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External trap-and-release membrane inlet for photoionization mass spectrometry: Towards fast direct analysis of aromatic pollutants in aquatic systems

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Abstract

RATIONALE:

Fast and sensitive detection of aromatic hydrocarbons (AHs) in water is of high importance because of their high impact on human health and the environment. For this, resonance-enhanced multiphoton ionization (REMPI) coupled to trap-and-release membrane-introduction mass spectrometry (T&R-MIMS) offers the possibility of sensitive on-line water analysis with minute time-resolution.

METHOD:

REMPI is a versatile tool for sensitive gas-phase analysis, in which AHs are selectively ionized in complex gas mixtures by the subsequent absorption of at least two photons. In T&R-MIMS, selective extraction and enrichment of analytes from the water can be achieved by using semipermeable membranes. By the subsequent stimulated desorption of enriched compounds mass spectrometric detection is enabled.

RESULTS:

We present an external T&R-inlet for hollow fiber membranes coupled to REMPI time-of-flight mass spectrometry (REMPI-TOFMS), which enables direct and sensitive detection of semi-volatile AHs in water. In laboratory experiments, spiked water samples were analyzed. For the investigated compounds, limits-of-detection (LOD) in the range of 1-47 ng/L were determined. The LODs are ca one order magnitude lower than in previously reported continuous membrane-introduction (MI) approach using a planar membrane. Further improvement of LOD may be realized by extending the trapping time and by increasing the release temperature. Furthermore, the system was applied to investigate different fuels suspended in water and real water samples. The obtained data is in good agreement with findings of a former study.

CONCLUSIONS:

In the framework of the present study, we demonstrate the high potential of the combination of REMPI and T&R-MIMS in the form of a newly developed external hollow fiber membrane inlet. With the developed system, semi-volatile AHs can be directly detected down to ng/L-levels on a minute time basis. The approach thus may pave the road to future ship application in marine sciences, natural resources exploration or pollutant and hazard detection.

Keywords: resonance enhanced multiphoton ionization, membrane introduction, mass spectrometry, trap-and-release, (polycyclic)aromatic hydrocarbons, water

1 Introduction

Aromatic hydrocarbons (AHs) in aquatic systems have been extensively monitored for decades due to their considerable impact on environment and health [1-4]. One commonly applied monitoring strategy for AHs is the collection of discrete water samples, their transport to the laboratories and proper storage, and their subsequent analysis [5-8]. The analysis thus comprises sample-preparation steps as well as the final detection and quantification of the analytes. In particular, the time-consuming sample-pretreatment procedures limit the number of samples to be analyzed. The sample number is further restricted by logistic limitations. The resulting low temporal and spatial resolution complicates early recognition of acute pollutions or neglects important intermediate events and, thus, ecological important aspects are not taken into account. Furthermore, it is possible that the transport and storage, as well as the preparation steps, influence the collected water samples (e.g. contamination, loss of substance, partitioning between dissolved and particulate fraction), which lead to the analyzed water not necessarily being representative of the water at the sampling site [9,10].

In recent years, several approaches were investigated to overcome the problems resulting from this traditional workflow. Solid-phase (micro-)extraction approaches (SP(M)E), for instance, were applied to on-line extraction of polycyclic aromatic hydrocarbons (PAHs) from different complex matrices [11,12]. In SP(M)E, compounds are enriched by sorption on a solid sorbent directly out of the water. The sorbent can be filled in cartridges, immobilized on disks as well as thin fused silica fiber. If SPME is combined with powerful analytical techniques, such as atmospheric pressure laser ionization mass spectrometry, very sensitive detection of PAHs can be performed [13].

A further possibility is the transfer of aqueous AHs into the gas phase followed by an immediate detection by e.g. mass spectrometry. For such an online detection of AHs in the gas phase, resonance-enhanced multiphoton ionization (REMPI) coupled to time-of-flight mass spectrometry (TOFMS) is one of the most sensitive on-line and real-time techniques, which is well known from many applications, such as combustion processes or environmental monitoring [14-18]. REMPI is a laser-based soft ionization technique producing mainly molecular ions. If a laser wavelength in the UV-region is used, the unique ionization scheme provides a selective ionization of AHs in complex gas mixtures, while other organic species e.g. alkanes as well as bulk gases such as N_2, O_2 or H_2O are disregarded.

REMPI has already been applied for the direct analysis of AHs in liquid samples (e.g. crude oils dissolved in acetonitrile/dichloromethane) by direct infusion [19]. However, the high matrix content of environmental water bodies impedes the application of this technique. As an alternative, membrane inlets for mass spectrometry can be utilized as introduction interfaces. Since its first application in the early 1960s by Hoch and Kok [20], membrane-introduction mass spectrometry (MIMS) has been proven to be a versatile tool for the fast analysis of dissolved gases and organic trace substances in aquatic systems [21-26]. In MIMS, selective extraction of dissolved compounds from the water phase into the MS is achieved by utilizing semi-permeable membranes. For non-polar compounds, membranes based on polydimethylsiloxane (PDMS) show the best performance and are widely used in the MIMS community. The underlying mechanism of MIMS is referred to as pervaporation, which can be described - in the case of amorphous membranes - by the solution-diffusion model of Reid and other workers [27,28]. In this process, dissolved analytes adsorb on the membrane surface at first and, by doing

this, a slight enrichment on the surface occurs. After this initial step, the adsorbed compounds dissolve into the membrane material and are transferred to the opposite side by diffusion. The subsequent evaporation from the opposing membrane surface releases the compounds into the gas phase. Hence, MIMS enables direct mass spectrometric analysis of dissolved organic compounds in environmental water.

