Analytical Fate of Ultra-Short Chain PFAS and Inorganic Fluorine in EOF and AOF

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Outline

Total Organic Fluorine Analysis Landscape

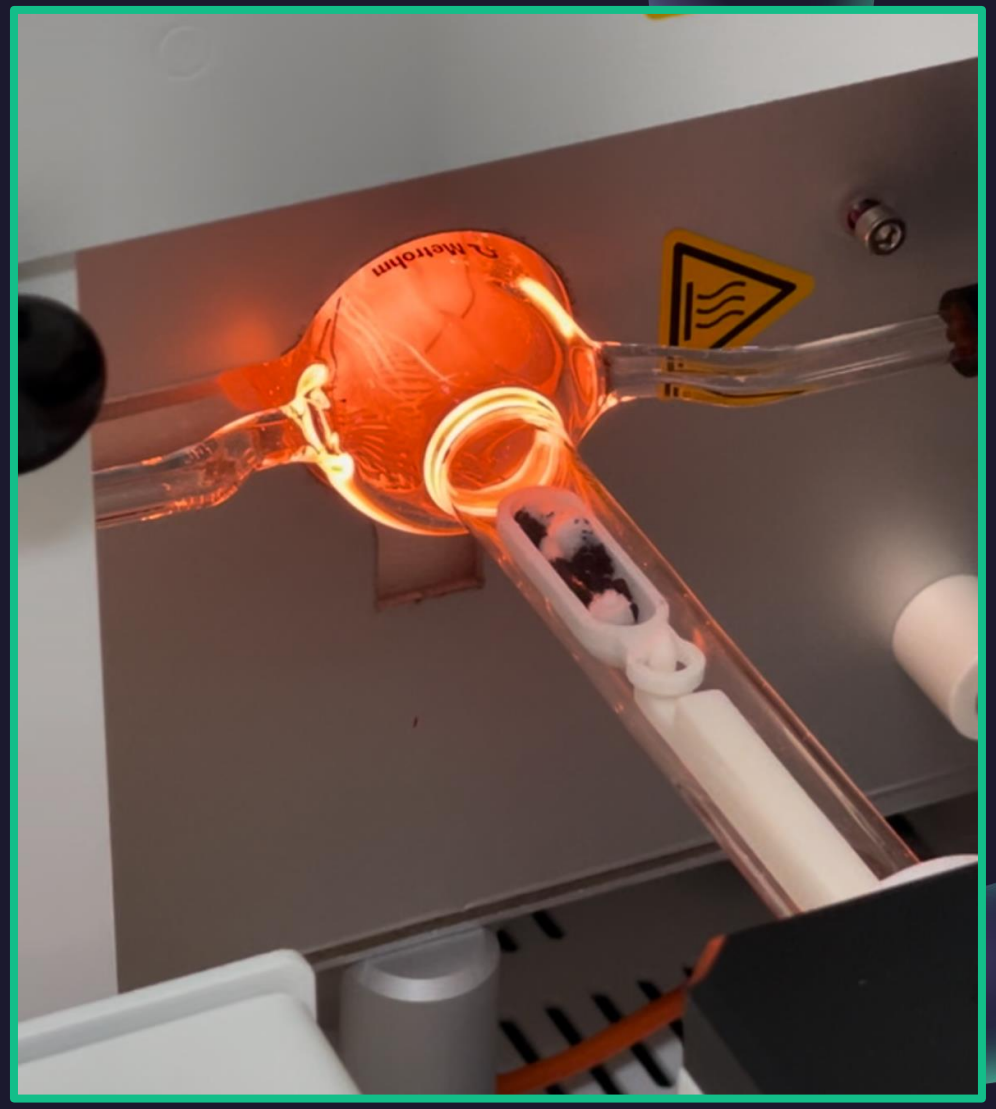
Methods Comparison Study (2023)

AOF vs EOF - Analytical Differences

Analyte Fate Studies for AOF and EOF

Case Study – EOF versus AOF in samples

Conclusion – Future of Organic Fluorine



Targeted methods alone cannot capture the entire PFAS burden in environmental samples.

Method Comparison Study

(2023 Focused on DW)

Ran multiple samples via AOF, EOF, PIGE, 19F-NMR and evaluated against targeted and non-targeted analyses and evaluated mass balance gap

All methods had limitations

19F-NMR availability. Tried Direct analysis and SPE prep with relaxants.

