

Paper Spray Mass Spectrometry with On-Paper Electrokinetic Manipulations: Sub Part-Per-Trillion Detection of Per/Polyfluoroalkyl Substances and Opioids in Water

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Abstract

This work describes a simple, 3D-printed device that enables low or sub part-per-trillion detection of per- and polyfluoroalkyl substances (PFAS), opioids, and other small molecules by paper spray mass spectrometry (MS) without solid phase extraction or other sample preparation. Using glass fiber filter papers within a 3D printed holder, the device stacks, separates, and desalts charged molecules on paper prior to spray into the mass spectrometer. Due to counter-balanced electroosmotic flow and electrophoresis, charged analytes stack on the paper and desalting occurs in minutes. One end of the paper strip was cut into a sharp point and positioned near the inlet of a mass spectrometer. The stacked analyte bands move toward the tip with the EOF, and paper spray ionization occurs directly from the tip. We demonstrated the practical utility of the device by quantitatively analyzing PFAS in tap water with sub-ppt detection limits in less than ten minutes with no sample pretreatment. The crucial parameters for successfully coupling electrokinetic manipulations with paper spray MS were investigated and optimized to enable stacking, separation, and MS ionization of both positively and negatively charged analytes.

Method

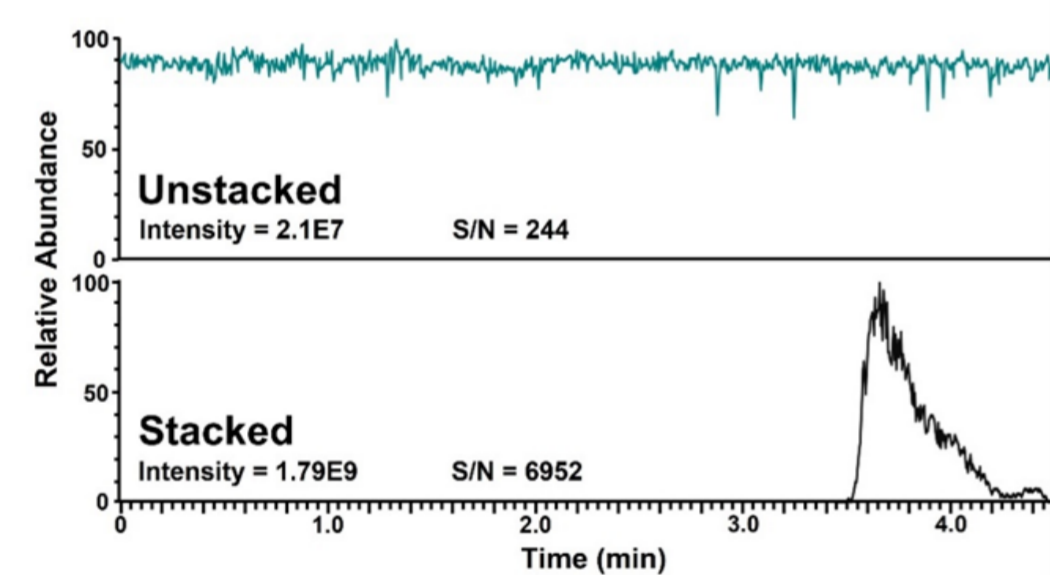
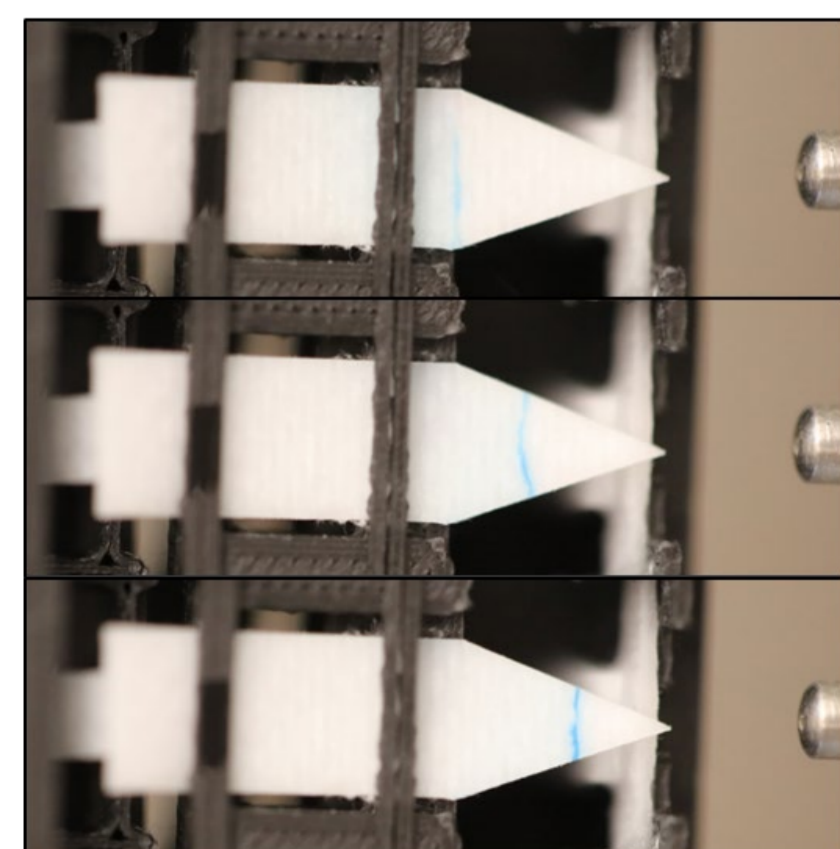
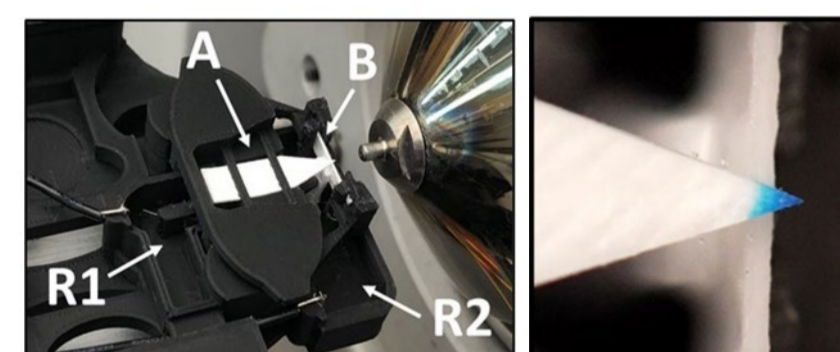


