

A new Online SPE/LC/MS/MS method for screening Perfluorinated Compounds (PFCs) in Waste Water

Carlos Gil¹; Norbert Helle²; Meike Baden²; Juergen Wendt³; ¹ Gerstel GmbH&CoKG Muelheim an der Ruhr, Germany; ² TeLA GmbH, Bremerhaven, Germany; ³ Agilent Technologies Sales and Support GmbH, Waldbronn, Germany

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Introduction

Perfluorinated compounds (PFCs) are a family of fluorine-containing chemicals with unique properties to make materials stain and stick resistant. Perfluorinated compounds are very stable, making their degradation in nature a slow process. International standardization established a method utilizing LC/MS/MS for the determination of PFQA and PFOS. Aside from these primary target compounds, other PFCs were brought into focus lately. Depending on the sample matrix, an extensive sample preparation is often necessary. This work describes a new SPE/LC/MS/MS method, which combines automated solid phase extraction with LC/ Triple Quadrupole MS for the screening of relevant perfluorinated compounds in waste water.

Experimental

Chromatographic separation and MS Detection were performed using an Agilent 1200 Rapid Resolution LC and a 6410 Triple Quadrupole Mass Spectrometer. A Gerstel MultiPurpose Sampler with an automated SPE accessory was integrated into the LC/MS/MS system. A complete picture of the system set-up is shown in **Figure 1**.

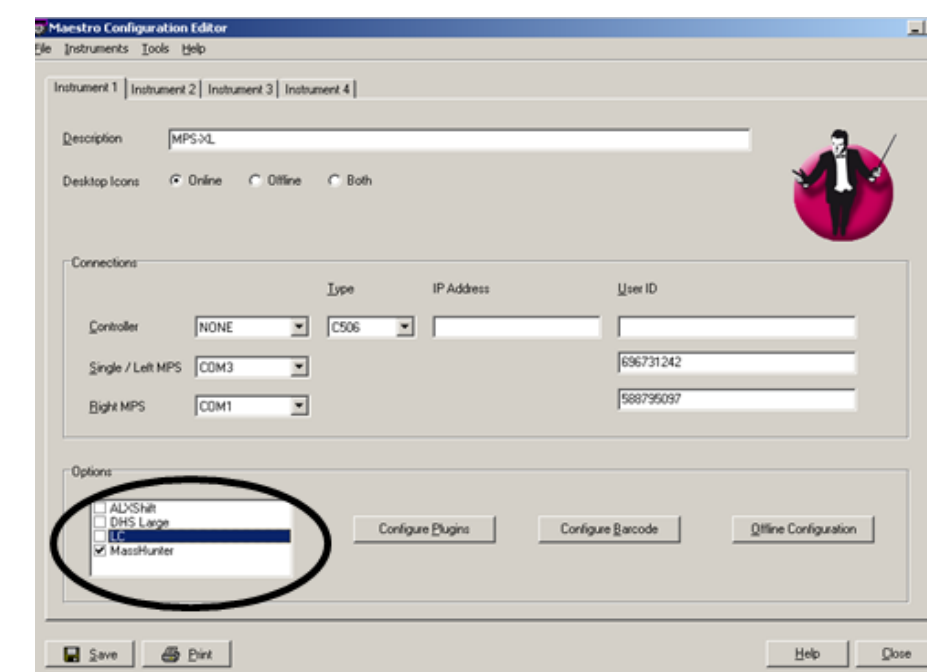
Figure 1) Instrument Set-up



The SPE system is controlled by the GERSTEL MAESTRO software. All parameters for the various SPE steps can be entered with the aid of the PrepBuilder. The result is a prep sequence, which can be saved, loaded and edited at any point in time. A link to the Agilent MassHunter Software, which controls the LC/QQQ system, is now implemented in MAESTRO Configuration Editor (**Figure 2**).

Experimental

Figure 2) MAESTRO Configuration Editor



The parameters for the complete LC/MS/MS method, including the MRM transitions, are summarized in **Table 2** and **3**.

Table 2) LC/MS/MS method

Column:	Maisch Reprosil C18HD (50*2,1 mm, 3 um)	MS: Agilent 6410 QQQ
Column temp:	40°C	Ionization Mode: ESI neg.
Mobile phase:	A: 5mMol Ammoniumacetate in water B: Methanol	Source Parameters:
Flow rate:	0.3 ml/min	Gas Temp: 350°C Gas Flow 10l/min
Gradient:	20 % B at 0 min; 100 % B at 10.0 min 100 % B at 14.0min; 20% B at 15.0 min	Nebulizer: 50 psi Capillary:3000 V
Stop time:	20 min	Post time: 5 min
Inj Vol:	2 ul	