Fundamental aspects of MIMS have been already reviewed in many publications [29-33]. Briefly, under steady state conditions, an equilibrium is established between compounds adsorbing on and those desorbing from the membrane. The resulting analyte flux through the membrane can be distinguished into steady-state and non-steady flux (I_{ss} and I_{ns}, respectively), whereas I_{ns} is referred to flux until reaching steady-state conditions. Derived from Fick's first law, I_{ss} and I_{ns} can be formulated as shown in Eq.1 and Eq.2, respectively.

$$I_{ss} = ADK \left[\frac{c_{sample}}{d} \right] \qquad (1)$$

$$I_{ns} = I_{ss} \left[1 - 2 \cdot exp \left(\frac{-n^2 \pi^2 Dt}{d^2} \right) \right] \qquad (2)$$

where A: membrane area; D: diffusion coefficient; K: distribution coefficient; c_{sample}: concentration of the analyte inside the sample; d: membrane thickness

It has already been shown that for volatile organic compounds (VOCs) the rate of the pervaporation process is determined by the diffusion through the membrane [34]. In contrast, for higher boiling point compounds the evaporation from the membrane surface can become the rate-limiting factor. The desorption of compounds from the membrane can be enhanced by different strategies. The temperature of the whole membrane can be controlled indirectly by thermalizing the water conducted to the membrane. Herein, the temperature of the membrane does not only affect the evaporation from the surface. Moreover, higher temperatures lead to an increase of diffusion through the membrane and, thus, to shorter response times. However, the solubility of organic compounds in PDMS generally decreases with increasing temperature [32]. Furthermore, the boiling point of water restricts the membrane temperature to values below 100°C, which is insufficient for most semi-volatiles. For an effective desorption from the membrane surface, different techniques can be applied. The utilization of laser desorption from the membrane surface, for instance, leads to increased sensitivity of MIMS for semi-volatile PAHs [35].

Alternatively, a promising approach for stimulated desorption from the membrane surface is trap-and-release (T&R), first utilized for MIMS by Lauritsen et al [36,37]. In their work, a hollow fiber membrane was placed directly inside an electron ionization (EI) ion source in close vicinity to the filament. By an alternating introduction of water and nitrogen into the membrane tube, semi-volatile organic compounds (SVOCs) were trapped and released depending on the heat capacity of the medium flowing through. By doing this, compounds such as toluene, phenol, phenanthrene and caffeine became accessible for MIMS.

Several papers have been published using T&R for the determination of organic compounds in air and water with MIMS [38-43]. For instance, Thompson et al used a coaxial heated membrane inlet design coupled to a Polaris-Q ion trap to determine SVOCs such as guaiacol, naphthalene and fluorene down to 4 ng/L in aqueous samples with a 10 min sampling/trapping time. Sparrapan et al determined LODs of phenolic compounds in water in the range of 2-15 µg/L using a similar design to Lauritsen et al [36,37]. Creaser et al[43] were able to determine dimethyl sulfoxide in equine urine at lowest concentrations of 6 mg/L with T&R-MIMS.

In contrast, other than the work of our group, only two studies have been exploited the high potential of the combination of REMPI and MIMS till now [44,45]. In both studies, direct insertion membrane probes (DIMPs) were utilized for the investigation of different AHs in spiked water. Soni et al were able to achieve LODs of 100 ng/L for pyrene using DIMP coupled to a GCQ ion trap equipped with a KrF-excimer laser (wavelength of 248 nm) for ionization. In the work of Oser et al DIMP was utilized for TOFMS with a Nd:YAG-laser (266 nm), while lowest LODs were achieved for xylene by extrapolation from measured concentrations in the range of 0.88 – 8.8 µg/L by 4 orders of magnitude down to ca 80 pg/L (calculated value for a signal-to-noise ratio (S/N) equal to three, as used in this work; calculation are based on presented LOD-values for a S/N=1 at a time resolution of 5s). However, DIMP setups need specially designed ion sources and bear a risk in case of membrane rupture.

External membrane inlets (EMIs) have already been proven as versatile and robust inlet devices for MIMS. EMIs can be easily interchanged between different analytical platforms. In addition, more than one can be used on one mass spectrometer, enabling the investigation of compounds with different polarities, if distinct membrane materials are used. Furthermore, in many cases the transfer line into the mass spectrometer can act as a security device restricting the water inflow in case of membrane rupture. Previously, we demonstrated the applicability of EMIs using sheet membranes for fast and continuous determination of different AHs by REMPI-TOFMS [46]. The published results therein indicate that for effective determination of higher boiling point compounds, stimulated desorption is of crucial importance.

Therefore, in this study we present an EMI setup for hollow fiber membranes, which can be used for sensitive and faster analysis of AHs by utilizing the T&R approach.

2 Materials and Methods

2.1 External Hollow Fiber Membrane Inlet (EHFMI)

FIGURE 1

The design of the final EHFMI as well as the whole experimental setup are presented in **Figure 1**. A polydimethylsiloxane (PDMS) hollow fiber membrane (Freudenberg Medical, Kaiserlautern, Germany; HelixMark, material: Wacker, Munich, Germany; Elastosil Rplus 4305/60; ID =1.47 mm; wall thickness = 250μm) is fitted with both ends on 1/16'' stainless steel capillaries (ID = 750 µm). For this purpose, the membrane was stored over several days in hexane. By doing this, the diffusion of hexane into the membrane leads to swelling of the PDMS and, thus, the inner diameter of the membrane increases. Afterwards, a spirally wound nickel wire (22 gauge) can be easily slid into the membrane tube, and the membrane can be subsequently tightly attached to the stainless-steel capillaries. This assembly is placed inside a 6 mm glass tube connected to the water stream by Swagelok connectors. The inner side of the membrane is supported by the nickel wire that is also used to resistively heat the membranes' inner surface. The water is transported by a gear pump (Model PQ12; Greylor Inc., Cape Coral, FL, USA) through the glass tube over the outside of the membrane at flow rates of 120 mL/min. Fast heating of the membrane is achieved, if the water is replaced by nitrogen. A small nitrogen gas stream is used to transfer the pervaporating molecules to the mass spectrometric system.

With the EHFMI setup, different techniques for measurements of water samples are possible, namely the open-end capillary approach (OEC) as well as the T&R technique. Briefly, in OEC, a continuous gas flow of nitrogen is guided through the inner side of the membrane tube and transfers the pervaporating molecules to the mass spectrometer. The gas flow is by the vacuum of the mass spectromemter, while valve V5 is open. In OEC, the membrane is continuously heated. The flowing water, however, cools the membrane to such an extent that no significant increase in membrane temperature occurs. After a defined sampling time has passed, the membrane is rapidly heated by replacement of the water surrounding the membrane by nitrogen.

In contrast, for T&R, the gas flow is prevented by closing V5, while cold sample water flows over the outside of the membrane tube. Thus, the compounds passing through the membrane, are trapped on the membranes surface or inside the membrane tube. After a defined trapping time, the water is pressed out of the glass tube as well as the connection between the glass tube and valve V6, and the membrane is dried to reduce the number of remaining water droplets. After switching valve V3, the analytes are released by rapid heating of the membrane and allowing a nitrogen flux similar to OEC (V5 open). The whole workflow of T&R is graphically summarized in **Figure 1**. It consists of four consecutive steps: trapping, washing, drying and release of the compounds. The optimized time intervals for each step are emphasized in Figure 3 with an overall analysis time of 280 s. These times are applied for each measurement if not otherwise stated. After each sample analysis the membrane was cleaned by washing with clean water and subsequent heating, which reduces possible carry-over effects.