Figure 1. Top: The unstacked paper spray MS extracted ion chromatogram. Bottom: paper spray MS with EK stacking of the same concentration

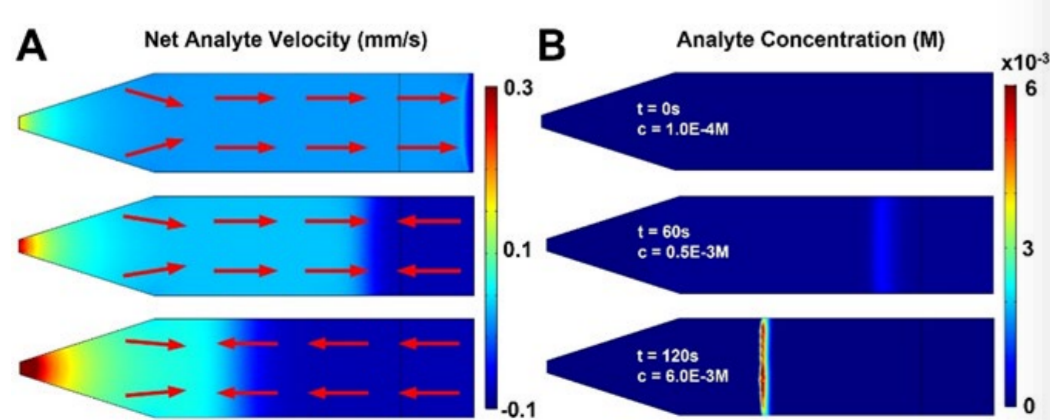
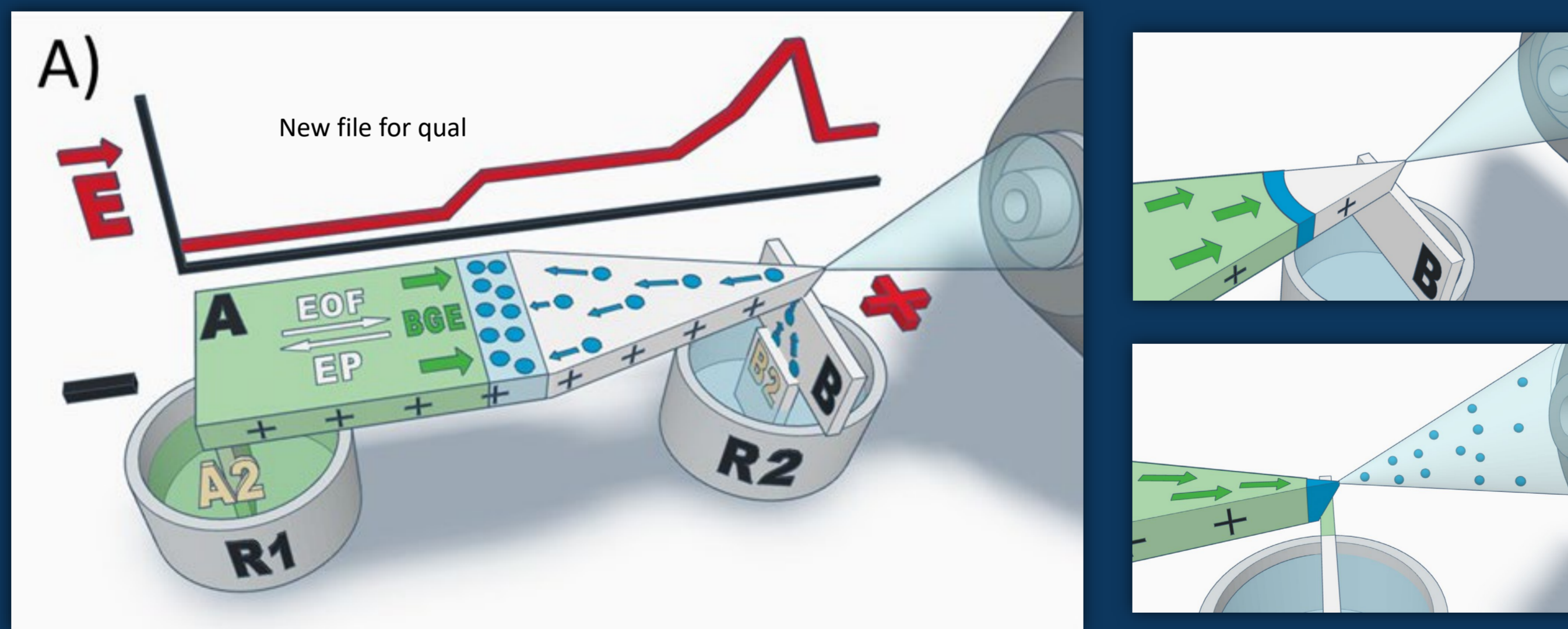


Figure 2. Methylene blue molecules stacked via FASS in the central region of the spray substrate. EOF in the direction of the spray tip transports the sample band towards the MS inlet.

Paper spray mass spectrometry with on-line electrokinetic stacking, separations, and desalting enables rapid, low-cost, and highly sensitive analysis.



