

Electronic Supporting Information
for
Photoacid generator formation for the selective enrichment of
perfluoroalkyl sulfonates and their direct analysis by MALDI-TOF-MS

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Mass spectra of PFOS using different matrices for MALDI-TOF-MS analysis

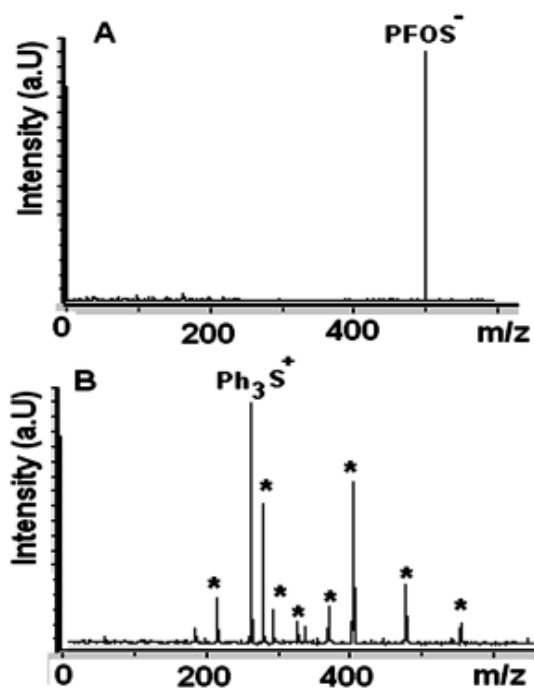


Fig. S1 A: mass spectrum of TPA (20 pg) in negative ion mode. B: mass spectrum of TPA (20 pg) in positive ion mode (Peaks denoted by “*” represent others product ions of TPA).

Matrix function of triphenylsulfonium group

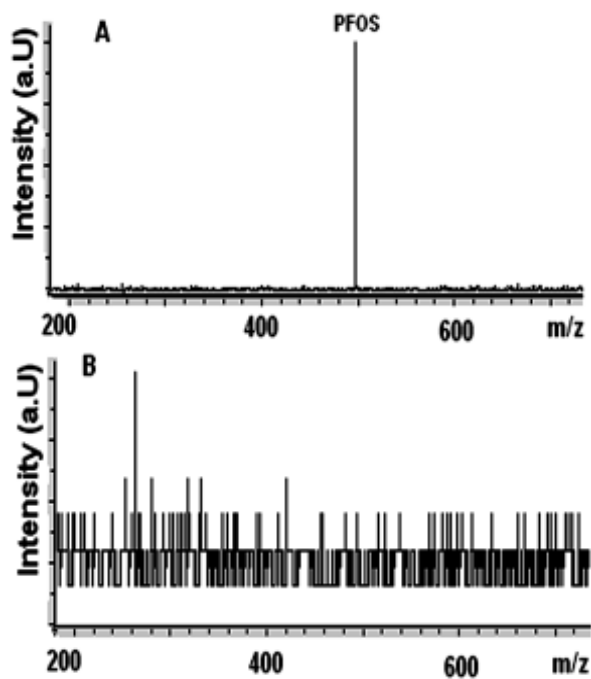


Fig. S2 A: mass spectrum of TPA (20 pg); B: mass spectrum of PFOS (20 pg without matrix assistant).

Table S1 The accuracy and precision of the described MALDI-TOF-MS method.

Analyte	Conc.level (ng/L)	Intraday (n=5) recovery % (RSD%)	Interday (n=25) recovery % (RSD%)
PFOS			
	0.3	92 ^a (11) ^b	88 (16)
	7.0	101 (9)	109 (12)

a The mean recovery

b The relative standard deviations (RSD%) are given in parentheses

Table S2 Matrix effect of environmental water samples on the recovery of PFOS in 500 mL water samples spiked with 2.0 ng L⁻¹ of standard PFOS(n=4).

Water samples	The mean recovery % of PFOS	% RSD (n=4)
Deionied water	98	5
Tap water	94	6
Gaobeidian wastewater	88	6
Xiaoqinghe river water	90	4

Table S3 Mean concentrations $\pm$ standard deviation ($n = 5$) of PFOS detected in real water samples, and the spiked recovery of PFOS obtained by spiking the target analytes.

Water Sample	PFOS (ng L ⁻¹) Detected by MALDI-TOF-MS	PFOS (ng L ⁻¹) Detected by LC-MS/MS ^[18]
Tap Water		
Background conc. (ng L ⁻¹ , n=5)	0.38 $\pm$ 0.10	nd ^a
Spike recovery (% n=5)	105 $\pm$ 4	112 $\pm$ 4
Xiaoqinghe River Water		
Background conc. (ng L ⁻¹ , n=5)	1.08 $\pm$ 0.06	0.96 $\pm$ 0.06
Spike recovery (% n=5)	93 $\pm$ 5	63 $\pm$ 2
Gaobeidian Wastewater		
Background conc. (ng L ⁻¹ , n=5)	3.30 $\pm$ 0.05	3.22 $\pm$ 0.02
Spike recovery (% n=5)	87 $\pm$ 5	65 $\pm$ 6

^a Not detected.