An alternative ionization technique for LC-MS/MS analysis of perfluoroalkyl substances (PFAS) in environmental samples

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INTRODUCTION

LC-MS/MS using Electrospray Ionization (ESI) is widely accepted as the standard technique for PFAS analysis. UniSpray Ionization (USI) is a novel atmospheric ionization technique for LC-MS/MS analysis that was evaluated with respect to PFAS analysis to determine if it provided enhanced ionization performance for this class of important compounds. Electrospray and UniSpray techniques were compared using the same set of water and soil samples and same analysis methods.

METHODS

How Does UniSpray Work?

UniSpray is a novel atmospheric ionization technique that allows for multimode ionization of both polar and non-polar analytes in a single injection. A simplified diagram of how UniSpray ionization works is show in **Figure 1**. The column effluent is nebulized by a grounded, heated probe and directed onto a high voltage stainless steel pin. Ionization occurs on impact. The nebulized flow bends around the surface of the impactor pin into the sample cone due to the Coanda Effect. This mechanism creates smaller droplets and allows for increased ionization and sampling efficiency.

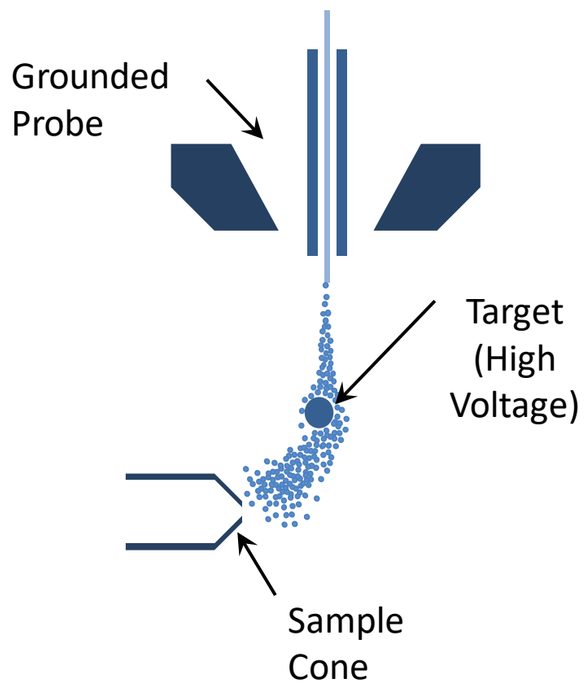

Figure 1. The ionization mechanism of the UniSpray source works by nebulizing flow onto an impactor pin.

Instrumental Conditions

UPLC System:	ACQUITY UPLC® I-Class PLUS
Column:	ACQUITY BEH C18 2.1x100 mm, 1.7µm
Mobile Phase A:	95:5 water:methanol + 2 mm ammonium acetate
Mobile Phase B:	Methanol + 2 mM ammonium acetate
Column Temp:	35°C
Sample Temp:	4°C
Strong Needle Wash:	90:10 methanol:water
Week Needle Wash:	50:50 water:methanol
Injection Volume:	30 µl

Gradient:

Time (min)	Flow (mL/min)	% A	% B
-	0.3	100	0
1	0.3	80	20
6	0.3	55	45
13	0.3	20	80
14	0.4	5	95
17	0.4	5	95
18	0.3	100	0
22	0.3	100	0

Mass Spectrometer: Xevo TQ-S micro

Electrospray	UniSpray
Capillary Voltage: 0.5 kV	Impactor Voltage: 1 kV
Desolvation Temp: 350°C	Desolvation Temp: 400°C
Desolvation Flow: 900 L/hr	Desolvation Flow: 900 L/hr
Cone Flow: 50 L/hr	Cone Flow: 100 L/hr

Water and soil samples were provided by the United State Environmental Protection Agency (USEPA). Water samples (5 mL) included reagent, surface, ground, influent, and effluent water. Sand, silt, fat clay, and lean clay were provided as soil samples (2 g). All samples were spiked with unknown concentrations of PFAS before receiving. Sample preparation was performed in accordance to ASTM 7979 (water) and ASTM 7968 (soil).

RESULTS AND DISCUSSION

The performance of UniSpray ionization for PFAS was compared to the well characterized technique of Electrospray. The same set of samples was analyzed using both ionization techniques. A majority of PFAS evaluated experienced an increase in intensity and peak area when using UniSpray ionization. Signal to noise (S:N), when using UniSpray as the ionization technique was equal or better for the PFAS evaluated when compared to Electrospray. A demonstration of the increase in S:N can be seen in **Figure 2**. The increase in both peak area and S:N allows for lower detection limits to be achieved. For the compounds that only had similar S:N but an increase in peak area, this allows for easier and more accurate quantitation at low concentrations.

