

Development and optimization of an external-membrane introduction photoionization mass spectrometer for the fast analysis of (polycyclic)aromatic compounds in environmental and process waters.

CHRISTIAN GEHM¹, THORSTEN STREIBEL^{1,2*}, SVEN EHLERT⁴, DETLEF SCHULZ-BULL³, RALF ZIMMERMANN^{1,2}

¹Joint Mass Spectrometry Centre, Chair of Analytical Chemistry, Institute of Chemistry, University of Rostock, Dr.-Lorenz-Weg 2, 18059 Rostock, Germany

²Joint Mass Spectrometry Centre, Cooperation Group Comprehensive Molecular Analytics, Institute of Ecological Chemistry, Helmholtz Zentrum München-German Research Center of Environmental Health (GmbH), Ingolstädter Landstrasse 1, 85764 Neuherberg, Germany

³Leibniz - Institute for Baltic Sea Research Warnemünde, Seestraße 15, 18119 Rostock – Warnemünde, Germany

⁴Photonion GmbH, Hagenower Strasse 73, 19061 Schwerin, Germany

*Correspondence: thorsten.streibel@uni-rostock.de, Tel.: +49-381-498-6527

ABSTRACT: The development of sensitive analytical techniques for the real – time detection of aromatic (AH) and polycyclic aromatic hydrocarbons (PAH) is of high importance due to their impact on human health and the environment. A promising approach, regarding to direct determination of (P)AHs in aqueous samples, is resonance-enhanced multiphoton ionization (REMPI) coupled to external-membrane introduction mass spectrometry (eMIMS). In eMIMS, analytes are extracted from the water phase into the gas phase, which is supplied to the MS by using an external semipermeable membrane setup. As a result, no laborious enrichment techniques are needed. With REMPI, ions are formed by the subsequent absorption of two photons via an excited molecular state. The unique ionization scheme of REMPI provides selective and sensitive detection of (P)AHs. When combining the capabilities of REMPI and MIMS, direct measurements of sub – µg/L concentrations of small (polycyclic)aromatic compounds are feasible. In this study, we present an external sheet membrane probe (ESMP) for the determination of selected (polycyclic)aromatic species in water samples by using REMPI time-of-flight mass spectrometry (REMPI-TOFMS). This inlet design shows promising results with respect to the direct analysis of (P)AHs in aquatic environments. With this early-stage system, concentrations down to tens of ng/L for selected small (polycyclic)aromatic compounds are accessible in minutes without any sample preparation.

INTRODUCTION

Fast and sensitive analysis of aromatic (AH) and polycyclic aromatic hydrocarbons (PAH) in aqueous matrices is vitally important due to their high impact on environmental and human health^{1,2}. The low concentrations of AHs and PAHs in environmental bodies of water complicate their monitoring³. Although available chromatographic offline techniques offer clear advantages in respect to sensitivity⁴⁻⁷, various laborious enrichment techniques (e.g. purge-and-trap, solid-phase extraction, liquid-liquid extraction) have to be applied to increase the concentrations to a detectable level⁸⁻¹⁰. For this reason, the development of online techniques moves into focus. A simplified analytical method for PAHs and similar compounds in complex matrices has been developed by Mirabelli et al. by using online solid-phase microextraction (SPME) coupled to atmospheric-pressure photo-ionization mass spectrometry (APPI-MS). They were able to reach limit-of-detections (LOD) down to 0.1 ng/L for PAHs.¹¹

Nevertheless, for this approach, analytes in the water samples have to be extracted and pre-concentrated by SPME before the SPME-fibers are separately introduced into the inlet system of the MS. On the other hand, a powerful analytical technique, for

online determination of PAHs in gaseous mixtures, is resonance-enhanced multiphoton ionization (REMPI) coupled to time-of-flight mass spectrometry (TOFMS)¹²⁻¹⁴. In REMPI ions are formed by the subsequent absorption of at least two photons including real molecular electronic states. Fundamentals of REMPI are described elsewhere¹⁵⁻¹⁷. One special feature of REMPI is the spectroscopic selectivity involved within the ionization process. Therefore, the unique ionization scheme of REMPI provides highly selective and sensitive detection of (polycyclic)aromatic species by using laser wavelengths in the UV - range. In recent years, REMPI-MS has been successfully applied to online determination of AHs and PAHs of various combustion processes and environmental monitoring¹⁸⁻²¹. Furthermore, complex liquid samples such as crude oils have been investigated via direct infusion technique²². Nevertheless, due to high matrix contents compared to low analyte concentrations the application of REMPI for aquatic systems is challenging.