2.2 Mass Spectrometric System
The homebuilt laser photo ionization mass spectrometry (PIMS) system has already been described in previous work [46]. Briefly, the TOF mass spectrometer (Stefan Kaesdorf GmbH,

Munich, Germany) comprises a two–stage Wiley/McLaren-type ion extraction, a two-stage ion-mirror and a multi– channel–plate detector. The homebuilt ion source is designed to accomplish the hyphenation of external as well as direct insertion membrane probes. The latter is planned to be tested in future studies for direct comparison of DIMP and EMI. Two turbomolecular pumps (TMU 521 and TMU 261, Pfeiffer Vacuum, Asslar, Germany) are used to differentially pump the ion source as well as the flight tube down to 2.2×10^{-5} mbar and 6.8×10^{-8} mbar, respectively. The TOF mass spectrometer is connected to the EHFMI via a heated fused silica capillary (inner diameter: 250μm; BGB Analytik, Rheinfelden, Germany) placed in close vicinity to the membrane, which restricts the gas flow into the ion source to ~ 2 mL/min and, in addition, acts as a security device in case of membrane rupture. A Nd:YAG laser (QuantaRay Indi 40-10; Newport Spectra-Physics, Darmstadt, Germany; averaged pulse energy: 1.8 mJ) is used to generate intense UV pulses of a wavelength of 266 nm (4th harmonic) at a repetition rate of 10 Hz, hitting the effusive molecular beam closely to the tip of the fused silica capillary. For data acquisition, two 8-Bit converter cards (Aquiris DP211 and DP110; Plane-les-Ouates, Switzerland) combined with a custom LabView program (Photonion GmbH, Schwerin, Germany) are used.

2.3 Investigated water samples

All chemicals were purchased as HPLC-grade from different suppliers. Mixed stock solutions were prepared by dissolving known amounts of selected AHs in isopropanol (Roth, Karlsruhe, Germany; purity 99.5). Aqueous standard solutions were prepared by diluting defined volumes of these stock solutions in tap water at a total volume of 1.0 L.

All the investigated compounds are listed in **Table 1**.

TABLE 1

3 Results and Discussion

3.1 Comparison of the open-end capillary (OEC) and the trap-and-release (T&R) approaches

FIGURE 2

For comparison of OEC and T&R, ion traces of toluene and *p*-xylene in spiked tap water obtained by EHFMI-REMPI-TOFMS @ 266 nm are presented in **Figure 2**. Before each measurement the membrane was washed with a continuous flow of tap water. In OEC, steady-state conditions are reached in approx. 1.5 min and 2 min of sampling time for toluene and *p*-xylene, respectively. These response times, however, are considerably longer than those of the sheet-membrane assembly presented in a former study[46] and can be attributed to increased thickness of the hollow fiber membrane. Nevertheless, both compounds show similar MIMS behavior, due to similarities in their vapor pressures. The detected differences in signal intensities are in good agreement with differences in the ionization yields of both substances with REMPI at 266 nm presented by Gehm et al [47]. For both compounds rapid heating of the membrane leads to an increase in signal intensity by a factor of 3 compared with steady-state flux due to enhancing evaporation rates from the membrane. Thus, the OEC approach is already

capable of improving signal to noise ratios compared with fully continuous measurements. Furthermore, **Figure 2** emphasizes that for toluene and *p*-xylene improved enrichment inside the membrane tube is achieved by applying T&R. By rapid heating, these compounds are transferred effectively as a peak into the mass spectrometer. If T&R is applied, signal heights compared with OEC are increased by a factor of 2 (1 min OEC vs 1 min T&R), and the whole analysis time can be reduced. Because of the enhanced sensitivity and shorter analysis times, T&R was chosen and optimized for all further experiments.

3.2 Determination of semi-volatile PAHs by T&R-EHFMI-REMPI-TOFMS

FIGURE 3

Representative ion traces of investigated PAHs in spiked tap water are shown in **Figure 3**. The trapping was performed at a water temperature of 20°C for a duration of one minute, followed by a 10 s washing step with clean tap water and one minute of drying the membrane with nitrogen. As expected ,the temperature inside the membrane tube drops if water evaporates from the membrane. **Figure 3** emphasizes that the compounds are effectively restrained by the cold membrane. The subsequent heating of the membrane up to temperatures of 170°C transfers the analytes as single peaks into the ion source of the TOF mass spectrometer. The corresponding peak widths are summarized in **Table 2** and refer to the width at 5% (FWFM) and 50% (FWHM) of maximum peak height. The FWFM values show lower variations than the values of FWHM, which can be attributed to variations in heating rates and, thus, variations in peak shapes. Effective desorption of compounds from the membrane is essential and can be provided by fast heating.

TABLE 2

Nevertheless, in some cases, water droplets remain on the membrane surface or between the membrane and the glass tube, which leads to much slower heating rates and impaired peak shapes. In addition, remaining water can produce cold spots resulting in double peaks as is presented in **Figure A1** (supporting information).

FIGURE 4

The repeatability of the system was tested by five consecutive measurements of the same samples (**Figure 4**). Between each measurement the membrane was cleaned two times by heating. For each cleaning step the whole sampling line was washed with pure water. The relative standard deviations of the peak areas of individual compounds range from 10 to 15%. Although these value are higher than obtained with other methods such as GC/MS, the results seem promising. In contrast, the signal heights show a much higher degree of variation (15-30%), which might result from the manual control of the valves and variations in heating rates. Therefore, the next step in progression and development will address these problems and eventually increase the performance of the whole system. For this, some strategies are possible. For instance, repeatability could be improved by the automatization of the workflow, especially the valve controls. Furthermore, the influence of the heating rate may be decreased, if a short cryo-focusing step is introduced between the EHFMI and the REMPI-TOFMS, similar to hyphenation of fast GC and photo ionization mass spectrometry [48]. For instance, if the compounds are desorbed from the membrane, they can be trapped on a fused silica capillary cooled by a Peltier element. After all the compounds are released from the membrane, the

capillary can be heated much faster, more reproducibly and up to much higher temperatures than the membrane. This might result in improved peak heights and shapes and, thus, in an improved overall performance of the system. Furthermore, by utilization of a Peltier modulator, more than one membrane module can be coupled to the mass spectrometric system, which enables much faster analysis. In addition, if different membrane materials are used the range of possible analytes can be extended. In general, good linear dependency of the peak areas on the analyte concentration was obtained for all compounds, except for pyrene (**Figure 4**; and **Figure A2,** supporting information).

