSD ≤ 20% Ongoing precision and recovery test(OPR) Recovery: 70-130%
Matrix spike	Recovery: 50-150%, RPD ≤ 30% deviation
Sample	(Non-dilution + 100 mL volume) Breakthrough ≤ 50%, inorganic fluoride < 8 mg/L

Table 1: EPA Method 1621 Specifications:
The table outlines the success criteria. The colors of the table correspond with the results in Tables 4 and 5.

INTRODUCTION

According to the database maintained by the EPA, the PFAS family is currently estimated to have more than 10,000 synthetic compounds. Due to the size of this group, speciation analysis has proven especially intricate. Amongst the options to analyze PFAS, speciation is commonly being done with LC-MS/MS. One of the most widely adopted approaches used by contract laboratories involves the analysis of 40 targeted compounds. Therefore, a screening method can be beneficial to gain additional information about the unaccounted-for compounds.

Adsorbable Organically Bound Fluorine (AOF) serves as a powerful screening parameter for monitoring persistent and diverse fluorinated compounds in the environment. AOF is included in PFAS, fluorinated pharmaceuticals, and pesticides. Its determination involves a multi-step process of adsorption, pyrohydrolytic combustion, and ion chromatographic detection. This work demonstrates the feasibility and effectiveness of upgrading an existing multi EA 5100, multi X 2500, and multi EA 5000 combustion furnace system to perform pyrohydrolysis, offering a cost-efficient alternative for laboratories aiming to comply with EPA Method 1621.

References:
1) Application Note · ICprep. (n.d.). Retrieved July 11, 2025, from https://www.analytik-jena.com/import/assets/12789180_AppNote_ICprep_0002_AOF_water_EPA_1621_en.pdf2) EPA Method 1621, January 2024: „Determination of Adsorbable Organic Fluorine (AOF) in Aqueous Matrices by Combustion Ion Chromatography (CIC)"
2) U.S. Environmental Protection Agency. Method 1633A. December 2024. EPA 820-R-24-007
3) U.S. Environmental Protection Agency (EPA). PFAS Structure List (PFASSTRUCTV5). CompTox Chemicals Dashboard. August 2022. https://comptox.epa.gov/dashboard/chemical-lists/PFASSTRUCT

METHODS

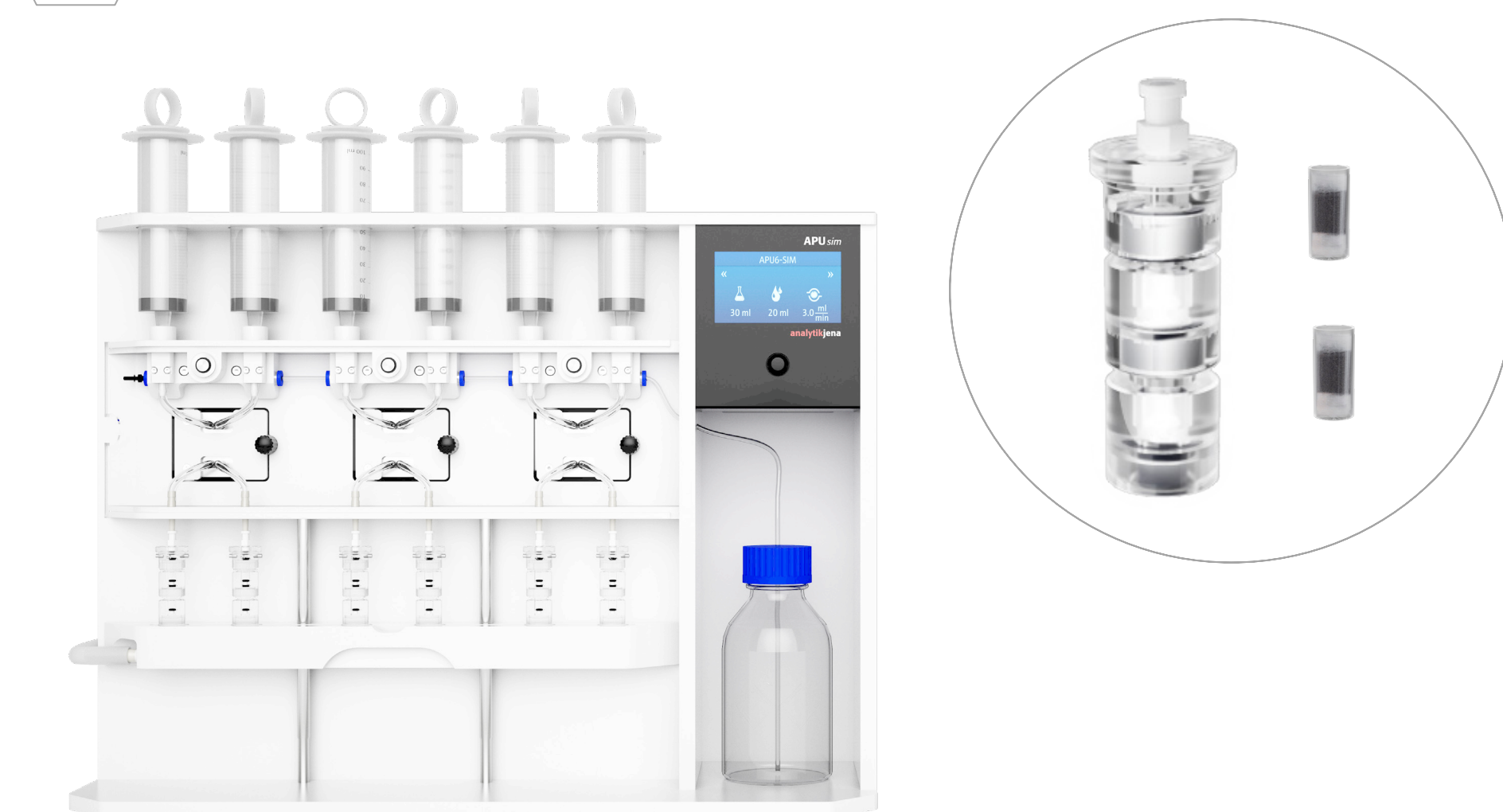### 1 Adsorption - Automated Column Preparation