Results

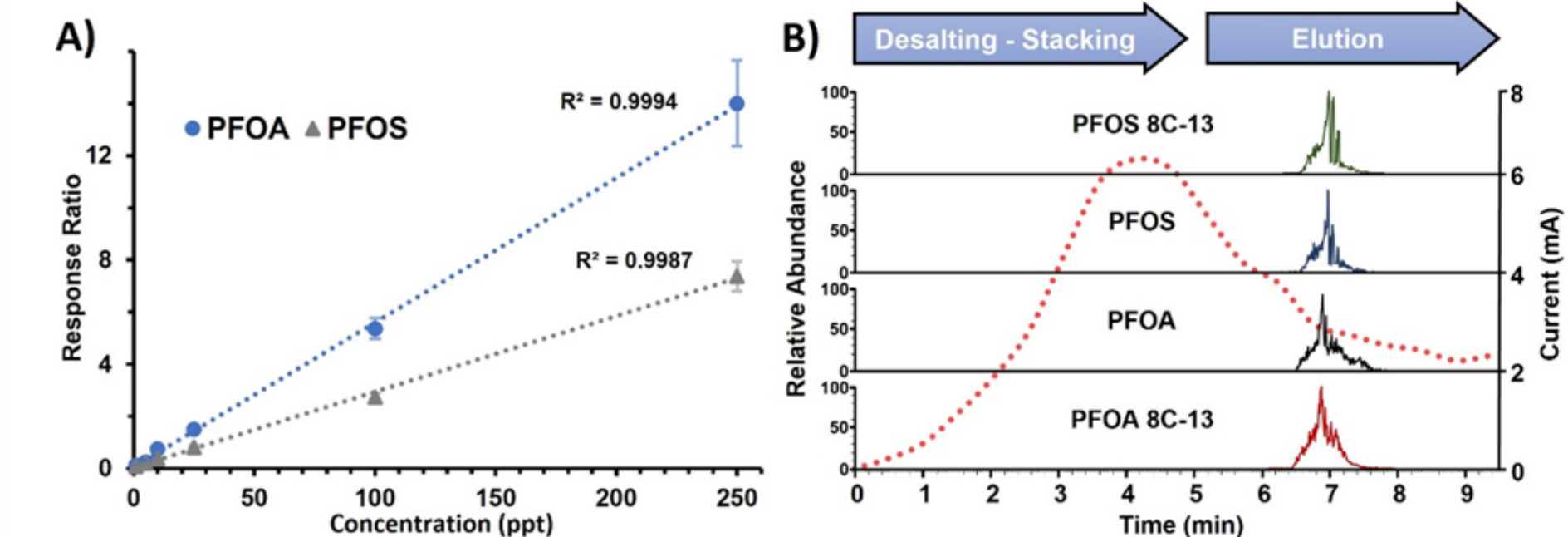


Figure 3: (A) Calibration curves for PFOA and PFOS. (B) MS/MS selected ion-monitoring electropherograms with overlaid current (dotted line) at 420 V of applied potential between R1 and R2.