TABLE 3

FIGURE 5

Limits-of-detection (LODs) were estimated for PAHs based on S/N=3 and are summarized in **Table 3** for trapping times of 1 min and 5 min. By extending the duration of the trapping (**Figure 5**), the S/N-ratios can be improved by a factor of 3.6 on average. An overview of the influence of the trapping time on peak areas is graphically given in **Figure A3** (supporting information). It was found that for most compounds with linearly increasing trapping times, the signal heights and peak areas linearly increase as well. Moreover, first results indicate that with higher desorption temperature the S/N-ratios as well as the rise and fall times can be improved (**Figure A5**, supporting information), which is in good agreement with observations presented by Riter et al.[49]. However, the use of desorption temperatures above 250 °C leads to a decreased lifetime of the utilized membrane. In addition, preliminary results for the sheet membrane setup suggest that, by utilizing high repetition lasers at a wavelength of 248 nm, the LODs can be improved by a factor 10. Thus, detection of sub-ng/L concentration of low molecular weight PAHs present in water, such as naphthalene or fluorene, would become feasible in less than 10 minutes of analysis time.

FIGURE 6

The results from a first test with complex samples are shown in **Figure 6A**. For this, tap water was contaminated with diesel as well as heavy fuel oil by suspending 2 µL of each fuel in 1.0 L of water. The results reflect the basic findings for an external sheet membrane setup described in Gehm et al.[46]: the most prominent compounds for water contaminated with diesel fuel are alkylated benzenes and indanes, whereas naphthalene and phenanthrene and their alkylated derivatives are the most abundant species for heavy fuel oil in water. Furthermore, in direct comparison with external sheet membrane setup [46], the utilization of T&R extends the spectrum of detectable analytes to higher molecular weights, while the LODs can be improved at the same time. A comparison of a measurement with both setups is given in **Figure A6** (supporting information). Much higher molecular weight compounds are not accessible via MIMS because of their much lower solubility in water.

The developed T&R-EHFMI-REMPI-TOFMS method was further applied to the measurement of real-world waters. For this purpose, water samples were taken from the estuary of the Warnow River, which flows into the Baltic Sea near Rostock, Germany. Representative ion traces of selected *m/z* values are shown in **Figure 6B**. The mass spectrum in **Figure 6B** was assembled by determining the corresponding maximum in signal intensity for each *m/z* value. Subsequently, the resulting mass spectrum was blank subtracted, and the mass spectrum for a pure water blank was obtained in a similar manner.

The detected major components can be assigned to alkylated indanes, naphthalenes and phenanthrenes as well as other small PAHs such as fluorene. Based on the measurements of pure fuels in water presented in **Figure 6A** and taking the location of the sampling site into account (near a high traffic road in the city harbor of Rostock), we assume that these contamination originate from diesel fuel as well as vehicle exhaust emissions.

4 Conclusion

In this study, an external trap-and-release hollow fiber membrane inlet (T&R-EHFMI) was utilized for REMPI-TOFMS. With this early stage system, fast and direct detection of volatile and semi-volatile aromatic species in water samples is accessible within minutes and without any sample preparation down to low ng/L-levels. T&R-EHFMI offers the advantage of a selective extraction of AHs from water samples, while REMPI-TOFMS is used for sensitive and selective detection of AHs. With the current setup, LODs for pyrene of our external membrane design are lower than those achieved with the DIMP-setup presented by Soni et al.[44]. The developed system, however, still offers potential for further methodological optimization. The valve-control can be automated, which will increase repeatability of the design. Furthermore, laser systems with a higher repetition rates as well as different laser wavelengths can be utilized. In preliminary tests, the use of an excimer laser (PhotonEx, Photonion GmbH, Schwerin, Germany; KrF, 248 nm 200 Hz repletion rate) with increased pulse frequency has already improved the detection limits by a factor of 10. In addition, by an additional focusing step behind the membrane, peak shapes may be improved. These approaches will be realized in further studies focusing on the development of a robust and versatile analysis system for continuous measurements on board marine research vessels or, in minimized form, in remotely operated underwater vehicles. For this purpose, external membrane introduction setups are needed, since in the event of membrane rupture, the failure of the entire measuring system can be prevented by fast shut-off of the MI unit. The MI-PIMS systems will be capable of directly determining AHs in open seawater, estuaries and freshwater at very low concentrations, and may be applied in marine sciences, natural resources exploration or pollutant and hazard detection.