One promising approach constitutes the utilization of membrane inlet mass spectrometry (MIMS). In MIMS, dissolved analytes are transported selectively from the water phase through a semipermeable membrane (e.g. PDMS) into the vacuum of the mass spectrometer, losing the matrix in the process.

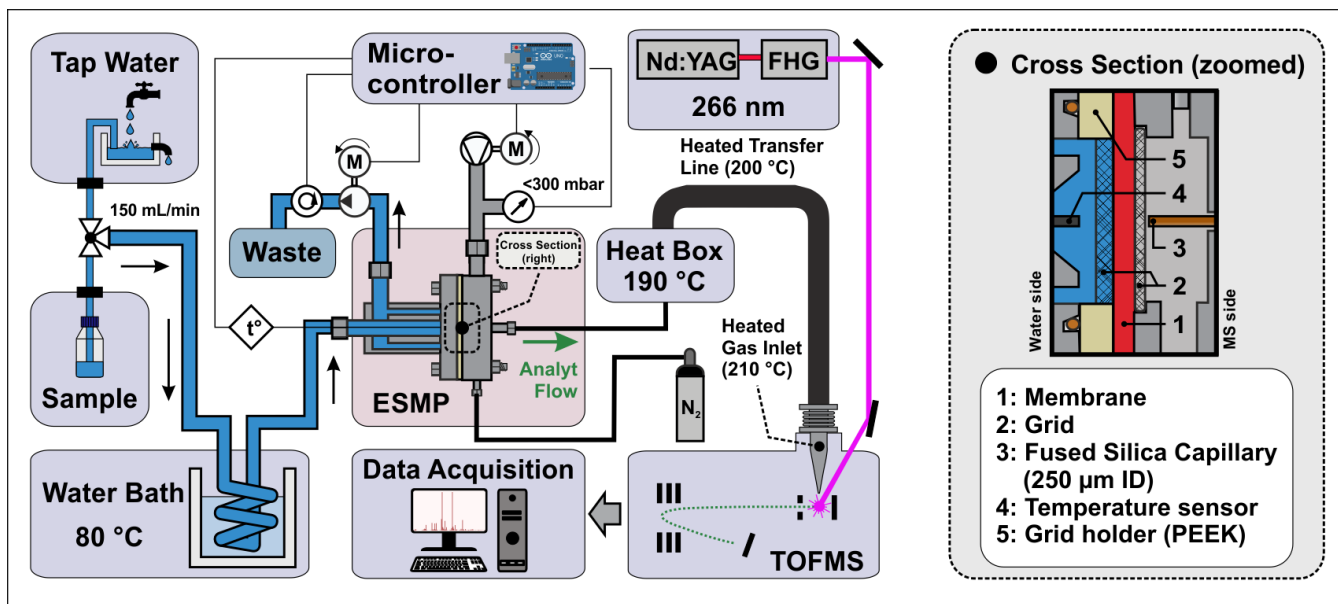


Figure 1. Experimental setup and scheme of the external sheet membrane probe (ESMP). Thermalized water is guided through the membrane probe centrally onto the membrane. The pervaporating molecules are transferred via a heated transfer line into the ion source. Molecular ions are produced by REMPI at 266 nm and are analyzed by TOFMS.

71 The fundamental process of MIMS is known as pervapora-
 72 tion and can be described by the solution-diffusion-model by
 73 Reid^{23,24}. In this model, the dissolved analytes first adsorb on
 74 the membrane surface. In this adsorption step, the analytes are
 75 slightly enriched on the membranes' surface²⁵. After adsorp-
 76 tion, the compounds dissolve into the membrane material, dif-
 77 fuse to the opposite side forced by the gradient of concentration
 78 and pressure, and are released into the vacuum by evaporation
 79 from the membrane surface. Consequently, no expensive en-
 80 richment techniques are needed and the analysis time is consid-
 81 erably reduced.²⁶⁻³¹

82 Up to now, two studies have been published describing the
 83 hyphenation of REMPI and MIMS using direct inlet membrane
 84 probes (DIMP). In these setups, the membrane is placed directly
 85 inside the high vacuum region of the ion source nearby the ion-
 86 ization volume. Soni et al.³² used a sheet membrane coupled to
 87 an ion trap MS to investigate aqueous laboratory samples of
 88 naphthalene and pyrene at a laser wavelength of 248 nm (KrF-
 89 Excimer laser). In this study, with REMPI-MIMS a limit-of-de-
 90 tection (LOD) for pyrene was achieved down to 100 ppt, which
 91 was 100 times lower than the LOD-value obtained by MIMS
 92 using electron-ionization (EI). The second paper was published
 93 by Oser et al.³³. They investigated laboratory water samples us-
 94 ing the fourth harmonic of a Nd:YAG laser (266 nm) with
 95 TOFMS. Besides the investigation of temperature effects on the
 96 MIMS response, they also determined LODs for single core ar-
 97 omatics down to 30 ppq (extrapolated values down to signal-to-
 98 noise ratio of 1). Both studies reflect the high potential of the
 99 combination of REMPI and MIMS. However, DIMP-type of
 100 coupling requires a suitable designed ion source and bears some
 101 risk in the case of membrane rupture.