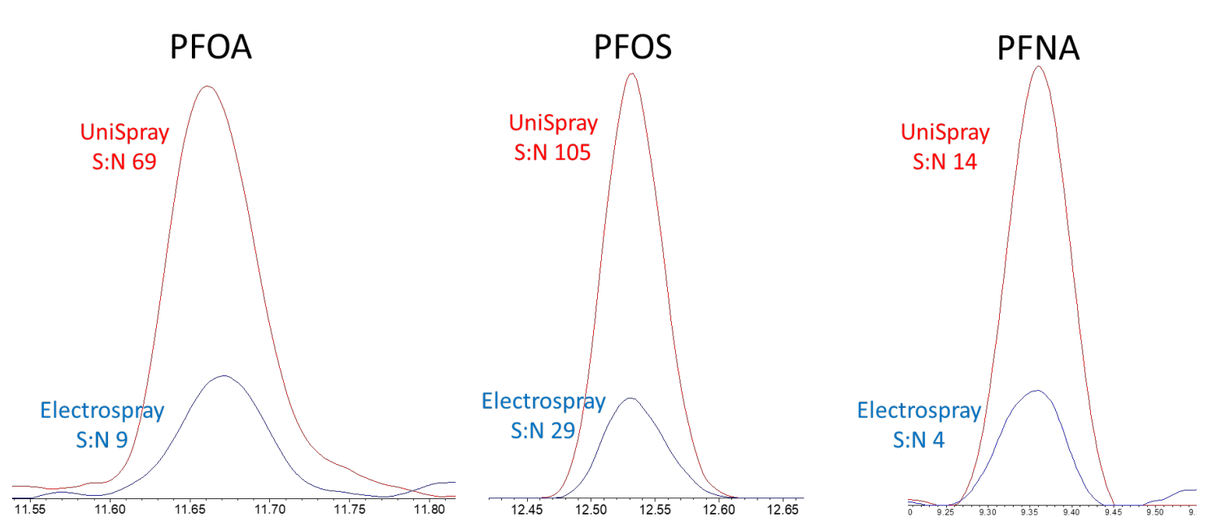

Figure 2. Signal:Noise (S:N) and peak response comparison between UniSpray (red) and Electrospray (blue) demonstrated with PFOA, PFOS, and PFNA peaks.

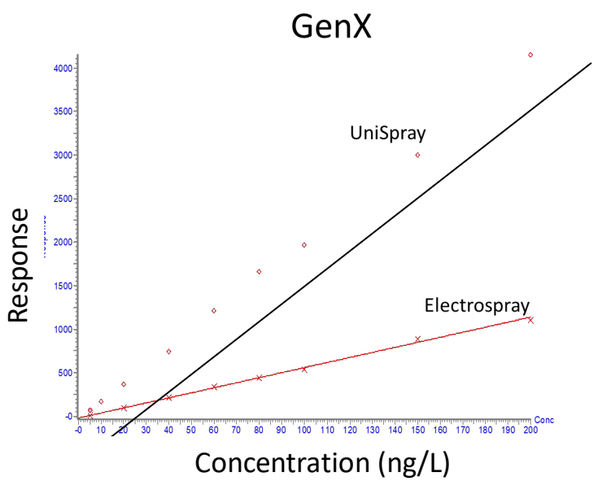

Figure 3. An example of GenX demonstrating the overall increase in peak response for GenX over the calibration range.

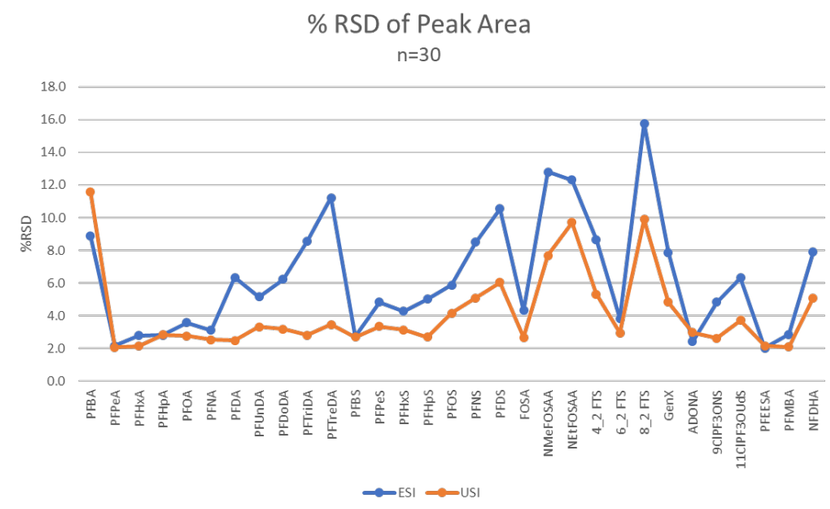

Figure 4. Evaluation of robustness of Electrospray (blue) and UniSpray (orange) over 30 injections of a surface water sample.