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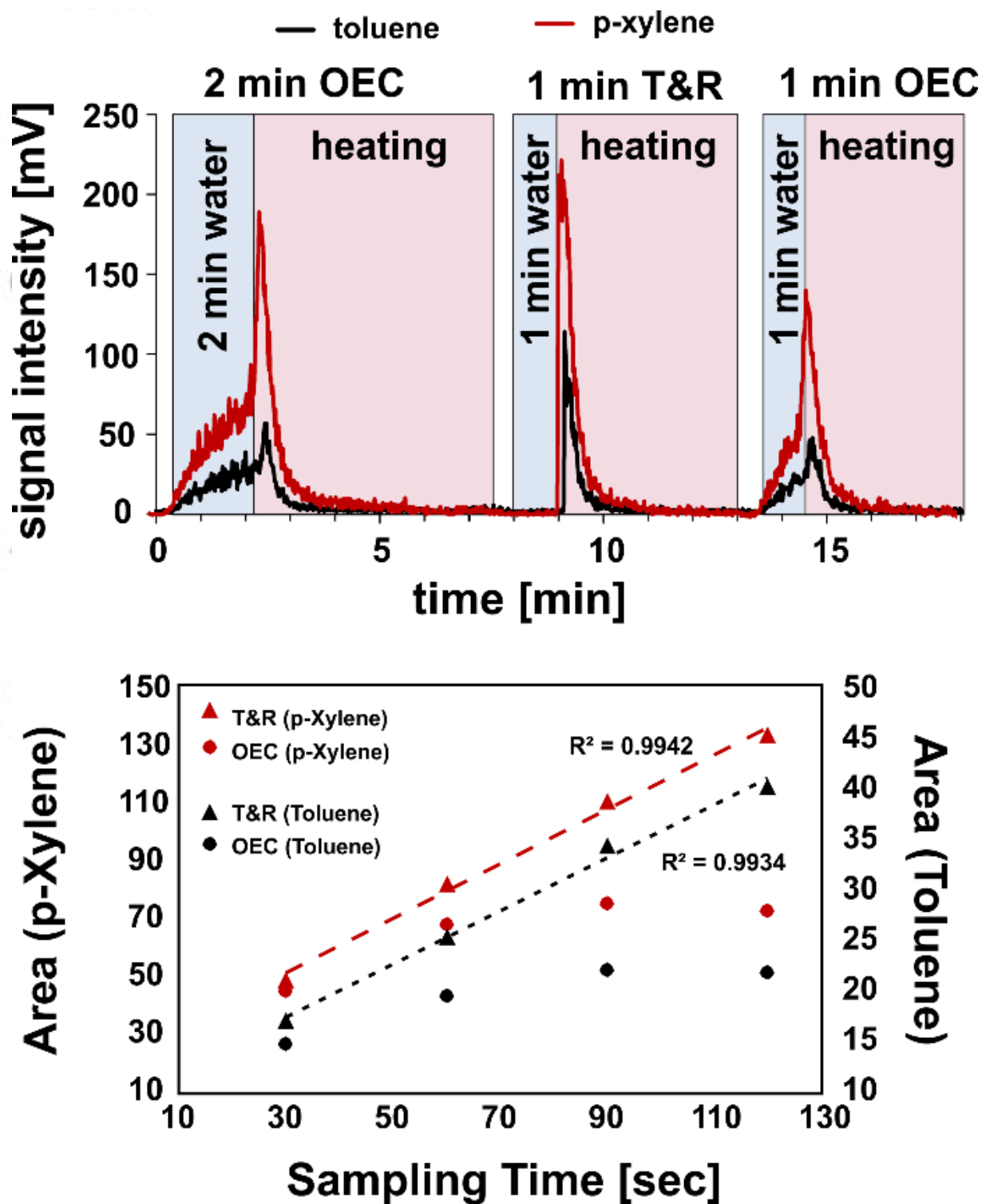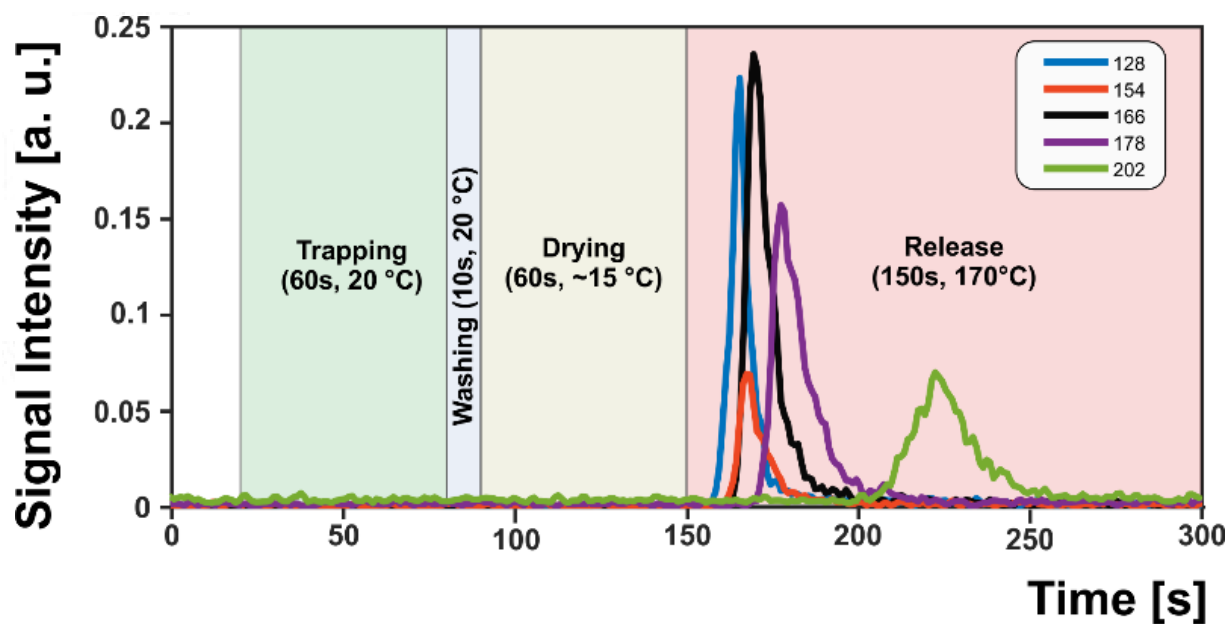
Figures