PIGE prep using 3.5 L makes it more sensitive. Availability an issue. Prep issues with ultra short PFAS and fluoride removal. Requires replicates.

AOF and EOF both had trade-offs. Seems like current direction.

Focus on AOF and EOF

Scalability, Acceptance, Sensitivity

Combustion Ion Chromatography Robust, Accurate, and Precise

Sensitivity Challenges may be overcome using specific prep procedures

EPA 1621 established some precedent for AOF

EOF Drinking Water Method

General Differences - AOF and EOF

ADSORBABLE ORGANIC FLUORINE

- Carbon Adsorption
- Background Fluorine
- Flow Rate 3-4 mL/min
- Particulate Limit
- Volume Loading Limited

• EXTRACTABLE ORGANIC FLUORINE

- Weak Anion Exchange
- Low Background
- Flow Rate 10-15mL/min
- Particulate Limited by SPE format
- Volume Loading Limit by SPE format

General Differences - AOF and EOF

ADSORBABLE ORGANIC FLUORINE

- Fluoride Removed by Nitrate
- RLs in 500ng/L range
- Entire Sample Used – single shot
- No Vap down
- Combust carbon/glass wool
- Result Orthogonal to Targeted Method (neutrals, volatiles, etc)

• EXTRACTABLE ORGANIC FLUORINE

- Fluoride Removed by Hydroxide
- RLs in 200ng/L range
- Extract may produce 2-3 analyses
- Extract Must be Evaporated to dryness
- Combust 100uL extract
- Result Aligned with Targeted Methods (EPA 533/1633)

Equipment

Metrohm Profiler-F

Metrohm Flex IC

Metrohm Eluent Production

Analytik Jena Combustion Module

Automatic Boat Loader Module

Analytik Jena APUSIM – AOF prep

Liquids Kit (for EOF work)

AOF and EOF results reveal different chemical space.

Analyte Fate Studies

Reveal underlying chemical space

Analyte Fate Study – Spike each analyte and process each method

Must do one at a time because AOF / EOF is PFAS aggregate

Similar studies have been done but did not include FTOH, Cationic, or ultra short sulfonamides

Needed to understand mass balance differences associated with methodology

Analyte Fate Studies
Ultra-short Carboxylates/Sulfonates

Parameter	EOF (WAX)	AOF (GAC)
Trifluoroacetic acid (TFA)	No – Lost in matrix spikes and during evap/drying	No - Breakthrough (conc dep.)
Perfluoropropanoic acid (PFPrA)	No – Lost in matrix spikes and during evap/drying	No - Breakthrough (conc dep.)
Trifluoromethanesulfonate (TFMS)	Yes	No – removed from nitrate F-removal
Perfluoroethanesulfonate (PFEtS)	Yes	No – removed from nitrate F-removal

Analyte Fate Studies
Result Highlights – Other classes

Parameter	EOF (WAX)	AOF (GAC)
Perfluorosulfonamides (eg: PFOSA) toxic and occur in DW [3,4]	No – Lost at extract dryness	Yes – C4, C6, **C8**, C10 > 85%
Fluorotelomer alcohols (FTOH)	No – Lost via breakthrough	Yes – 6:2 and 8:2 FTOH >70%
Cationic PFAS (AFFF relevant)	No – quat N unretained on WAX	Yes – N-TAmP-FHxSA, N-AP-FHxSA, N-CMAmP-6:2FOSA >80%
Hexafluorophosphate PF_6^- (Not OF)	Yes – retained on WAX, and High Combust. Eff.	No
Tetrafluoroborate BF_4^- (Not OF)	Yes – retained on WAX	No

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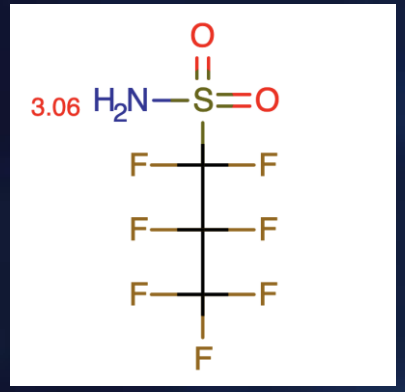
Relevance to Real World Samples

