RESTEK Pure Chromatography

# Rapid quantification of PFAS compounds in water utilizing a weak anion exchange coated blade spray mass spectrometry (CBS-MS)

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## PFAS and EPA 1633

PFAS compounds are synthetic organofluorine chemicals that have been produced since the 1940's and have been used in a variety of consumer products and industries.

EPA 1633 analyzes **40 PFAS compounds** in aqueous, solid, and tissue samples. This method utilizes a weak anion exchange (**WAX**) SPE cartridge for clean-up, with LC-MS/MS analysis on a C18 column.

## Statement of Problem

EPA Method 1633 analyzes **large volume** samples of **complex matrices** with significant solids content.

- Sample preparation is difficult, time consuming, and has high potential for contamination.
- LC-MS analysis requires **long analysis times** and is also rife with potential sources of contamination.

## The Solution = Coated Blade Spray

Coated Blade Spray (CBS) is an **easy to use** open-bed SPME device that can be directly interfaced with mass spectrometry (MS) instrumentation as a substrate electrospray ionization device.

- **No cartridge, no clogging!**
- Less than **15 second** analysis time.
- **Green**: consumes a fraction of the solvent needed for a traditional LC-MS analysis.
- **CBS is an excellent screening analysis** to reduce laboratory workload.

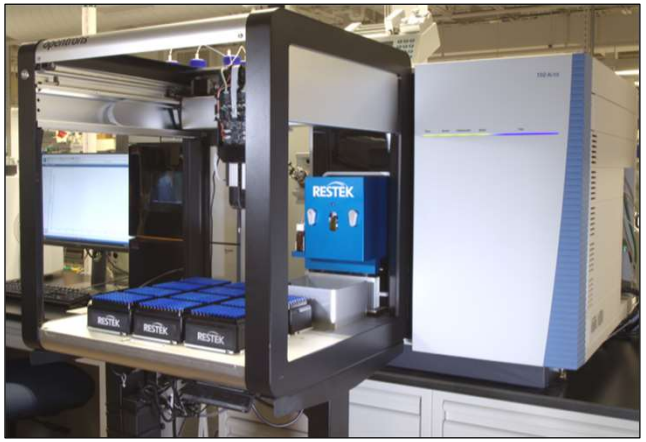
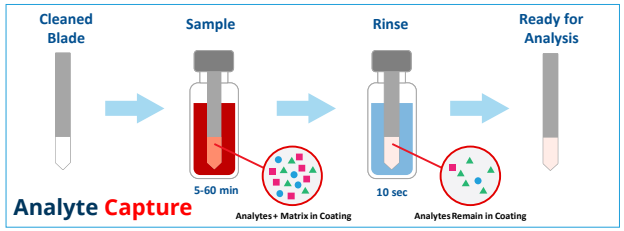
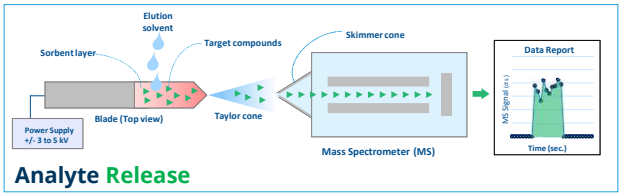



**Figure 1.** CBS-MS Total Solution employing an Opentrons OT-2 and a Thermo TSQ Altis.

## Coated Blade Spray is a simple process!

**Capture** the target analytes on a blade, then **release** them into the mass spectrometer.



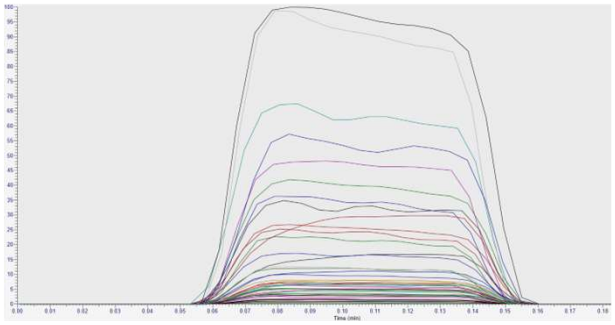

## Experimental Conditions

40 PFAS compounds from the EPA 1633 list were extracted from **substitute wastewater** (ASTM D5905-98) with a **WAX-coated blade** and analyzed with an Opentrons OT-2 liquid handler attached to a Thermo TSQ Altis.

| Capture | Release |
|---|---|
| **Sample Volume:** 500 µL | **Spray Solvent:** 9:1 MeOH:$CHCl_3$, 1% $NH_4OH$ |
| **Extraction Time:** 60 minutes | **Elution Volume:** 10 µL |
| **Rinse:** Water | **Elution Time:** 3 s |
| **Rinse Time:** 10 s | **Electrospray voltage:** -2800 V |
| **Shaker Speed:** 1200 rpm | |

## > 70 Transitions in a five second spray

A **five second spray** is enough to achieve **quantitative** results, even for large panels. This work monitored over 70 MRM transitions utilizing a 2 ms dwell time to achieve **20 scans** per compound.



