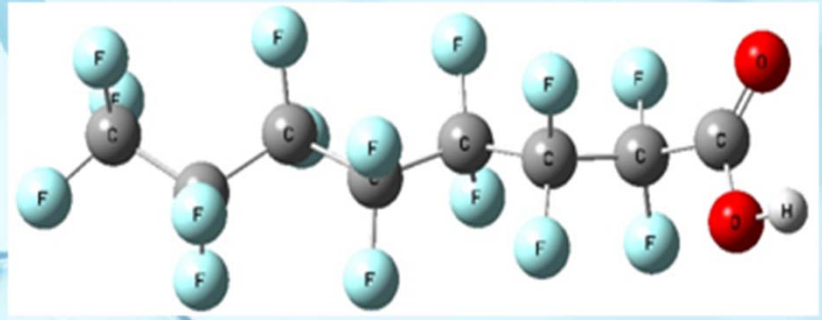
PFAS in Different Water Matrices and Related Matrix Effects



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Introduction

PFAS testing is an important component of the overall effort to identify, remediate and eliminate source materials in an effort to help our environment and protect human health.

As we learn more about these compounds and find more ways to identify the broader class of PFAS materials, the analytical testing has to keep step with the ever-expanding knowledge base.

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Introduction

Understanding analytical results for PFAS and the quality control that supports the data is a critical tool in making decisions in the field.

The PFAS list of target analytes is growing. State of Michigan is currently looking at a compound list of 28 target analytes.

State of Wisconsin is currently looking at a compound list of 36.

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Introduction

Other states are interested in an even larger list of PFAS compounds. We anticipate that this trend will continue.

As newer replacement PFAS compounds are used by industry, environmental factors may be found to be dangerous for our planet.

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Instrument LC/MS/MS

New technology allows for more sensitivity.

Advantages:

- Improved sensitivity bring down the baseline
- Ability to speciate a wider range of compounds

Toxicologists will continue to add new compounds and push for lower reporting limits for human health.

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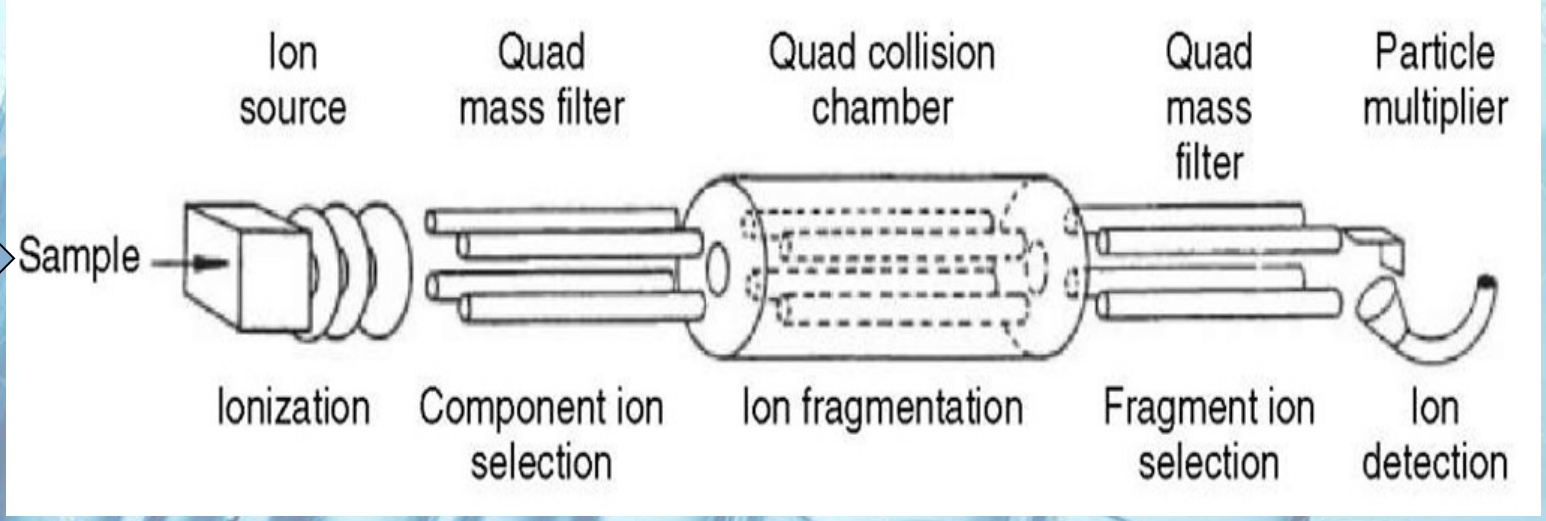
LIQUID CHROMOTOGRAPHY

IONIZE

Quad sorts by color

Fragment the Red M&M to find what's inside

Final fragment shows its PB&J



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How the LC/MS/MS works

Motivation

The demand for lower reporting limits of detection are also a consideration when analyzing samples and different matrices.