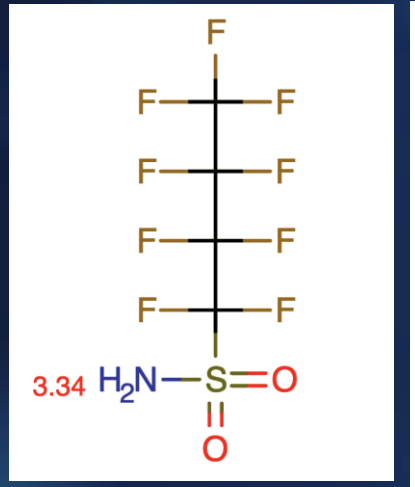
PerFluoro-Sulfonamides

Relevant class missed by complete dryness of extract (EOF)
Detected PFOSA/PFBSA in 9 pre-treated groundwater samples using alternative technique
Perfluoropropanesulfonamide (PFPSA) presence

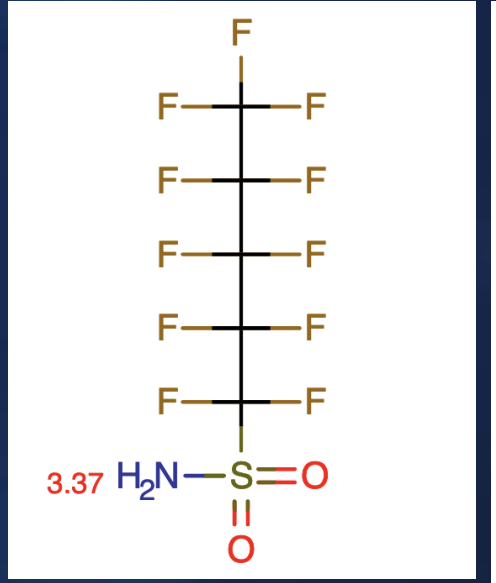
C3 - PFPSA



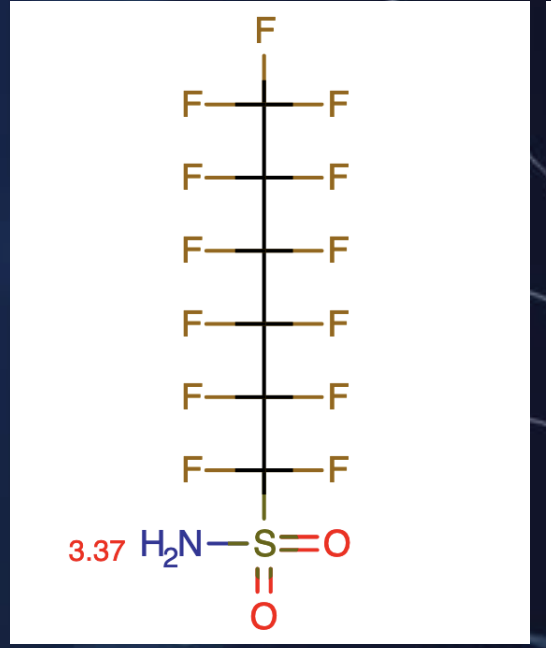
C4 - PFBSA