Experimental Setup
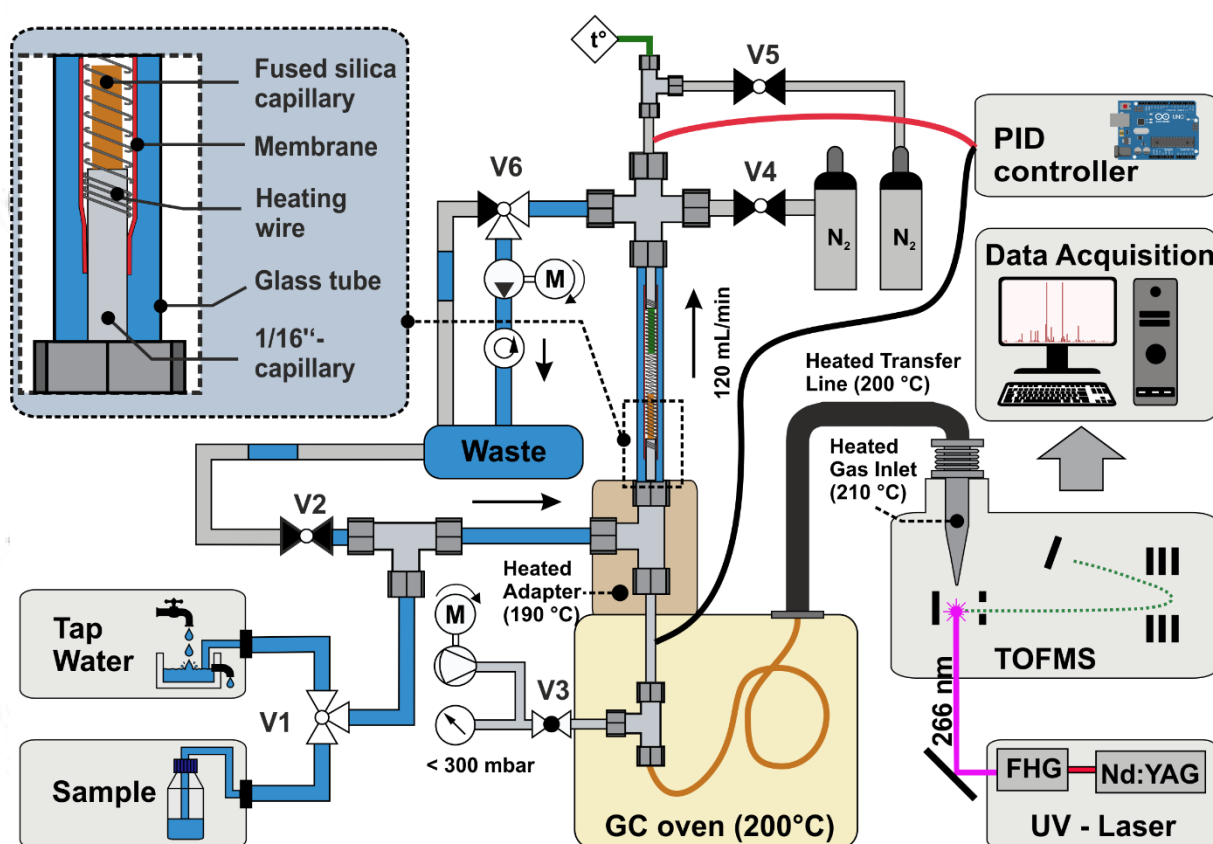
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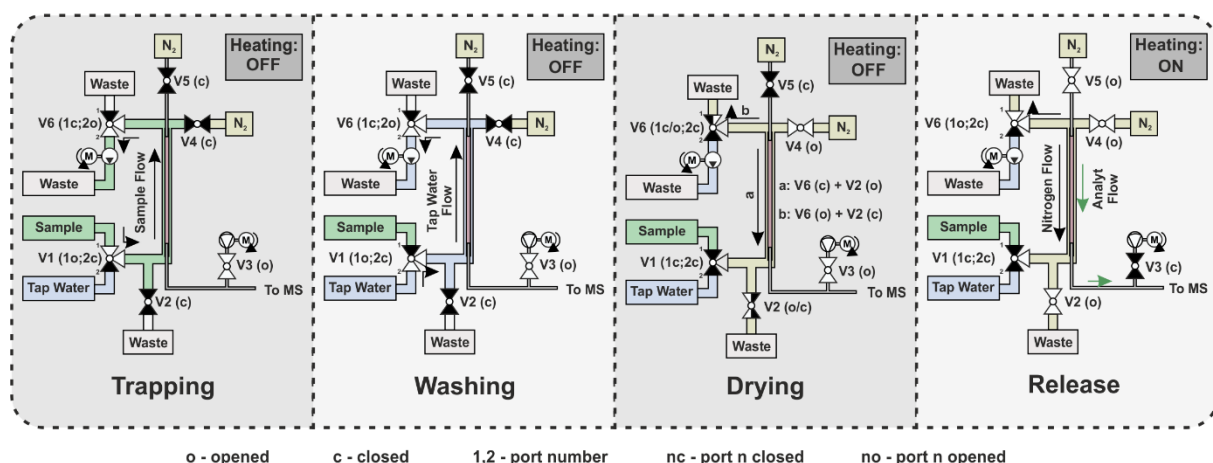
Figure 1: Scheme of the experimental setup of external hollow fiber membrane inlet (EHFMI) coupled to photoionization mass spectrometry (PIMS). instrument(top); Workflow for trap-and-release (T&R). Analytes are selectively extracted from the water and are enriched in the cold membrane (trapping). By rapid heating of the membrane, trapped compounds are transferred effectively to the PIMS instrument. The washing and drying steps are applied to improve repeatability as well as the whole performance of the EHFMI-PIMS system (bottom).

Figure 2: Comparison of two sequential analysis approaches for external hollow fiber membrane inlet (EHFMI) coupled to photoionization mass spectrometry (PIMS): open-end capillary (OEC) and trap-and-release (T&R). With OEC and T&R, higher signal intensities than with fully continuous analysis can be obtained. Furthermore, by utilizing T&R, a higher degree of enrichment with increasing sampling times can be achieved.