Figure 2 | Column Method Preparation System APU sim (left) picture with column holder and columns (right):
Per EPA 1621, blanks, samples, and standards must all be run in duplicate with 2 columns. The second responsible for catching breakthrough, which must not exceed 50%.
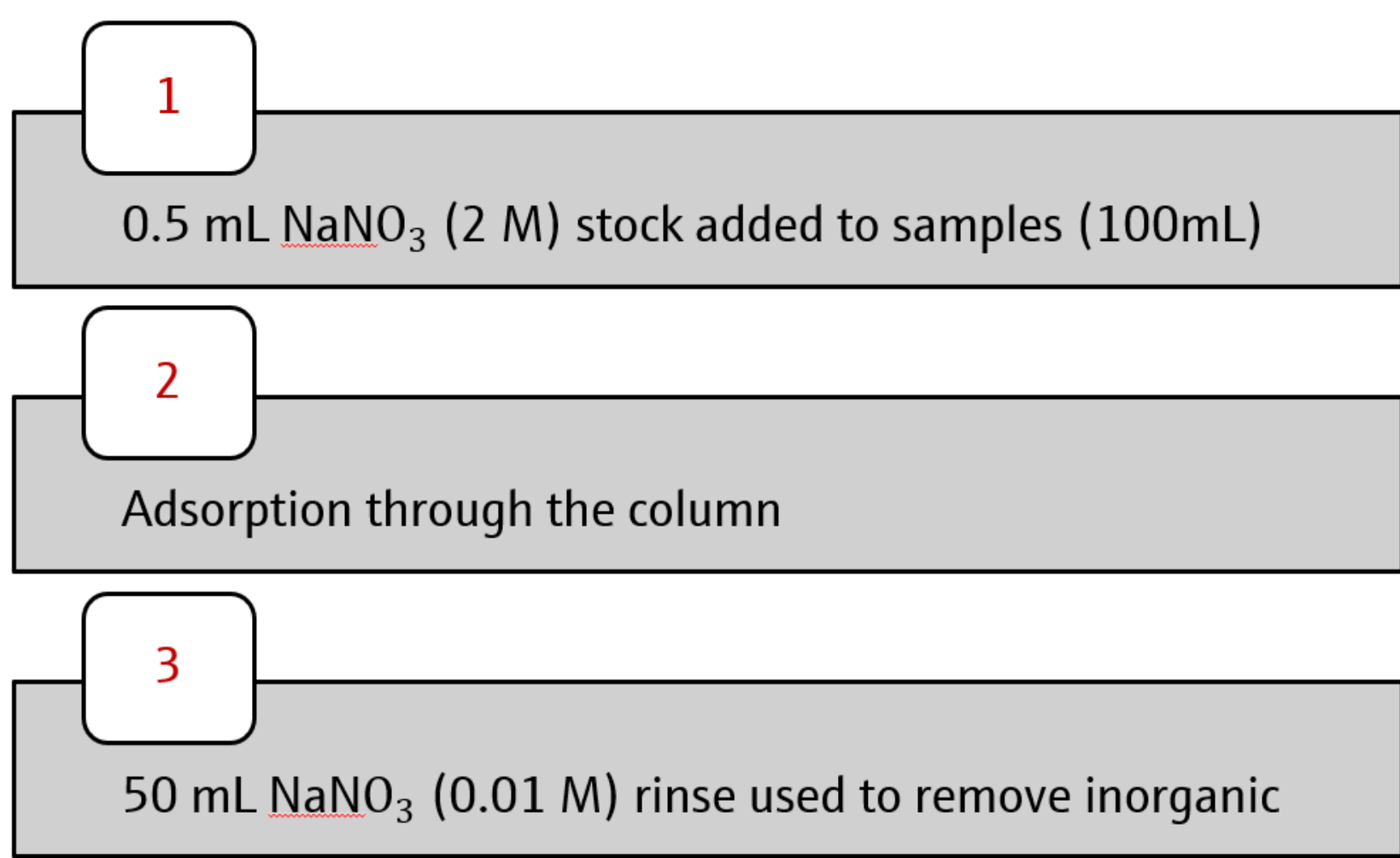
1 0.5 mL NaNO₃ (2 M) stock added to samples (100mL)