102 In contrast, for external membrane assemblies, the membrane
 103 probe is placed outside of the MS and is connected to the ion
 104 source via a transfer capillary³⁴⁻³⁶. The advantage of this setup
 105 lies in its simplicity, robustness and versatility. In case of mem-

106 brane failure, the transfer line acts as a security device and re-
 107 stricts the water flow into the MS. Additionally, external mem-
 108 brane probes can be easily utilized for a wide variety of different
 109 mass spectrometers and are already applied in many publica-
 110 tions³⁷⁻³⁹. However, external setups in combination with
 111 REMPI are not published yet.

112 Therefore, as a proof of principle, we present the first labor-
 113 atory measurements of water samples with a homebuilt REMPI-
 114 MS system equipped with an external inlet for sheet membranes
 115 (REMPI-eMIMS). With the aid of this setup, selected AHs and
 116 small PAHs are investigated in different water matrices.

117 EXPERIMENTAL

118 External Sheet Membrane Probe (ESMP)

119 The setup of the external sheet membrane probe (ESMP) is
 120 based on the work of Hou et al.³⁴. It consists of two stainless
 121 steel flanges illustrated in Figure 1. Between these flanges, a
 122 sheet membrane (Wacker, $d = 10$ mm; thickness = 150 μm) is
 123 placed orthogonally to the water flow direction. The reason for
 124 this arrangement is to improve the pervaporation processes by
 125 reducing the boundary layer between the water phase and the
 126 membrane. The membrane is stabilized on the vacuum side as
 127 well as on the water side by two stainless steel grids. On the
 128 vacuum side, the ESMP is connected to the REMPI-TOFMS
 129 via a fused silica capillary (ID=250 μm). In this setup, the mem-
 130 brane is heated indirectly by heating the inflowing water up to
 131 80 °C via a water bath. The MS side of the membrane flange
 132 can be evacuated down to 300 mbar by a small diaphragm pump
 133 (30 KNDC, KNF Neuberger, Freiburg, Germany). A small gear
 134 pump (PQ12; Greylor Inc., Cape Coral, US) transfers the water
 135 to the membrane. The setup is equipped with different sensors
 136 to continuously monitor the pressure (MPX5700AP, Conrad
 137 Electronic SE, Hirschau, Germany), water temperature and wa-
 138 ter flow rate (FCH-m-PP-LC, BIO TECH, Vilshofen, Ger-
 139 many).

140 **Table 1. Physico-chemical properties of the investigated (polycyclic) aromatic hydrocarbons**

Substance	m/z	Boiling Point ^a	Density ^a	Vapor pressure ^a	Solubility ^a	Lg K _{ow} ^a	Lg(Diffusivity)	Rel.PI-CS ^d
benzene	78.11	80.09	0.8765	1770	12690	2.13	-9.87 ^b	0.05
toluene	92.14	110.63	0.87	530	3790	2.73	-9.94 ^b	1
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
3-methylphenanthrene	192.26	350	1.025	0.26	0.019	5.08	-	-

a: Data obtained from ⁴⁰; 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 ⁴¹; Diffusivity in m²/s
c: Data obtained from ⁴²; Diffusivity in m²/s
d: Data obtained from ⁴³; REMPI – cross section relative to toluene

141

142 An arduino-based microcontroller was programmed with a
143 custom program to read and visualize sensor data, and to control
144 both pumps.