Figure 3: Ion traces of investigated polycyclic aromatic compounds (PAHs; β=500-750 ng/L; see Table 2) obtained by trap-and-release external hollow fiber membrane inlet (T&R-EHFMI) coupled to photoionization mass spectrometry (PIMS). With T&R-EHFMI-PIMS, analysis of small PAHs is possible at concentration levels down to 5-50 ng/L in less than five minutes.
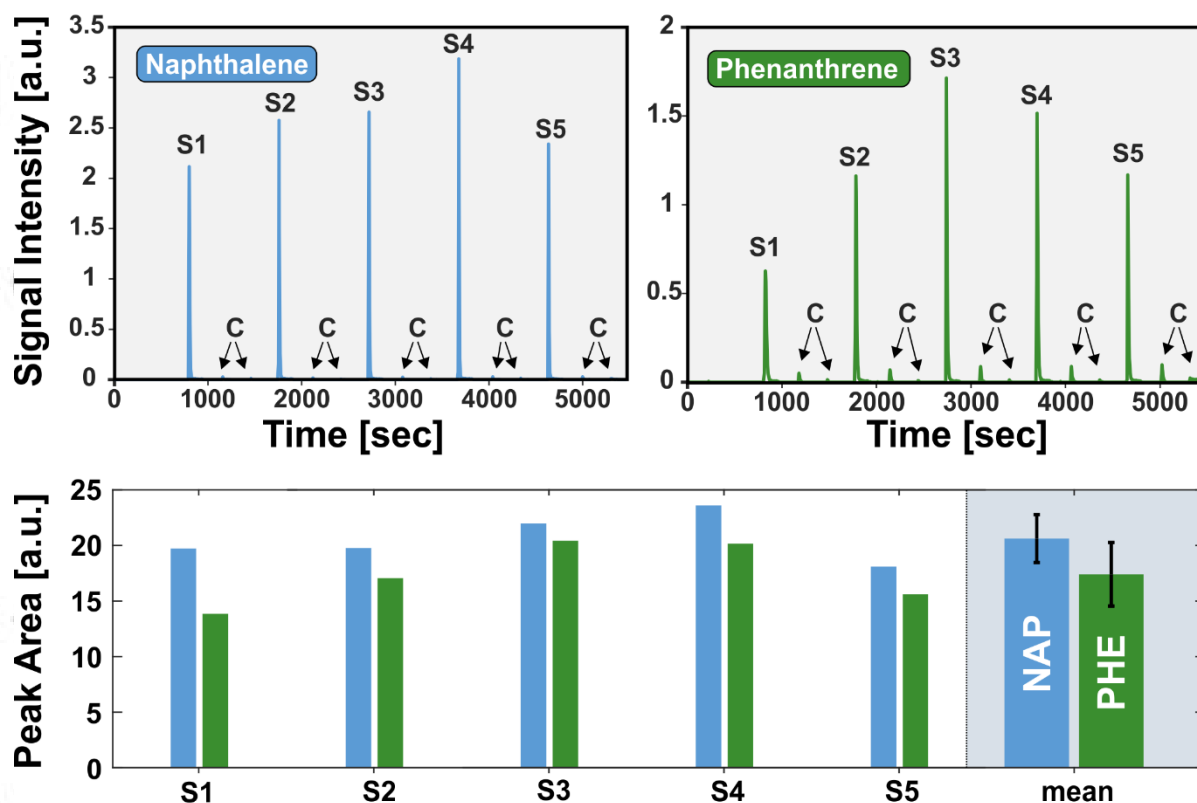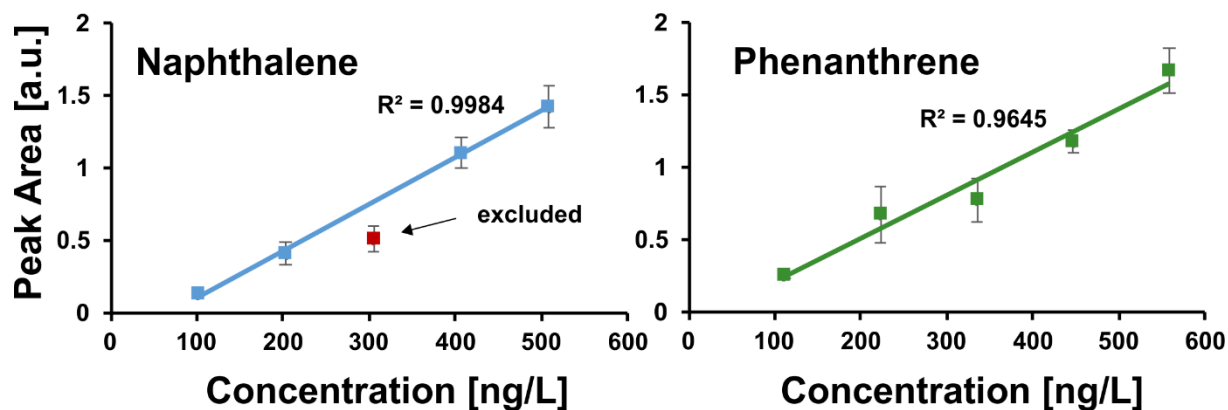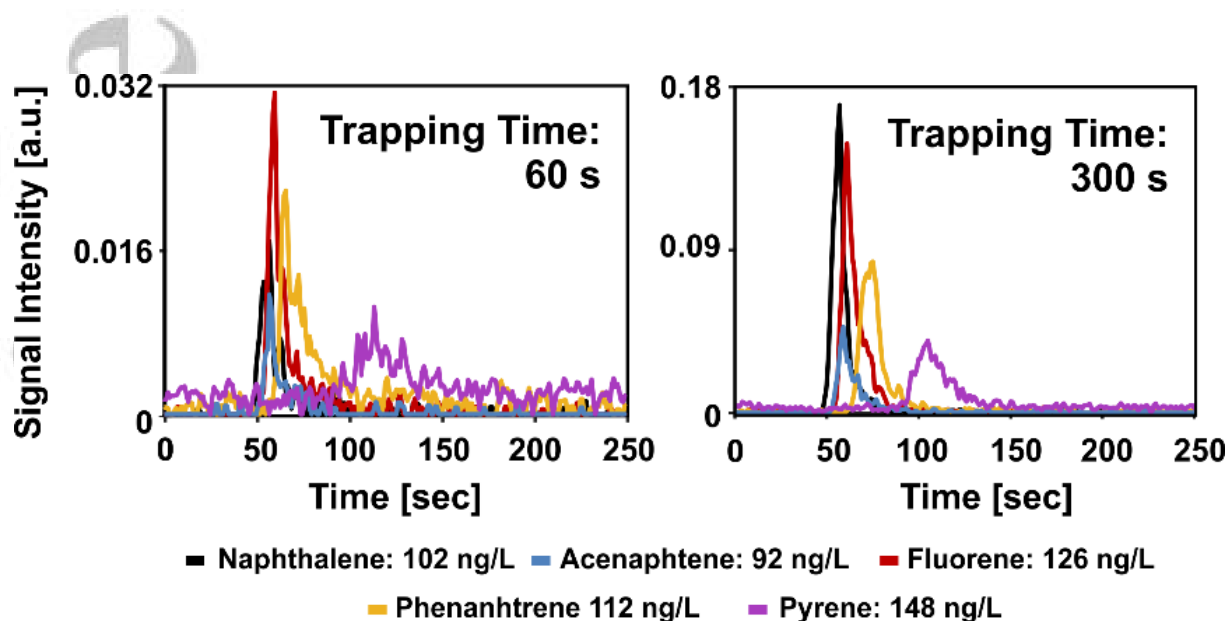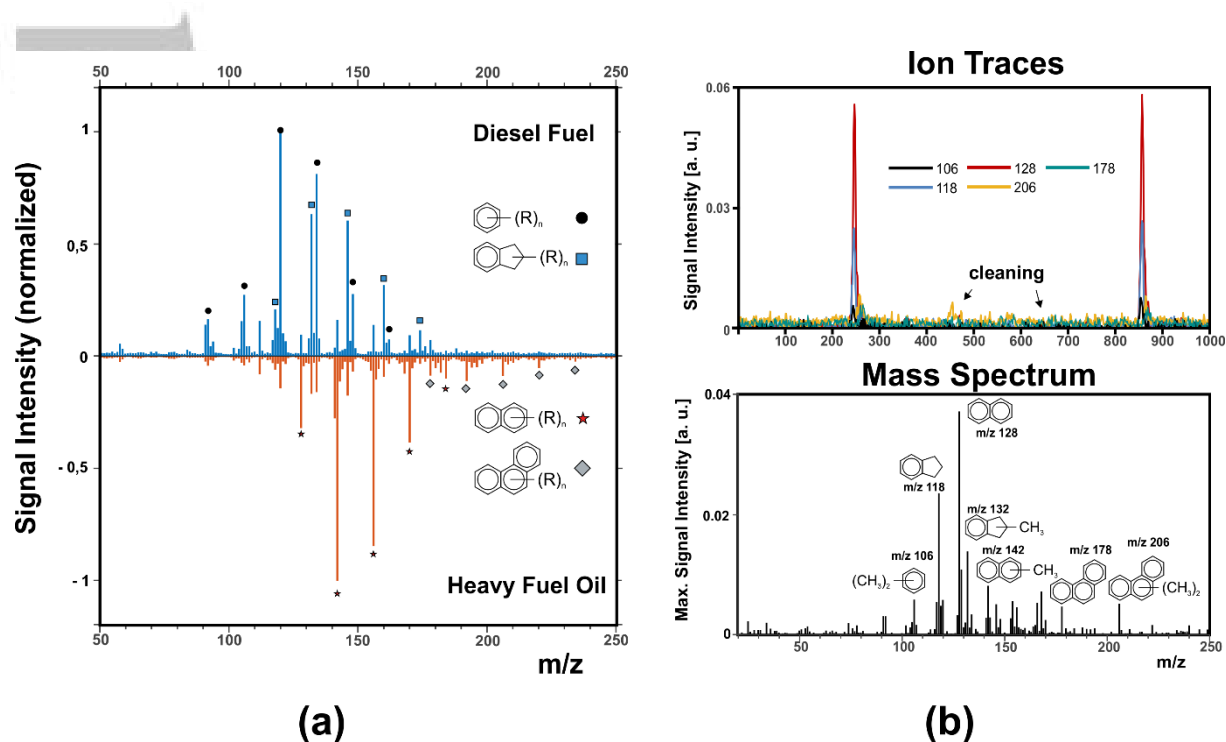
Figure 4: (A) Repeatability of the developed system for trap-and-release (T&R) external hollow fiber membrane inlet (EHFMI) coupled to photoionization mass spectrometry (PIMS). Between each sample measurement (S), the membrane was cleaned by heating (C). For signal intensities variations in the range of ± 15-30%, while for peak areas standard deviations between 10 and 5% were obtained. An extended overview of all investigated compounds is presented in Figure A4 (supporting information); **(B)** Calibration curves of naphthalene and phenanthrene. Good linear behavior was found for naphthalene, acenaphthene as well as fluorene (see Figure A3, supporting information).