Table 3) MRM transition of the PFTs

Compound	Precursor [M-H]	Frag(V)	CE1(V)	Product Ion 1 [m/z]	CE2(V)	Product Ion 2 [m/z]
PFPeA	263	60	1	219	-----	-----
PFHxA	313	80	1	269	10	119
PFHpA	363	80	5	319	15	169
PFOA	413	80	5	369	15	169
PFNA	463	80	10	168	15	138
PFOS	499	120	15	127	15	97
PFDA	513	80	40	165	50	153

Table 1) SPE-Method

Sample is filled in a 20 ml vial and the vial is placed in the MP-Sampler

Automated SPE:

- Conditioning of the SPE cartridge (Oasis WAX, 150mg) using 2 ml MeOH/NH₃, 2ml MeOH and 2 ml H₂O
- Introduction of 10 ml sample to the cartridge
- Drying of the cartridge with N₂ for 1 min
- Rinse with 2 ml Acetate-Buffer
- Drying of the cartridge with N₂ for 1 min
- Elute with 2ml MeOH and 2ml NH₃/MeOH
- Transport vial to the sample tray for injection

Results and Discussion

Figure 3) Workflow of a conventional sequence vs. Prep Ahead

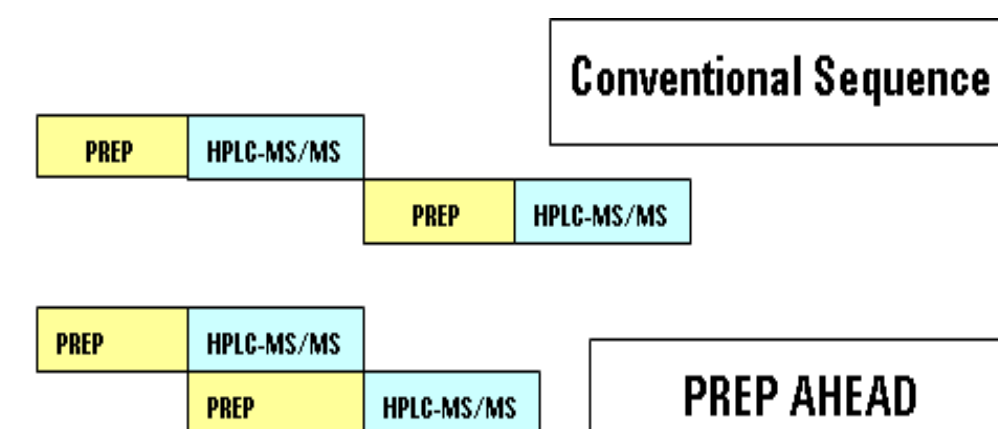


Figure 4) Overlay of 8 separate sample preparations of a waste water sample, spiked with 0.5 ng/ml