## Results and Discussion

The table below shows signal-to-noise (S:N) values at six different concentrations. "Cal 1" represents samples at one quarter the minimum concentration level described in EPA 1633. **34 compounds at this level yield S:N values greater than three.**

| Compound | Cal 1 | Cal 2 | Cal 3 | Cal 4 | Cal 5 | Cal 6 |
|---|---|---|---|---|---|---|
| PFEESA | 66 | 112 | 246 | 411 | 596 | 1,277 |
| 6:2FTS | 52 | 91 | 211 | 325 | 451 | 1,532 |
| 8:2FTS | 50 | 91 | 210 | 318 | 460 | 2,063 |
| 9Cl-PF3ONS | 49 | 94 | 206 | 321 | 463 | 1,157 |
| 11Cl-PF3OUdS | 39 | 69 | 155 | 266 | 360 | 1,069 |
| 4:2FTS | 36 | 57 | 128 | 201 | 281 | 797 |
| PFHxS | 29 | 48 | 106 | 173 | 243 | 509 |
| PFPeS | 25 | 43 | 94 | 161 | 216 | 444 |
| ADONA | 21 | 37 | 84 | 134 | 182 | 556 |
| PF5OHxA | 21 | 34 | 75 | 119 | 170 | 502 |
| FPrPA | 20 | 28 | 66 | 119 | 175 | 939 |
| PFHpS | 18 | 33 | 74 | 111 | 154 | 348 |
| FPePA | 16 | 31 | 71 | 138 | 189 | 1,177 |
| 3,6-OPFHpA | 16 | 23 | 54 | 81 | 112 | 343 |
| PFBS | 14 | 24 | 51 | 84 | 118 | 236 |
| PF4OPeA | 13 | 21 | 46 | 72 | 105 | 301 |
| N-EtFOSAA | 12 | 20 | 48 | 76 | 107 | 801 |
| PFNA | 12 | 22 | 50 | 73 | 105 | 403 |
| L-PFDS | 11 | 18 | 43 | 63 | 87 | 219 |
| HFPO-DA | 10 | 16 | 35 | 59 | 90 | 288 |
| PFDA | 9 | 16 | 35 | 51 | 74 | 315 |
| FHpPA | 7 | 15 | 34 | 59 | 82 | 607 |
| PFTrDA | 7 | 10 | 24 | 36 | 48 | 199 |
| PFHpA | 7 | 12 | 26 | 42 | 58 | 185 |
| PFPeA | 7 | 11 | 22 | 35 | 51 | 141 |
| PFUnA | 6 | 11 | 23 | 34 | 47 | 214 |
| PFTeDA | 6 | 9 | 21 | 28 | 39 | 176 |
| PFHxA | 6 | 9 | 20 | 32 | 45 | 138 |
| PFDoA | 5 | 8 | 16 | 27 | 35 | 148 |
| L-PFNS | 5 | 8 | 15 | 24 | 32 | 93 |
| N-MeFOSAA | 5 | 9 | 18 | 28 | 42 | 303 |
| PFOA | 5 | 8 | 16 | 26 | 34 | 120 |
| PFOS | 4 | 7 | 14 | 21 | 30 | 72 |
| FOSA | 3 | 5 | 12 | 19 | 30 | 220 |
| PFBA | 3 | 4 | 7 | 11 | 15 | 38 |
| L-PFDoS | 2 | 4 | 7 | 15 | 17 | 44 |
| N-MeFOSA | 2 | 2 | 5 | 8 | 12 | 59 |
| N-EtFOSA | 1 | 1 | 3 | 4 | 5 | 23 |

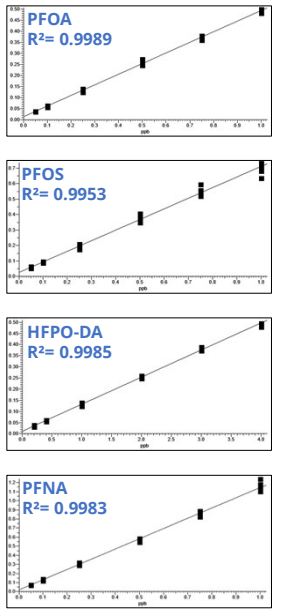



**Figure 2.** Table of S:N values at six concentrations (left). Calibration curves for four prominent compounds (right).

Quantitative results were promising:

- 19 compounds with $R^2 > 0.99$
- 34 compounds with single or double digit ppt MDL blank

During tuning two compounds underwent in-source fragmentation, resulting in MRMs indistinguishable from N-MeFOSA and N-EtFOSA. Therefore, results for these pairs of compounds are summed together.

CBS-MS quantitatively identified **37** PFAS compounds extracted from substitute wastewater at **1/1000th** the typical sample volume of EPA Method 1633.

## Acknowledgements

Janusz Pawliszyn is the inventor of CBS and a collaborator of Restek.

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WAX sorbent was purchased from Suzhou Nanomicro Technology Co.
The authors declare no competing financial interest.