145 Mass Spectrometric System

146 The utilized TOFMS (custom-built by Stefan Kaesdorf
147 GmbH, Munich, Germany) has a mass resolution of 1100 at
148 m/z 78 and consists of a two – staged Wiley and McLaren ion
149 source, ion optics for the parallelization and adjustment of the
150 ion beam, a reflectron and a multi – channel – plate as detector.
151 The ion source and the flight tube are differentially pumped by
152 turbomolecular pumps (TMU 521 and TMU 261, Pfeiffer Vac-
153 uum, Asslar, Germany) down to a pressure of 3.4×10^{-5} mbar
154 and 6.8×10^{-8} mbar, respectively. The introduction of the per-
155 vaporating molecules into the TOFMS is realized by a heated
156 gas inlet. It consists of a hollow thermo-conductive ceramic,
157 pointing to the center of the ion source. Inside the ceramic a
158 deactivated fused silica capillary (250 μ m ID, BGB Analytik,
159 Rheinfelden, Germany) is used to introduce gaseous molecules
160 into the ion source as an effusive molecular beam. The capillary
161 is guided through a vacuum seal and is connected to the external
162 membrane probe. The capillary restricts the gas flow into the
163 ion source to ~ 2 mL/min. The molecules are irradiated by UV
164 – laser pulses in close vicinity to the tip of the capillary. UV
165 photons with a wavelength of 266 nm (fourth harmonic of a
166 Nd:YAG – laser (QuantaRay Indi 40-10; Spectra Physics, Santa
167 Clara, US; 10 Hz repetition rate; pulse length: 8 ns; averaged
168 pulse energy: 3 mJ)). Two 8-Bit converter cards (Aquiris
169 DP211 and DP110; Plan-les-Ouates, Switzerland) are used to
170 acquire mass spectral data, whereas data sets are recorded by a
171 custom LabView routine (Photonion GmbH, Schwerin, Ger-
172 many).

173 Standard solutions

174 All investigated AHs and PAHs (various distributors; purity
175 98% - 99.6%) are listed in Table 1. Mixed stock solutions were
176 prepared by dissolving different amounts of these compounds
177 in isopropanol (Roth; purity 99.5%). These stock solutions were
178 used to prepare a dilution series (1:10 dilution factor) down to
179 10^{-5} in isopropanol. Eventually, aqueous standard solutions

180 were prepared by diluting known amounts of these dilution
181 stages in tap water at a total volume of 1000 mL and a maximum
182 concentration of isopropanol of 78 mg/L. All standard solutions
183 were measured as triplicates.

184 RESULTS AND DISCUSSION

185 Laboratory Measurements

186 Based on the solution-diffusion model, the diffusive transport
187 of compounds through the membrane is the rate determining
188 step of pervaporation. Under steady-state conditions, there is an
189 equilibrium between analytes adsorbed on one side of the mem-
190 brane, and those, which are desorbed from the other side. This
191 results in a constant flux of compounds through and from the
192 membrane. This steady-state flux (I_{SS} , (Equation 1)) can be de-
193 rived from the first *Fick's* law and is decisive for sensitivity in
194 MIMS.

$$I_{SS} = A \cdot D \cdot K \cdot \frac{c_{sample}}{d} \quad (\text{Equation 1})$$

195

196 Here, A is the membrane area, D the diffusivity, K the distri-
197 bution ratio between water and membrane, c_{sample} the concentra-
198 tion of the analyte in the sample and d the membrane thickness.
199 The flux until reaching steady-state conditions is known as non-
200 steady state flux (I_{NS} , (Equation 2)) and can be calculated based
201 on the second *Fick's* law.

202

$$I_{NS} = I_{SS} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \cdot \exp\left(\frac{-n^2 \pi^2 D t}{d^2}\right) \right] \quad (\text{Equation 2})$$

203

204 I_{NS} approaches I_{SS} asymptotically and determines the re-
205 sponse time of a compound. Here, instead of using the whole
206 time period until reaching I_{SS} , response times often refer to the
207 time for achieving 90% of I_{SS} starting from 10% of I_{SS} ($t_{10\%-90\%}$).
208 Based on the work of Pasternak et al.⁴⁴ and LaPack et al.²⁹, $t_{10\%-}$
209 90% can be approximated as in (Equation 3). With (Equation 3)
210 diffusivity constants can be estimated.

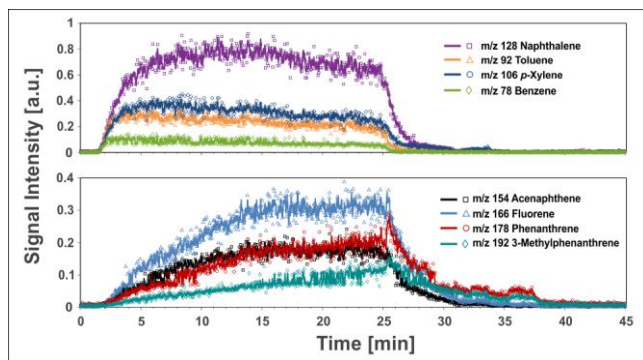


Figure 2. Extracted ion traces of selected aromatic and polycyclic aromatic species in spiked tap water obtained by REMPI-eMIMS. The concentration levels are in the $\mu\text{g/L}$ range. For volatile compounds fast response times ($t_{10\%-90\%}$) from several tens of seconds up to 2.5 min are determined. The $t_{10\%-90\%}$ are higher for semi-volatile species. The symbols mark the data points. The solid lines are calculated by moving median over 5 data points.