2 Adsorption through the column

3 50 mL NaNO₃ (0.01 M) rinse used to remove inorganic

Figure 3 | AOF Sample preparation steps

2 Combustion

Parameter	Setting
Furnace Temperature	1050 °C
O₂ Main Flow	300 mL/min
Ar Flow (inlet)	150 mL/min
O₂ Flow (inlet)	150 mL/min

Table 2: Combustion instrument parameters

3 Absorption

Parameter	Setting
Water dosage	0.2 mL/min
Absorber supply	2 mL
Post purge volume	1 mL

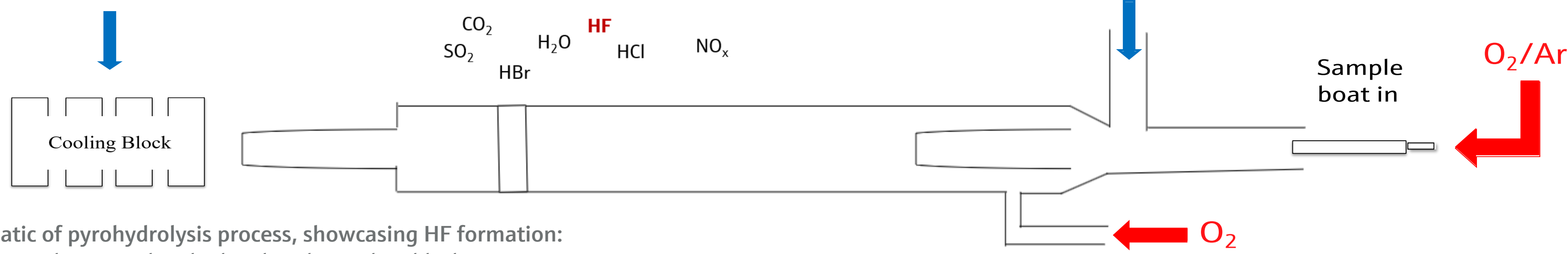Table 3: Absorption instrument parameters

H_2O (Absorber Solution)

Figure 5 | Schematic of pyrohydrolysis process, showcasing HF formation:
Post combustion, sample gas is absorbed within the cooling block.

Figure 4 | Complete ICprep Solution for AOF sample preparation:
It includes the automated boat drive (bottom right), combustion module (bottom center), absorber/humidifier module (top center), and fraction collector (far left).

After the columns are prepared, they are placed onto the 35-position tray on the multi-matrix sampler (MMS) shown on the right side of Figure 4. The samples are then introduced into the sample port. From here, the introduction rate is automated utilizing the Flame Sensor to ensure complete and controlled combustion.
Phase 1 begins when the sample is introduced into an argon-rich environment to be volatilized. Combustion takes place in the second phase. During this process, water is metered to increase the conversion rate of fluorinated organic compounds to HF.

RESULTS

Sample ID	Meas. 1 [µg/L]	Meas. 2 [µg/L]	Meas. 3 [µg/L]	Meas. 4 [µg/L]	Mean value [µg/L]	Recovery [%]	RSD [%]
Method blank	0.98	0.75	0.63	0.7	0.76		20
PFAS standard	23.7	23.5	23.6	23.8	23.6	95	0.5

Table 4: Initial performance and recovery test (IPR) with duplicates

Sample ID	AOF [µg/L], measurement 1	AOF [µg/L], measurement 2	AOF [µg/L], mean value	SD [µg/L]	Recovery rate [%]
Method blank	1.1	0.86	0.98	0.17	-
Standard solution with 25 µg/L AOF	23.3	23.1	23.2	0.14	93
Wastewater	7.43	8.09	7.76	0.47	-
Surface water	1.68	1.9	1.79	0.16	-
Matrix spikes	12.5	12.6	12.6	0.07	86

Table 5: Measurement sequence per EPA 1621:
This includes method blanks, standards, samples, and spikes in duplicate.

CONCLUSION

In this analysis, the ICprep digestion system meets all EPA Method 1621 performance criteria for AOF determination, including recovery (> 85% for standards and spikes), precision (RSD < 0.5%), and low method blank values (0.76 µg/L). The system enables reliable and reproducible results, even for low-concentration samples. Its separation from the detection unit allows flexible operation and efficient use of existing ion chromatography systems. ICprep offers a cost-effective alternative to coupled CIC systems, especially for labs handling smaller sample sizes.

FURTHER STEPS

To advance this evaluation, a possible next step is to analyze extractable organic fluorine (EOF) using the ICprep system in combination with a separate ion chromatography (IC) system for detection. Alternatively, analysis can be performed using a High-Resolution Continuum Source Atomic Absorption Spectrometer (HR-CS AAS). The ICprep system enables efficient combustion of both AOF and EOF samples, significantly broadening the range of environmental matrices that can be assessed. This expanded capability allows for more comprehensive quantification of diverse sample types, including complex materials such as soils.

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