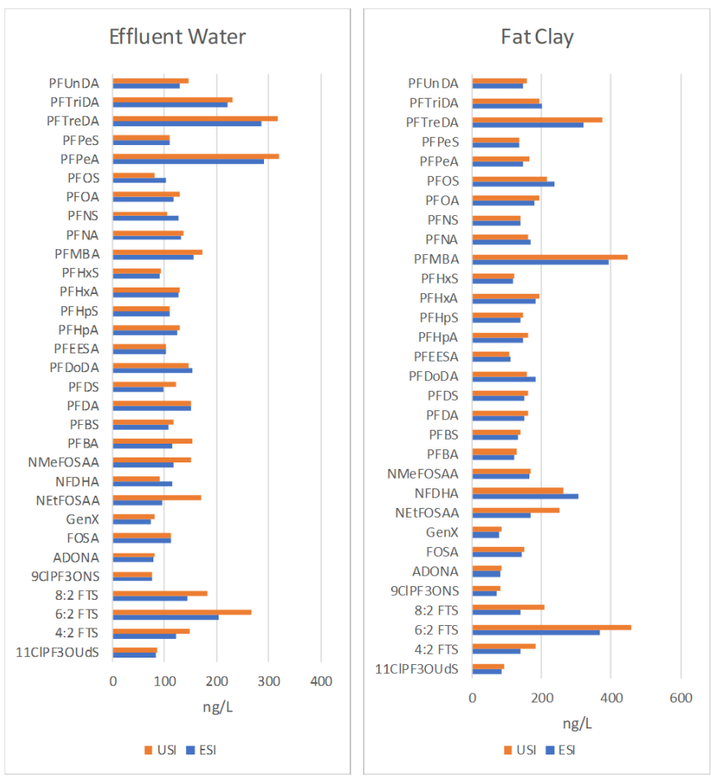

Figure 5. Quantitative comparison of PFAS in effluent water (left) and fat clay (right) extracts using UniSpray (orange bars) and Electrospray (blue bars).

A variety of water and soil extracts were evaluated using both ionization techniques. Figure 5 shows the calculated concentrations determined in two of the samples (effluent water and fat clay) using both ionization techniques. The calculated concentrations from UniSpray and Electrospray were very comparable demonstrating UniSpray is a suitable alternative ionization technique for routine sample analysis and quantitation. This also demonstrates the increase of ionization experienced in UniSpray does not create any increase in matrix interference or matrix effects.

Figure 3 uses the PFAS compound GenX (HFPO-DA) to demonstrate the increase in response seen using UniSpray over the calibration range, where response is plotted on the y axis and concentration on the x axis. This increase in response, especially at lower concentrations, allows for easier automated integration and more accurate quantitation.

The robustness of each ionization technique was also evaluated by performing 30 replicate injections of a surface water sample. The %RSD of the peak areas across the 30 injections were all within 15 % (**Figure 4**). A majority of the peak area RSDs from the Electrospray injections were under 10%, while a majority were under 5% for UniSpray. The slight reduction of RSD experienced by UniSpray could potentially be attributed to the increased peak areas which inherently will reduce uncertainty in these values.

CONCLUSIONS

- **The direct injection technique for PFAS was adapted to a novel ionization technique**
- **The UniSpray ionization source provided enhanced ionization of most PFAS studied when compared to Electrospray ionization.**
- **UniSpray produced increased response and peak areas allowing for more robust quantitation at low concentrations**
- **An enhancement in signal to noise was experienced with some compounds when analysis was performed using UniSpray allowing for lower detection limits of these compounds.**
- **UniSpray ionization was determined to be as robust of an ionization technique as Electrospray for the analysis of PFAS in a variety of water and soil samples with RSDs < 10%.**
- **UniSpray has been demonstrated to be a viable alternative ionization technique for LC-MS/MS analysis of PFAS in complex environmental matrices.**

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