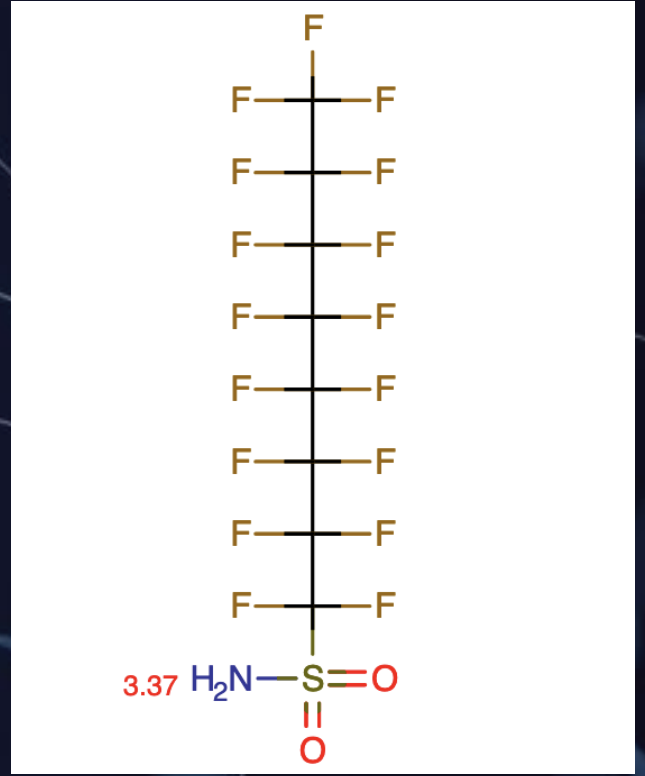
C5 - PFPeSA



C6 - PFHxSA

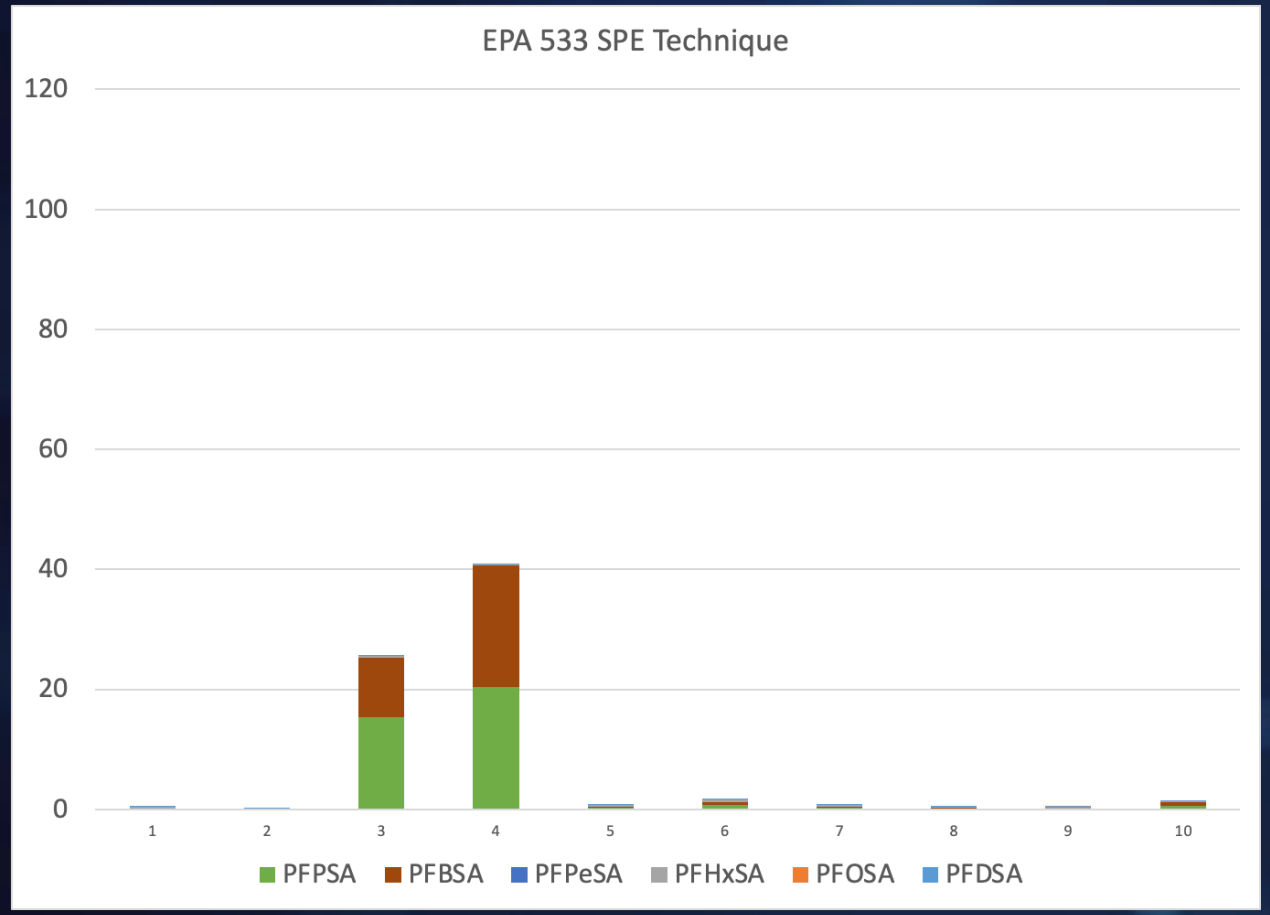


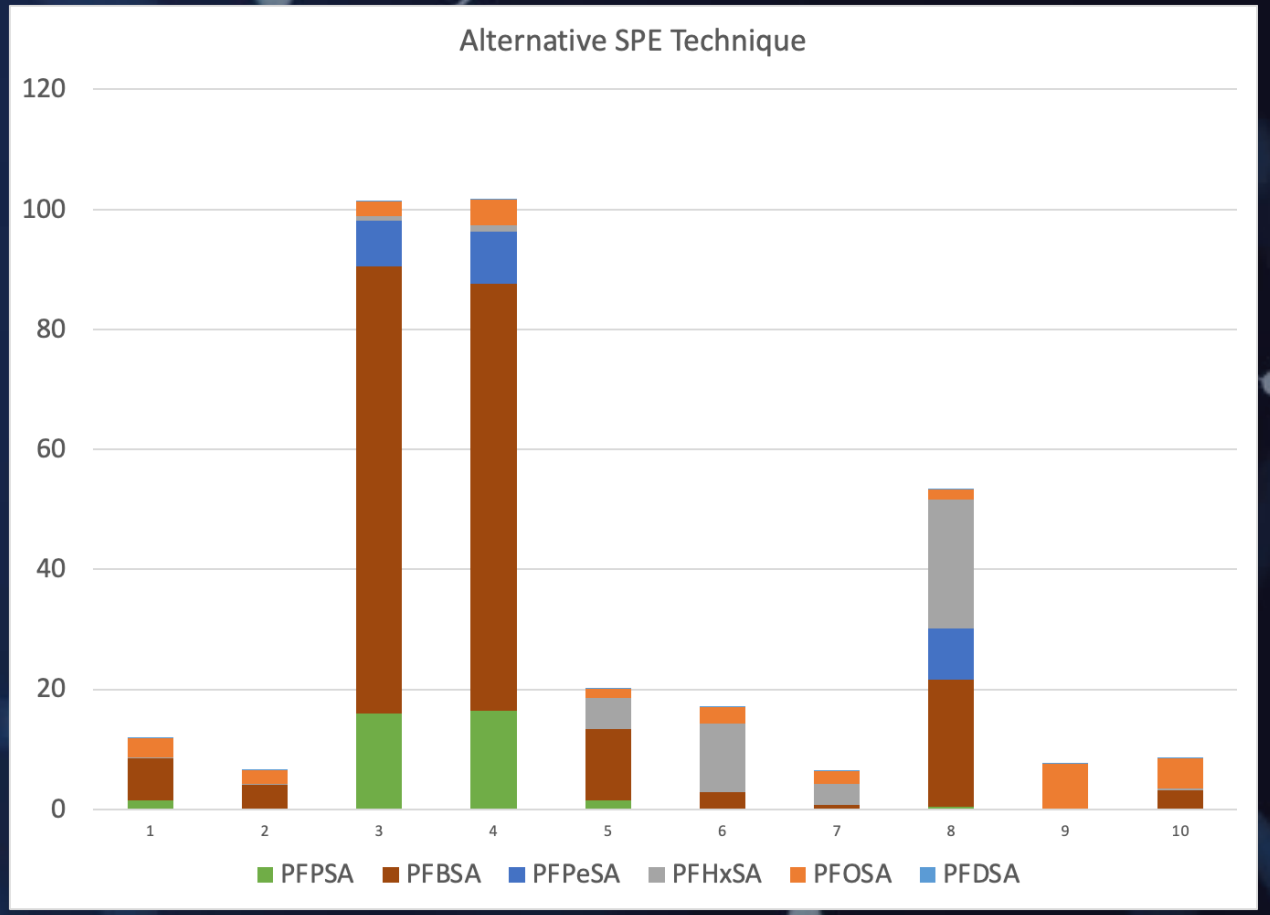
C8 - PFOSA



PF-Sulfonamides

- Relevant class underestimated by complete dryness of extract (EOF)
- Detected PFOSA/PFBSA in 9 pre-treated groundwater samples drying to fixed volume
- High-Res MS showed Perfluoropropanesulfonamide (PFPSA) presence equal in both extracts





Combustion Observations

- Hexafluorophosphate (PF6) revealed potential multi-step mechanism

PF6 recovery consistently high >160%

PF6 decomposes at 200 C
(NaF melts at 993C)

PF6 hydrolyzed by water

Hexavalent P may promote F atom release

Samples with PF6 may need special calibration
(EOF recovers PF6, AOF does not)

What Does This Data Mean?