Figure 5: Selected ion traces of polycyclic aromatic compounds (PAHs obtained by trap-and-release (T&R) external hollow fiber membrane inlet (EHFMI) coupled to photoionization mass spectrometry (PIMS) at one-minute and five-minute trapping time. By extending the duration of trapping, the signal intensity in the mass spectrum and, thus, the signal-to-noise ratio (S/N) can be improved.

Figure 6: (A) Mass spectra of diesel fuel and heavy fuel oil suspended in water obtained by trap-and-release (T&R) external hollow fiber membrane inlet (EHFMI) coupled to photoionization mass spectrometry (PIMS). For diesel fuel most prominent compound classes are alkylated benzenes and indanes, while for heavy fuel oil naphthalene and phenanthrene as well as their alkylated derivatives show highest abundance **(B)** Selected ion traces and mass spectrum of water from the Warnow river estuary obtained by T&R-EHFMI-PIMS at one-minute trapping time. The detected aromatic compounds can be assigned to contamination from diesel fuel as well as vehicle exhaust emissions originating from a nearby heavy traffic road.

Table 1: Physico-chemical Properties of the Investigated (Polycyclic) Aromatic Hydrocarbons

p-xylene	106.17	138.37	0.88	180	1167	3.15	-10.34 [b]	3.0
Naphthalene	128.17	217.9	1.03	31	11.27	3.3	-10.09 [c]	22.9
Acenaphthene	154.21	279	1.222	3.8	0.311	3.92	-10.22 [c]	28.5
fluorene	166.22	295	1.203	1.9	0.088	4.18	-10.26 [c]	54.6-61.0
Phenanthrene	178.23	340	0.98	1.1	0.025	4.46	-10.28 [c]	99.4-144
Pyrene	202.25	404	1.271	0.000882	0.148	4.88	-10.47 [c]	14-223
a: Data obtained from [50]; Density in g/mL at 20°C; Vapor Pressure in Pa at 25°C; Solubility in mg/L at 25°C b: Data obtained from [51] ; Diffusivity in m²/s c: Data obtained from [52] ; Diffusivity in m²/s d: Data obtained from [47] ; REMPI – cross section relative to toluene								

Table 2: Peak areas and peak widths at 5% (FWFM) as well as 50% (FWHM) of maximum signal heights (Figure 4).

Compound	*m/z*	β [ng/L]	Peak Area	FWFM (5%)	FWHM (50%)
Naphthalene	128	510	1.42 ±0.14	24 ± 3	7 ± 2
Acenaphthene	154	460	0.55 ±0.05	27 ± 3	11 ± 3
Fluorene	166	630	1.83 ±0.23	29 ± 5	11 ± 3
Phenanthrene	178	560	1.66 ±0.16	32 ± 3	13 ± 3
Pyrene	202	740	1.12 ±0.02	33 ± 2	17 ± 1

Table 3: Comparison of signal-to-noise ratios (S/N) and LODs (S/N=3) for one minute and five minute trapping time

Compound	1min		5 min		Improvement
	S/N	LOD in ng/L	S/N	LOD in ng/L	factor
Naphthalene	55	5.6	279	1.1	5
Acenaphthene	43	6.4	96	2.9	2
Fluorene	70	5.4	250	1.5	4
Phenanthrene	24	14.0	90	3.7	4
Pyrene	9	46.8	26	17.0	3