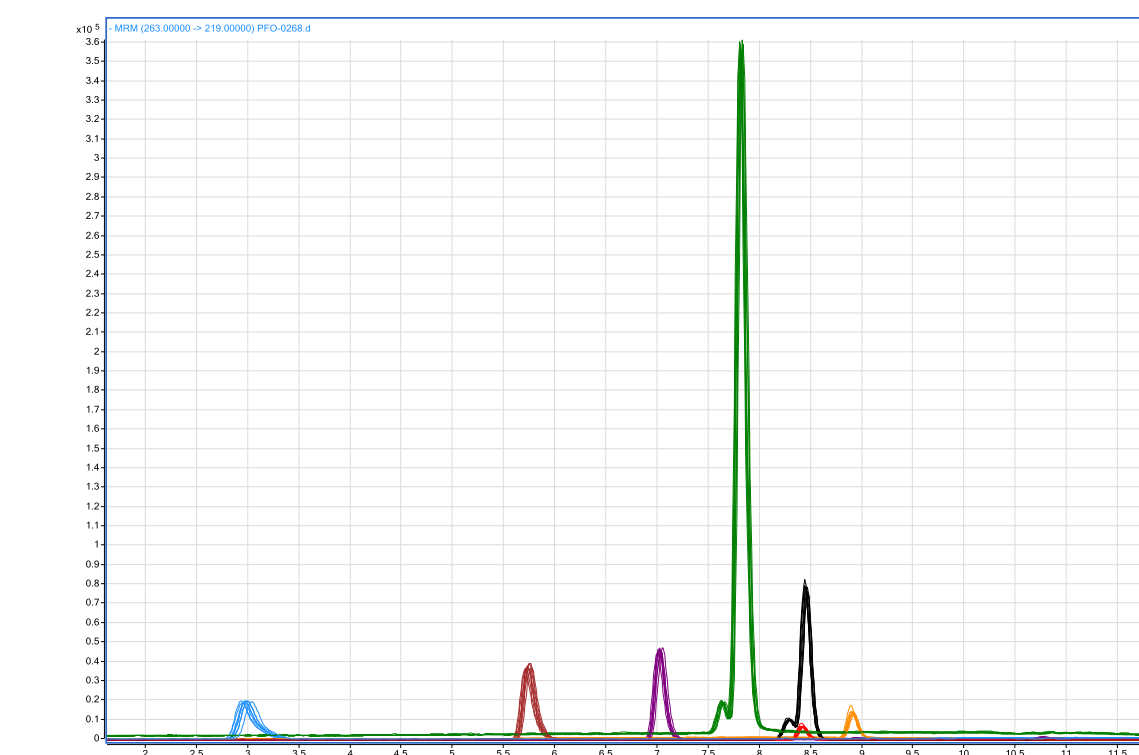


Figure 5) Reproducibility of the SPE-Method (Waste water spiked with 5 ng/ml PFT)

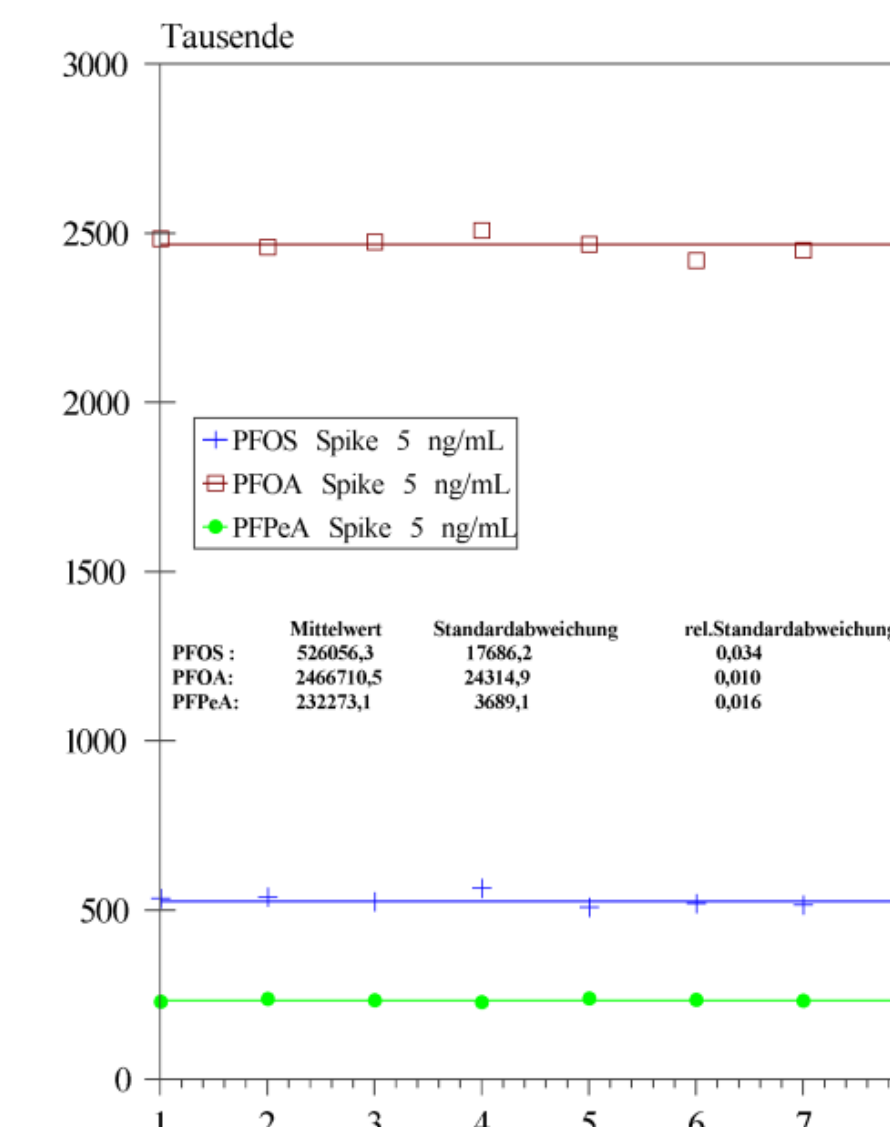
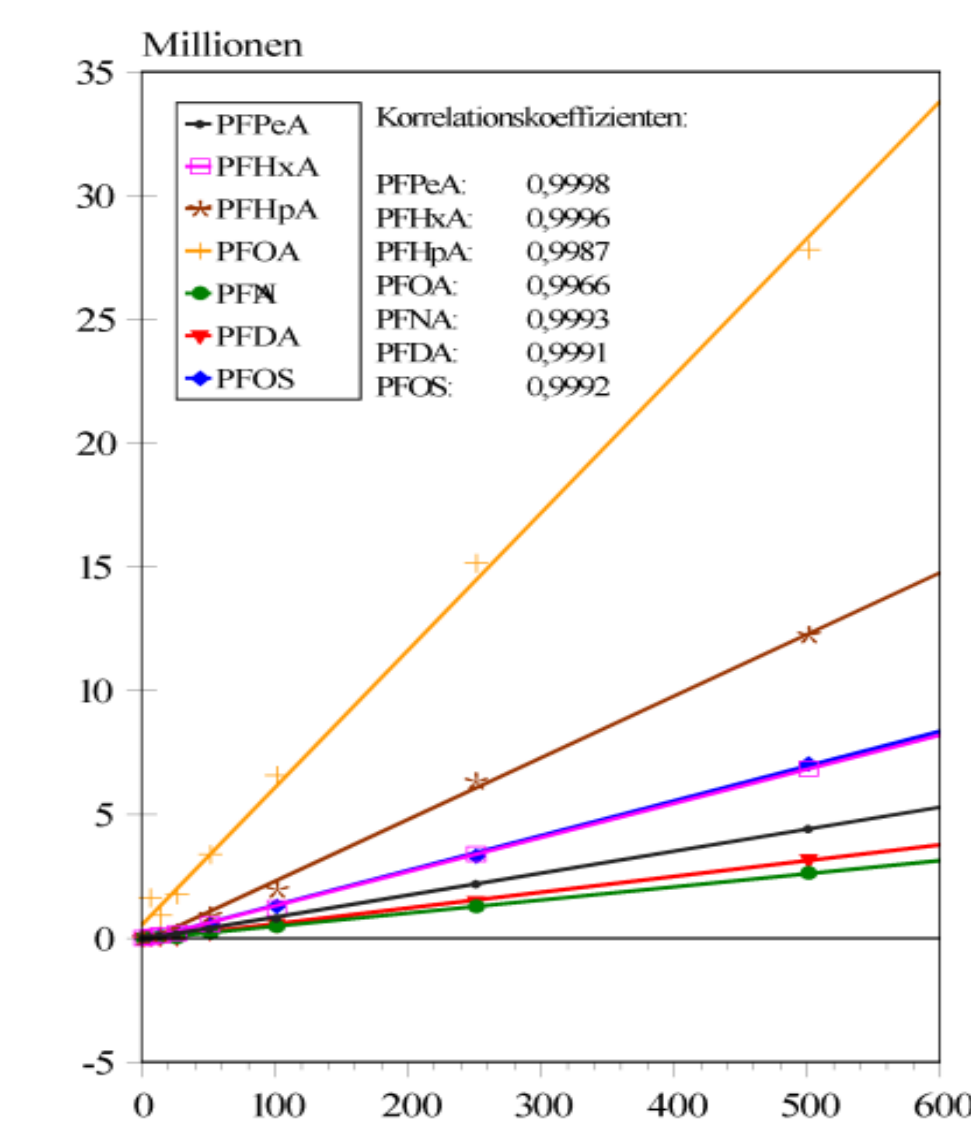