$t_{10\%-90\%} \approx 0,237 \cdot \frac{d^2}{D}$	(Equation 3)
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211

212 Figure 2 illustrates measurements of spiked tap water sam-
 213 ples containing selected AHs and PAHs. Additionally, I_{SS} and
 214 $t_{10\%-90\%}$ are summarized in Table 2. For all of the investigated
 215 AHs short response times from approx. 30 seconds up to two
 216 minutes were achieved. Except for benzene (1720 $\mu\text{g/L}$), good
 217 signal intensities of I_{SS} compared to the corresponding concen-
 218 trations were detected. Even though benzene has a high volatil-
 219 ity and diffusivity, it is poorly ionized at 266 nm, which is dis-
 220 cussed by Gehm et al.⁴³ In contrast, toluene (155 $\mu\text{g/L}$) and *p*-
 221 xylene (78 $\mu\text{g/L}$) show larger two-photon ionization cross sec-
 222 tions. For our REMPI-eMIMS measurements, the differences in
 223 signal heights of the I_{SS} between toluene and *p*-xylene, and tol-
 224 uene and benzene are in good agreement with the differences in
 225 ionization ratios of these compounds at 266 nm presented in Ta-
 226 ble 1. Therefore, we assume that these compounds show similar
 227 behavior in the pervaporation process under the applied condi-
 228 tions.

229 In general, PAHs have much higher REMPI cross sections
 230 than single core aromatics. For example, in gas phase measure-
 231 ments, naphthalene is ionized approximately twenty times bet-
 232 ter with REMPI at 266 nm than toluene. The corresponding
 233 REMPI-eMIMS response is reduced to a relative value of ap-
 234 prox. six.

235 **Table 2. Calculated LODs and Response times**

Substance	LOD [ng/L]	t_{10-90} (without pump) [s]	t_{10-90} (with pump) [s]
benzene	n.d.	36	11.5
toluene	53	65.98	21.995
<i>p</i> -xylene	16	106	29.985
naphthalene	20	227.01	65.01
acenaphthene	30	513.01	123.5
fluorene	22	587.02	166.005
phenanthrene	10	644	361.995
3-methylphenanthrene	52	719.03	520.505

236 In contrast to *p*-xylene and benzene, naphthalene shows clear
 237 differences in the pervaporation process compared to toluene
 238 based on physico-chemical parameters. Nevertheless, due to its
 239 high volatility and diffusivity, promising signal heights of I_{SS}
 240 and $t_{10\%-90\%}$ can be detected for naphthalene as well.

241 For the investigated semi-volatile PAHs good signal intensi-
 242 ties compared to the concentrations of 40-60 $\mu\text{g/L}$ were
 243 achieved. Herein, fluorene shows the most intense REMPI-
 244 eMIMS response, whereas acenaphthene has the shortest re-
 245 sponse time of all tested SVOCs. Based on physico-chemical
 246 data presented in Table 1, it is evident that in direct comparison
 247 with fluorene, acenaphthene is transferred more effectively
 248 through the membrane. In addition, the evaporation of acenaph-
 249 thene from the membrane surface can be assumed to be higher.

250 This leads to shorter response times of acenaphthene com-
 251 pared to fluorene. On the other hand, fluorene is ionized more
 252 efficiently due to a larger photoionization cross section at 266
 253 nm. Therefore, higher signal intensities in mass spectra are rec-
 254 orded. Even though phenanthrene is ionized much more effi-
 255 ciently at 266 nm than acenaphthene, both substances show
 256 similar signal intensities in REMPI-eMIMS. Additionally, the
 257 response time of phenanthrene is approximately 60 s longer
 258 compared to fluorene. This behavior can be explained by the
 259 much higher boiling point and lower diffusivity of phenan-
 260 threne. Methylphenanthrene has the highest boiling point and
 261 the lowest diffusivity of the selected substances, which results
 262 in the longest response time of all investigated compounds.

263 As illustrated in Table 2, the $t_{10\%-90\%}$ values can be improved
 264 by a factor of two to four by differentially pumping the MS-side
 265 of the membrane flange. At the same time, the signal intensities
 266 are decreased by a factor of ten. The reason for this can be at-
 267 tributed to higher diluting factor of the gas mixture on the MS-
 268 side of the membrane by the increasing nitrogen flux. However,
 269 much faster measurements of AHs and PAHs in liquid samples
 270 are possible. Such fast measurements can be essential for appli-
 271 cations, where relatively high concentrations ($\mu\text{g/L}$ – mg/L) of
 272 (polycyclic)aromatic species are present.

