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Technical Report

PFAS: Essentials for Analysis by LC-MS/MS

Abstract:

Per- and polyfluoroalkyl substances (PFAS) are currently of great public health and environmental concern. Often referred to as forever chemicals, their ubiquitous use has led to demands for more regulations and analysis. Analysis of PFAS is complicated by the use of laboratory materials that may already contain PFAS. This report describes a modification that ensures a PFAS-free background while maintaining the benefits of a standard LC configuration.

Keywords: PFAS, LC-MS/MS

Laboratories face the challenge of implementing high-throughput workflows while ensuring high and consistent sensitivity and performance, as well as user-friendly methodologies for analysts with varied expertise using LC-MS/MS instruments. Several components of LC-MS/MS instruments (e.g., degassers, solvent lines) and consumables (e.g., caps, syringe filters) commonly used in the laboratory may contain materials derived from individual PFAS, such as PFOA. Historically, to prevent background contamination from these components during PFAS analysis, hardware was reconfigured to eliminate as many PFAS-based components as possible. As a result, purchasing, maintaining, operating and troubleshooting the LC became more cumbersome.

Through thorough evaluation, we confirmed that a standard LC configuration, with PTFE tubing and degasser in-line, can be successfully used for trace analysis of PFAS. There is one essential modification required: installing a *delay column*.

Mobile phase contaminants continuously eluting from the system have the effect of raising the background signal. However, it is common for mobile phase contaminants such as PFAS to be retained on the column during system equilibration and the weak portion of the gradient. Then, when the gradient reaches sufficient strength, the accumulated contamination is eluted as a discreet peak. An additional LC column installed after the mixer and before the autosampler accumulates mobile phase contaminants and retards their elution from the primary analytical column during a gradient. This delay column ensures a retention time separation between the contaminant peak and the peak of interest.

In this study, long equilibration times were used to accumulate measurable PFAS mobile phase contaminants. After 120-minute equilibration periods, a series of in-vial 1 ppb standard and blanks (80:20 MeOH:H_2O) were injected without and with a delay column (**Figure 1**). The simple modification of installing the delay column between the mixer and autosampler (**Figure 2)** was sufficient to ensure a PFAS-free background while maintaining the benefits of a standard LC configuration with its clear and flexible PTFE solvent lines and in-line degassing.

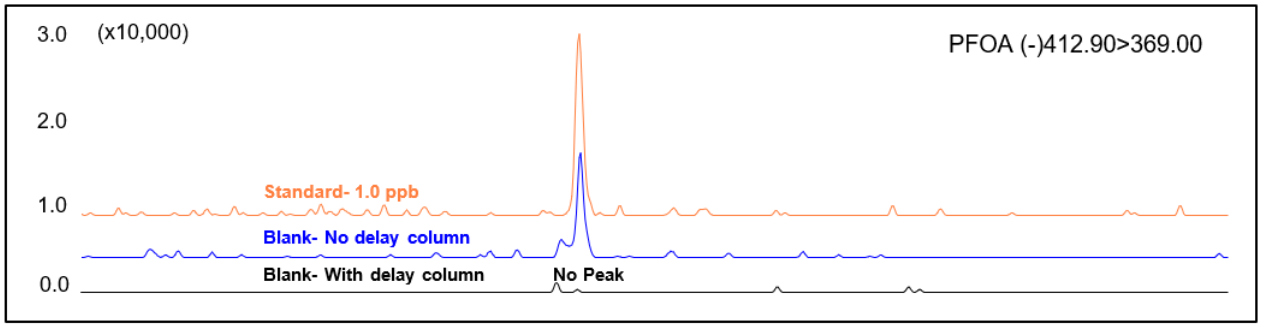

Figure 1: Chromatograms for a PFOA 1.0 ppb Standard (concentration in vial) (orange), blank without delay column (blue), and blank with delay column (black).

Figure 2: Installation of delay column

Another common practice for the trace analysis of PFAS has been to modify the standard vial and cap selection most commonly used by laboratories. The use of polyproplyene vials and enclosures is common, however, polypropylene caps have the disadvantage of not resealing after injection, thus risking compromise to sample integrity.