Figure 6) Calibration Curves for the PFTs from 5-500 ng/ml (in matrix) using the SPE-LC/MS/MS method



Results and discussion

Online SPE combined with a direct sample introduction into the LC/MS/MS system enabled an automated clean-up step immediately followed by the analysis of seven perfluorinated compounds. In order to increase the sample throughput, the SPE/LC/MS/MS-system was operated in PREP AHEAD mode (**Figure 3**). This means that the automatic sample preparation (20 min) and the LC/MS/MS-analysis were nested. While measuring sample 1, the sample preparation of sample 2 was executed in parallel and the eluate could be injected directly after the end of sample run 1. The TICs of eight separate sample preparations of a waste water sample are overlaid in **Figure 4**., demonstrating a good reproducibility for all compounds. A statistical evaluation of the reproducibility is summarized in **Figure 5**. The RSD% for PFOS, PFOA and PFPeA are in the range from to 1.0-3.4 %, with recovery rates from 82-106%.

The defined calibration range for the PFTs in waste water was 5-500 ng/ml. A seven level calibration with three replicate injections for each compound was measured. The calibrations were linear over the range range tested and the correlation coefficients were > 0.99 for all seven perfluorinated compounds (**Figure 4**).

Conclusions

- The described Online SPE/LC/MS/MS system enables an automated clean-up by SPE immediately followed by analysis of the perfluorinated compounds.
- The PREP AHEAD mode allows a higher sample throughput, while sample preparation and LC/MS/MS analysis are nested.
- The method shows good reproducibility and recovery for the PFT in the difficult matrix waste water.
- In the future, other PFTs, which are defined in the german DIN 32 645, will be integrated in the described Online SPE/LC/MS/MS method.