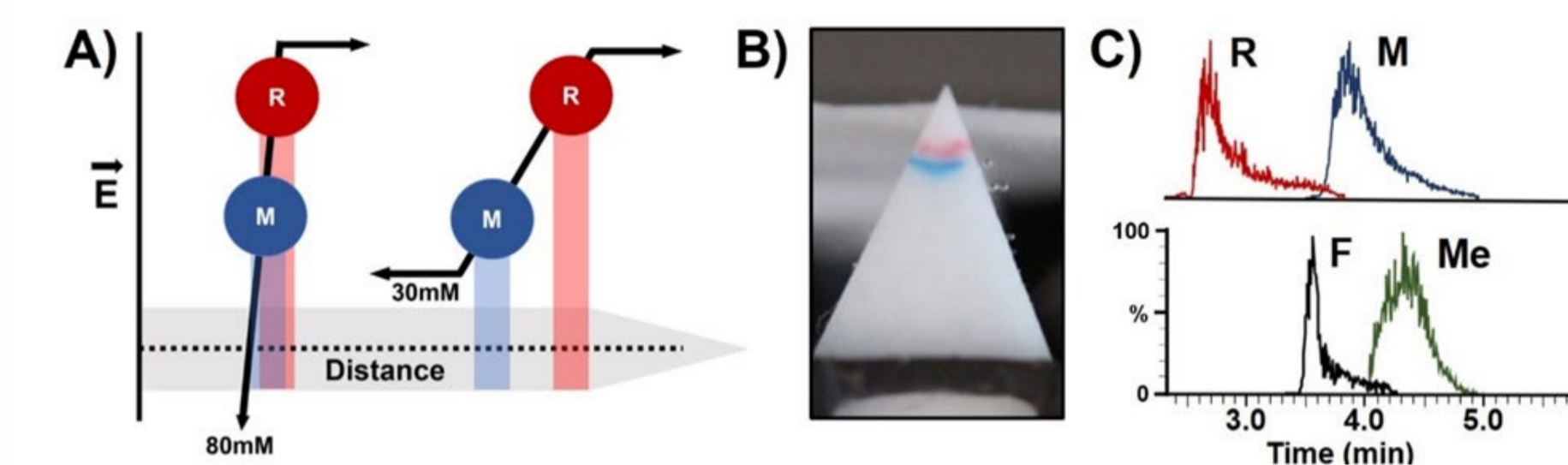


Figure 4: (A) FASS separation of methylene blue [M] and rhodamine 6G [R] occurred because the mobility of M is higher than R, causing it to stack farther down the electric field gradient. Reducing the steepness of the conductivity gradient promoted separation

	Table 1. LODs for Selected Analytes	
	Stacked	Regular
Cocaine	7.2 ppt	137 ppt
Fentanyl	3.9 ppt	80µl Positive mode 155 ppt
Morphine	9.5 ppt	931 ppt
Angiotensin II	0.1 ppb	20 ppb
PFOS	0.29 ppt	500µl Negative mode 270 ppt
PFOA	0.72 ppt	205 ppt

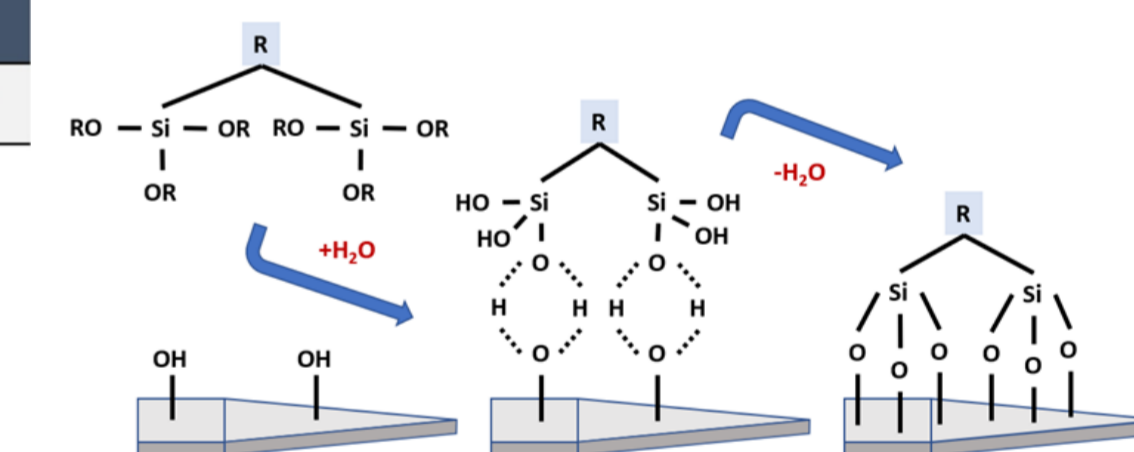


Figure 5. Silane reagents were used to impart positive surface charge onto the filter membranes

Conclusions

- This stacking device can accommodate large volumes of dirty samples for MS analyses in minutes
- The technique is much simpler and faster than solid-phase extraction followed by LC-MS
- PFAS contaminants were detected at sub-ppt levels from tap water without any sample cleanup.
- Mass-production of the cartridges could enable rapid and timely analyses, while the improved sensitivity and simplicity of the equipment could enable use of portable mass spectrometers



Acknowledgements

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