Therefore, PTFE lined silicone rubber caps were evaluated for contamination. Thirty consecutive injections were made from the same vials, and no PFAS contamination was observed in any of the runs. Figure 3 shows the 30th injection of one such test.

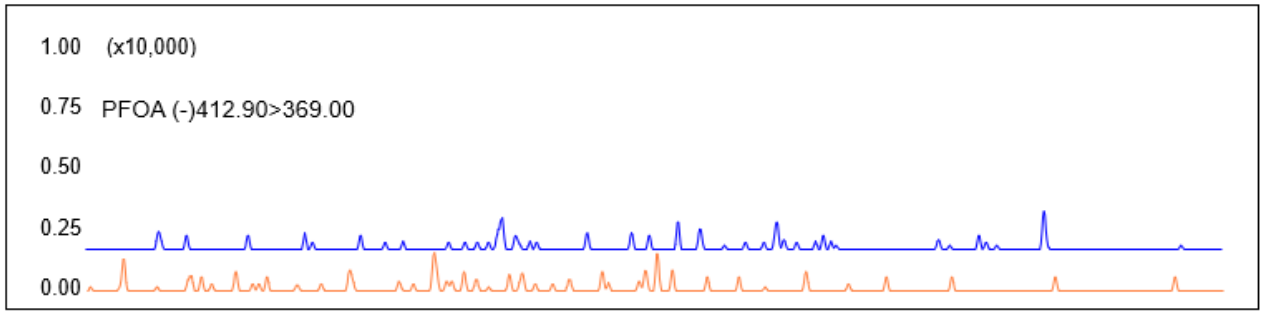

Figure 3: PFOA transition in blank comparisons of a polypropylene cap and vial (blue) to PTFE cap with silanized glass vial (orange) after 30 consecutive injections.

Table 1: Consumables recommended for PFAS analysis.

LC-MS/MS CONSUMABLES		
Part Number	**Description**	**Comment**
220-97331-68	Vials, 1.5mL Amber Silanized Glass Vials w/cap & Septa, Short thread, 12 x 32mm, 9mm opening, 100pk	Caps and vials
227-32007-02	Column, LC, Shim-pack Velox C18 1.8µm, 2.1 x 50mm	Analytical column
220-91394-07 220-91394-02*	Column, LC, Shimadzu Nexcol C18 5µm, 50 x 3.0mm Column, LC, Shimadzu Nexcol C18 5µm, 50 x 3.0mm w/Test Mix	Delay column *Comes standard with HPLC install

Table 2: Summary of current standardized methods for PFAS analysis.
(*)Not published and with name subjected to change.

METHOD	EPA 537/537.1	EPA 533	EPA 8327	EPA Draft 1633	ASTM D8421-22	ASTM D7968-19
Sample	Drinking Water	Drinking Water	Ground/Surface/ Wastewater	Aqueous, solid (soil, biosolids, sediment), tissue samples	Aqueous (municipal and industrial wastewater, leachate)	Soil, Sediment, Sludge
Sample Preparation	Solid phase extraction (polymeric sorbent)	Solid phase extraction (anionic sorbent)	Cosolvation + direct injection	Solid phase extraction (anionic sorbent) or solvent extraction + clean-up	Cosolvation + direct injection	Solvent extraction + direct injection
Quantitation	Internal standard calibration (1 MRM)	Isotopic dilution	External calibration	Isotopic dilution	External calibration (2 MRMs) Isotopic dilution optional	External calibration (2 MRMs + ion ratio)
Targets	EPA 537.1 – 18 EPA 537 – 14	25	24	40	44	21
Shimadzu Platform	**Triple Quad** LCMS-8045 LCMS-8050	**Triple Quad** LCMS-8045 LCMS-8050	**Triple Quad** LCMS-8050 LCMS-8060 LCMS-8060NX	**Triple Quad** LCMS-8045 LCMS-8050 LCMS-8060 LCMS-8060NX	**Triple Quad** LCMS-8050 LCMS-8060 LCMS-8060NX	**Triple Quad** LCMS-8050 LCMS-8060 LCMS-8060NX

ULTRA FAST MASS SPECTROMETRY


LCMS-8040


LCMS-8045


LCMS-8050


LCMS-8060NX


LCMS-2020


LCMS-2050


Q-TOF LCMS-9030

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