Conclusions

- Neither AOF nor AOF capture all TFA (Trifluoroacetic acid) and PFPrA (Perfluoropropanoic acid)
  - Ultra-short chain targeted methods can capture these as well as TFMS, PFEtS, PFPrS, and Bistriflimide
- There is no total OF method that captures everything
  - Primary Trade-off is sensitivity for selectivity in EOF over AOF
- Analyte fate studies can be used to establish the chemical space bounds of both AOF and EOF
- Both EOF/AOF still perform very well for common PFAS analyte lists (C4+ carboxylates, sulfonates C3+, FTS C6+) [1,2]
- EOF may have lower achievable reporting levels, but misses relevant PFAS classes if conc. is high enough (study to be released 2024)
- AOF offers orthogonal chemical space capture that may be beyond those tested (FTOH, cationic, and PF sulfonamides)
- Mass balance efforts largely impeded by chemical space of aggregate organic fluorine tests

Thank you

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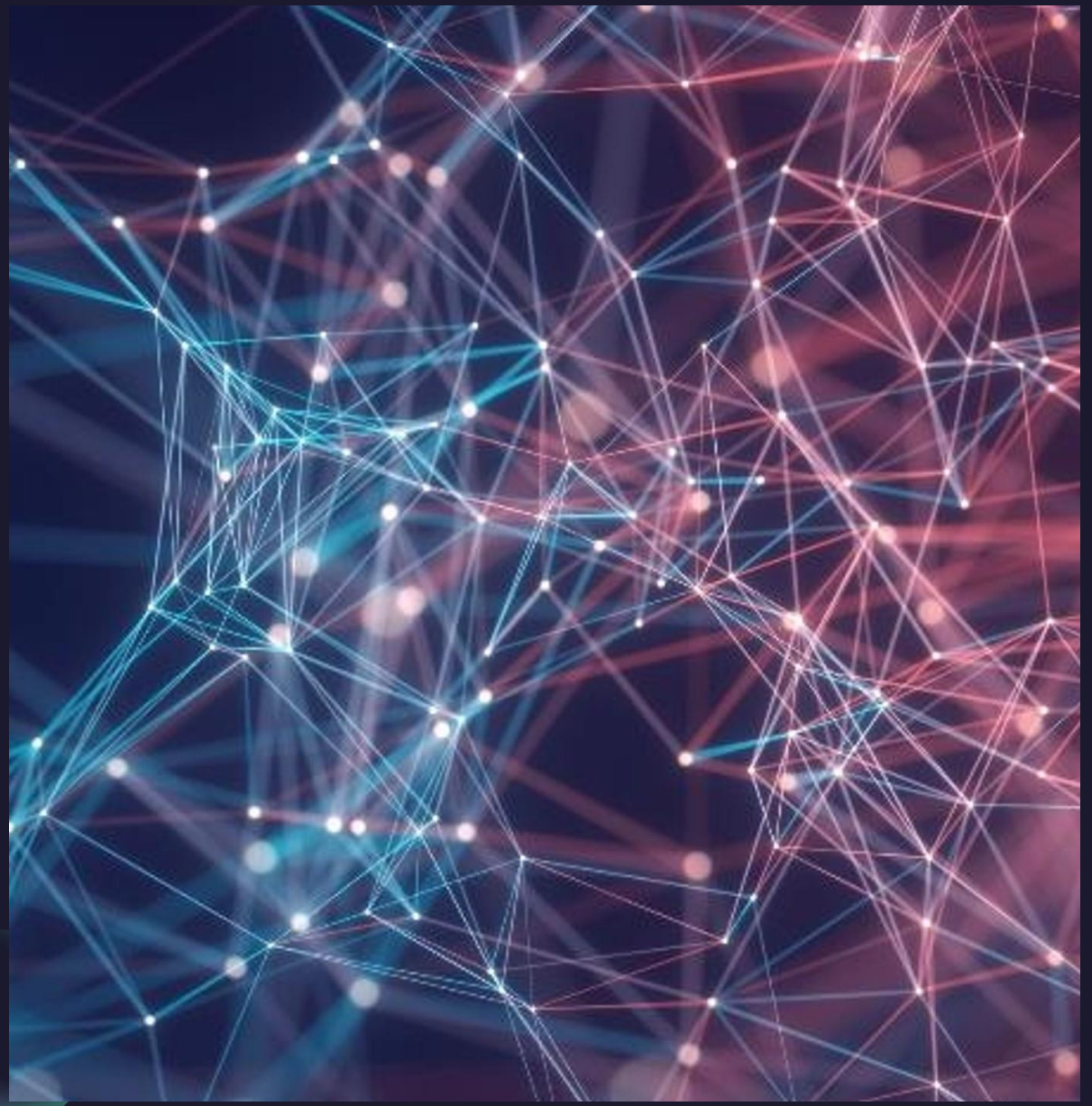

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