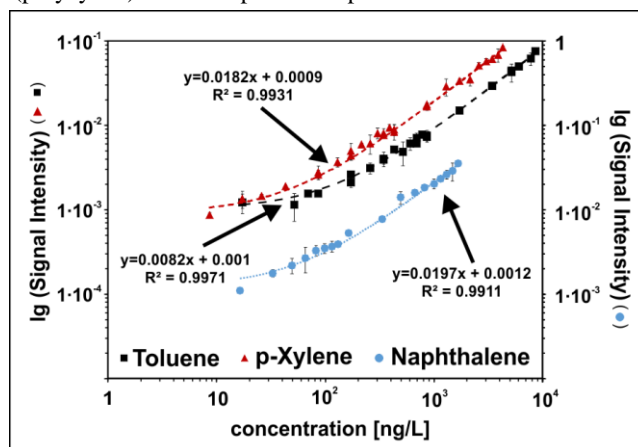


Figure 3. Linearity of the developed ESMP-REMPI-TOFMS

273 The linearity of our ESMP-REMPI-TOFMS is presented in
 274 Figure 3 for toluene, xylene and naphthalene. For all three com-
 275 ponents, a good linear behavior was found over 2.5-3 orders of
 276 magnitude.

277 The LODs of all investigated (polycyclic)aromatic species were
 278 calculated based on calibration curves given in Figure A1
 279 (Suppl. Information, SI) and are summarized in Table 2. For all

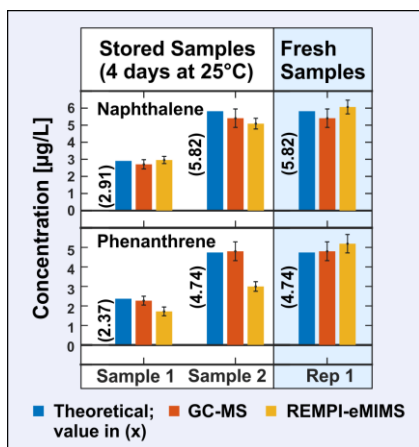


Figure 5. Comparison of REMPI-eMIMS and GC-MS. For naphthalene good agreement between both techniques was found. For phenanthrene, deviations result from sample storage.

compounds, LODs of 10-60 ng/L can be determined. The most important limiting factors for LODs are memory effects. These memory effects result from insufficient diffusion through the membrane and the following evaporation from the relatively cold membrane surface. In addition, the deposition of SVOCs on cold metal surfaces might play an important role. Due to the experimental setup of the ESMP, the MS-flange is not heated directly. Therefore, the wall of this flange might act as a cold spot, where SVOCs can adsorb. The following desorption is slow and leads to steady emission of compounds. These memory effects might be reduced by implementing additional heating of the MS-flange.

The LODs could be improved by stimulating the evaporation from the membrane surface by additional heating or by laser-desorption of the MS-side of the membrane. In addition, first results suggest that, by heating the membrane surface, the performance of the system can be extended to higher boiling point compounds, which was previously shown in the work from Soni et al.⁴⁵. Memory effects can be reduced as well. Another opportunity is the usage of laser systems with higher repetition rates or alternative laser wavelengths. Preliminary results, using a KrF-excimer laser (248 nm; 200 Hz repetition rate) with a non-heated MI-REMPI-TOFMS setup, indicate significant improvement in performance (Figure A5, SI). Another interesting approach without the need of heated transfer lines is condensed phase MIMS (cp-MIMS), in which analytes are extracted by the membrane from the water into a liquid acceptor phase⁴⁶⁻⁴⁸. Due to the fact that the compounds are directly washed away from the membrane surface by the liquid, this technique is independent of the evaporation process. In combination with EI, comparable LODs in the range of 270-330 ng/L for naphthalene can be observed as we determined in our study⁴⁹. Additionally, the investigation of compounds with low vapor pressures are accessible with short analysis times. The advantages of REMPI and cp-MIMS can be combined by introducing the acceptor phase directly into high vacuum of the MS, which was presented by Kruth et al.¹⁷, or to couple a suitable cp-MIMS setup with capabilities of APPI.

The performance of our REMPI-eMIMS system was tested against gas chromatography coupled to EI-MS (GC-MS). For this, different samples of pure water were spiked with known amounts of naphthalene, acenaphthene, fluorene and phenanthrene. The overall sample volume was 2L. From these samples

subsamples were analyzed in parallel by GC-MS as well as REMPI-eMIMS. For GC-MS measurements, the corresponding water sample was extracted by liquid-liquid extraction with hexane. The extract was restricted to 1 mL, which was analyzed by an Agilent 7010A Triple Quadrupole GC/MS. REMPI-eMIMS measurements were performed 4 days after water samples were prepared. An excerpt from the results is given in Figure 5, whereas a complete graphical overview is presented in Figure A3 (SI). For Naphthalene, the concentrations obtained by REMPI-eMIMS match well to the corresponding values determined by GC-MS. In contrast, a clear deviation can be observed for phenanthrene especially at higher concentrations. Therefore, new samples with the same concentrations were prepared in pure water and were measured directly after preparation. The measured concentrations of the new samples are now consistent with GC-MS data. Thus, we assume that the storage of the samples has an influence on values measured with our system, which can be attributed to wall effects of the used sample vessels.