For example, compounds that could have been detected at an acceptable level on an LC/MS or GC/MS previously, now require an LC/MS/MS or GC/MS/MS, to reach the required limits of detection.

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Technology

In addition, LC/MS/MS technology is continually advancing. Merit's experience with the ASTM D7979 method between two different Agilent instrument models show a 5-fold reduction in reporting limits for most PFAS compounds.

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Instrumentation LC/MS/MS

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Instrumentation GC/MS/MS

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Instrumentation

From our own experience, samples analyzed by the ASTM D7979 method:

- Agilent MS/MS Model #: 6495B gives RLs of **2 ppt** for most of the compounds on the Michigan 28 compound list
- Agilent MS/MS Model#: 6470 is **10 ppt** for the same list.

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Solvent Dilution Method

When using ASTM D7979 method:

- 15 ml centrifuge tube, 5 ml sample volume
- Add Surrogate (i.e. internal standard for isotopic dilution) This is allowable by the method.
- Add 5 ml MeOH directly into sampling bottle
- Add Acetic Acid
- Analyze using LC/MS/MS

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Solvent Dilution Advantages

This method introduces the PFAS chemicals to the instrument without any selectivity (that can lead to losses).

Due to the nature of PFAS chemicals and their ability to adhere to different materials, this method eliminates additional surfaces for the samples to come in contact with.

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Solvent Dilution Advantages

By capturing everything in the original sampling vial and injecting it directly into LC/MS/MS, it creates less potential error by removing additional sample handling procedures.

This methodology does not rely on a selectivity of a cartridge, therefore, you can analyze solvents and other non water matrices that may affect SPE effectiveness.

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Solid Phase Technology

SPE -03 8-Channel automated SPE from PromoChrom Technologies

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SPE Method

When using EPA Drinking Water Method 537 or other solid phase extraction protocols:

- Preserves 250 ml plastic bottles w/TRIZMA (TRIS buffer/base)
- Solid Phase Extraction
- Internal Standard Calibration or Isotopic Dilution
- Analyzed using LC/MS/MS

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SPE Advantages

250 ml samples concentrated down to a smaller final extract allows for greater sensitivity and gives a lower level of detection and adds a layer of selectivity in the analytical process.

The selectivity process eliminates additional interferences that do not interact with the SPE cartridges, allowing for faster run times and simplified reporting.

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SPE Limitations

This selectivity also opens things up for matrix effects.

Our experience after analyzing a substantial amount of drinking water samples from a wide variety of sources in the State of Michigan, we observed a pattern of matrix interference with the longer chained PFAS compounds on the drinking water list.

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SPE Limitations

Our colleagues at the EGLE (State of Michigan) laboratory found a correlation between the amount of iron present and the effect that we noticed during solid phase extraction.

When analyzing similar samples using a different methodology, for example, ASTM D7979 (solvent dilution and injection), would not have the same recovery issues for longer chained PFAS compounds.

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Solvent Dilution Limitations

Solvent dilution does not utilize selectivity of the extraction procedure, this can present matrix interference issues.

Complex matrices significantly enhance the ionization potential of the FTS compounds (4:2, 6:2, 8:2 FTS) in the MS/MS source.

This results in greatly increased response of these compounds and their corresponding isotopes. This fact is also referenced in EPA Method 533.

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Solvent Dilution Limitations

The sensitivity is not as good as the SPE, because the sample is diluted and not concentrated.

Due to the lack of selectivity, the solvent dilution requires longer run times, in order to sufficiently separate compounds into individual peaks.

Introducing the sample with little manipulation has the potential of lowering the life of the analytical column.

Method Comparisons

DOD PFAS method, which also uses solid phase extraction, includes the addition of carbon clean-up procedure in an attempt to remove coextracted materials that may cause interference.

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Matrix Influences

The solid phase extraction method, although great for more sensitive analyses, is limited by the cartridges ability to capture PFAS analytes in different matrices.

Some matrices, such as solvents, high concentration samples, strongly alkaline samples, and matrices with high level of metals will affect the cartridge negatively.

The required QC parameters can fail, resulting in flagged data.

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Method Optimizations

The use of an LC/MS/MS helps reduce matrix interferences and depending on characteristics of different sample matrices, some methods may be more optimal than others.

Both SPE and Solvent Dilution are strong methods for detecting PFAS compounds. Both methods allow for isotopic dilution, which depending on the matrix is advantageous.

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Conclusion

When analyzing samples, understanding the matrix and having the flexibility to use different methods provides great advantages.

As more PFAS compounds are added, and more matrices need to be analyzed, understanding the advantages and disadvantages of available methods helps to navigate the increasingly demanding and challenging world of PFAS.

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THANK YOU!

QUESTIONS?

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