Influence of Water Temperature

Pervaporation is influenced by different parameters, such as membrane material, membrane thickness, temperature, and flow rate. Variations of membrane material or thickness were not in the scope of this study, but are comprehensively summarized in^{26,50}. For the extraction of non-polar species out of water samples, PDMS is mentioned as the most suitable membrane material.

Water temperature affects the I_{SS} as well as the $t_{10\%-90\%}$. In our experiments, we found a direct proportional relationship of water temperature and I_{SS} (Figure 4), which can be attributed to increasing diffusion and desorption rates at higher temperatures. Additionally, by increasing water temperature the response times are reduced. Figure 4 also indicates 80 °C as the optimal water temperature for our system. Water temperatures above 85°C lead to a high degree of bubble formation causing reduction of signal stability and I_{SS} . These findings are in good agreement with data presented in previous^{26,33} studies.

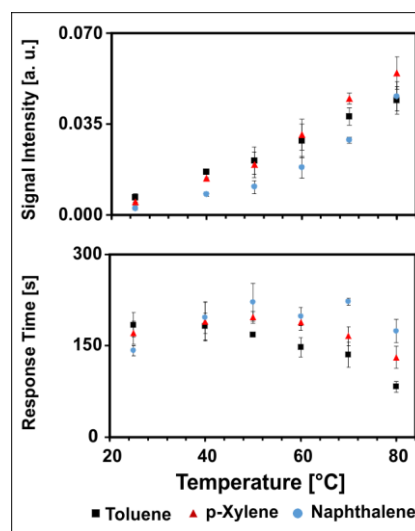


Figure 4. Influence of water temperature on I_{SS} (top) and $t_{10\%-90\%}$ (bottom)

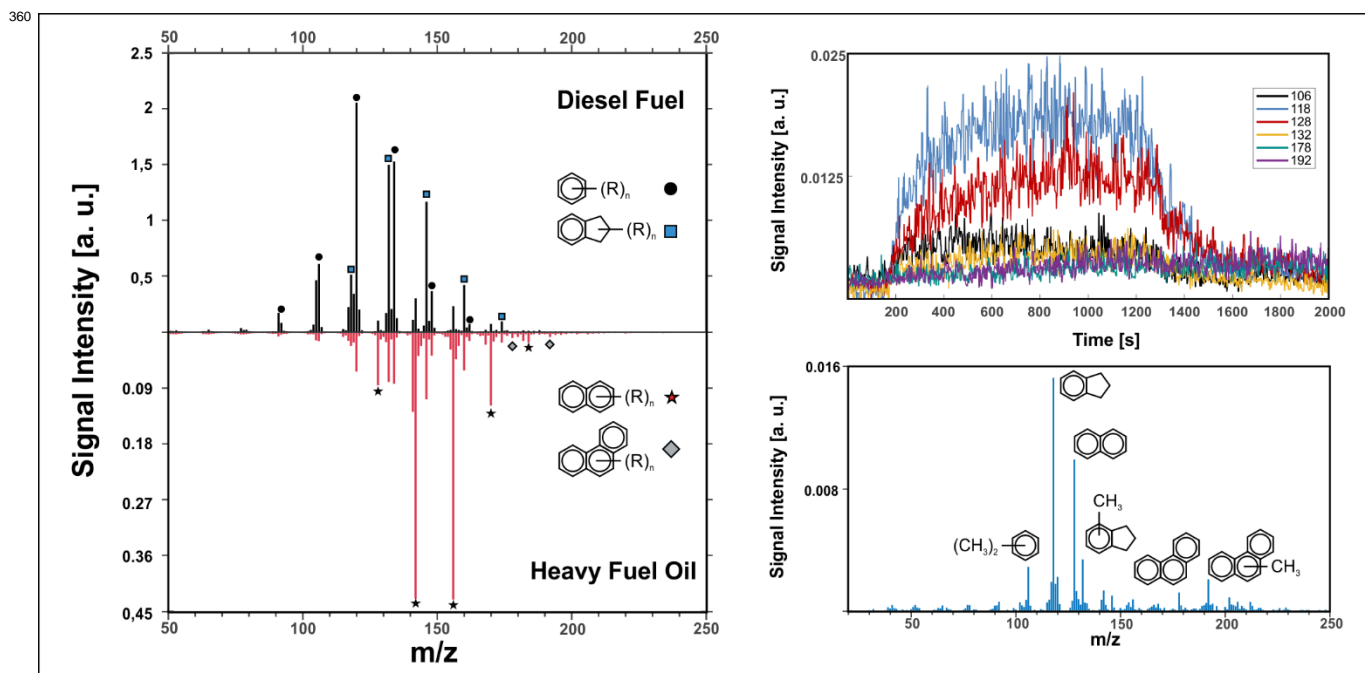


Figure 6. REMPI-eMIMS mass spectra of brackish water spiked with diesel fuel (DF) and heavy fuel oil (HFO) (left). In DF alkylated benzenes and indanes are the most prominent species. For HFO, a clear mass shift to higher m/z -values can be detected.; Ion traces and extracted mass spectrum of water from the Warnow river estuary (right). The river sample was additionally characterized by GC-MS. The REMPI-eMIMS value for naphthalene corresponds well with the GC-MS data. Additionally, with REMPI-eMIMS xylene and indane can be detected.

361

362 Investigation of Real World Samples

363 For the application of our ESMP-REMPI-TOFMS to real
 364 world samples it was tested beforehand, which compounds are
 365 detectable in contaminated waters. For this, brackish water of a
 366 harbor region was sampled. Known amounts of diesel fuel (DF)
 367 or heavy fuel oil (HFO) were added to 1 L of the water to simu-
 368 late a high contamination with these commonly used shipping
 369 fuels. The blank - subtracted mass spectra are shown in Figure
 370 6 (left). Clear differences between both contaminated water
 371 samples in respect to the detected compounds can be found. In
 372 the DF-contaminated sample alkylated benzenes and indanes
 373 show the highest prominence, whereas for HFO-contaminated
 374 water alkylated naphthalenes were the most dominant species.
 375 Additionally, phenanthrene and its alkylated derivatives can be
 376 detected in the HFO-water. In general, there is a shift to higher
 377 m/z from DF to HFO. These findings are well supported by ana-
 378 lyzing the evaporating gases of the pure DF and HFO at 80°C
 379 with REMPI-TOFMS (Figure A2, SI).

380 After these initial experiments, the ESMP-REMPI-TOFMS
 381 was used to investigate real world samples. A water sample was
 382 taken from the Warnow river estuary. Selected ion traces and
 383 the blank-subtracted mass spectrum are presented in Figure 6
 384 (right). The water sample was additionally characterized by
 385 GC-MS. Besides indane and xylene, small PAHs such as naph-
 386 thalene, acenaphthene, and fluorene were detected. A compari-
 387 son of GC-MS and REMPI-eMIMS is given in Table 3. For
 388 naphthalene, the concentration obtained by REMPI-eMIMS is
 389 in excellent agreement with GC-MS data. A similar statement
 390 can be applied to acenaphthene and fluorene, but it has to be
 391 noted that these concentrations are very close to the respective
 392 LODs. For phenanthrene a clear difference of the concentration
 393 value between both techniques was determined. An explanation

394 for this can be attributed to the extraction process for GC-MS
 395 analysis, in which the dissolved, the particle-bounded PAHs as
 396 well as compounds, stuck to the walls were extracted and ana-
 397 lyzed. With MIMS, in contrast, only dissolved organic com-
 398 pounds can be determined. In addition, the amount of particu-
 399 late matter in the analyzed sample was relatively high and the
 400 sample was stored over 3 days at 8°C. Therefore, and based on
 401 the large $\lg K_{ow}$ -value of phenanthrene, it can be expected that
 402 the majority of phenanthrene is bound to the particulate matter
 403 and wall of the sampling vessel.

404 **Table 3. Comparison of REMPI-eMIMS and GC-MS data**

Substance	REMPI-eMIMS [ng/L]	GC-MS [ng/L]
Naphthalene	121	115
Acenaphthene	(48)	13
Fluorene	(17)	16
Phenanthrene	87	679

405

406 Application to Process Analysis

407 Besides environmental application of REMPI-eMIMS, the
 408 presented setup can be easily adapted to process analysis. As an
 409 example for such a process, the online extraction behavior of
 410 coffee was monitored (Figure 7). For the extraction of coffee
 411 powder, the sample-side in the front-end was replaced by a filter
 412 setup (Figure 1). Additionally, the water outlet was guided back
 413 on top of the filter to enable continuous extraction and sam-
 414 pling. Representative traces of selected ions are shown in Figure
 415 7. At the beginning, only 1 L of water was circulating through
 416 the system.

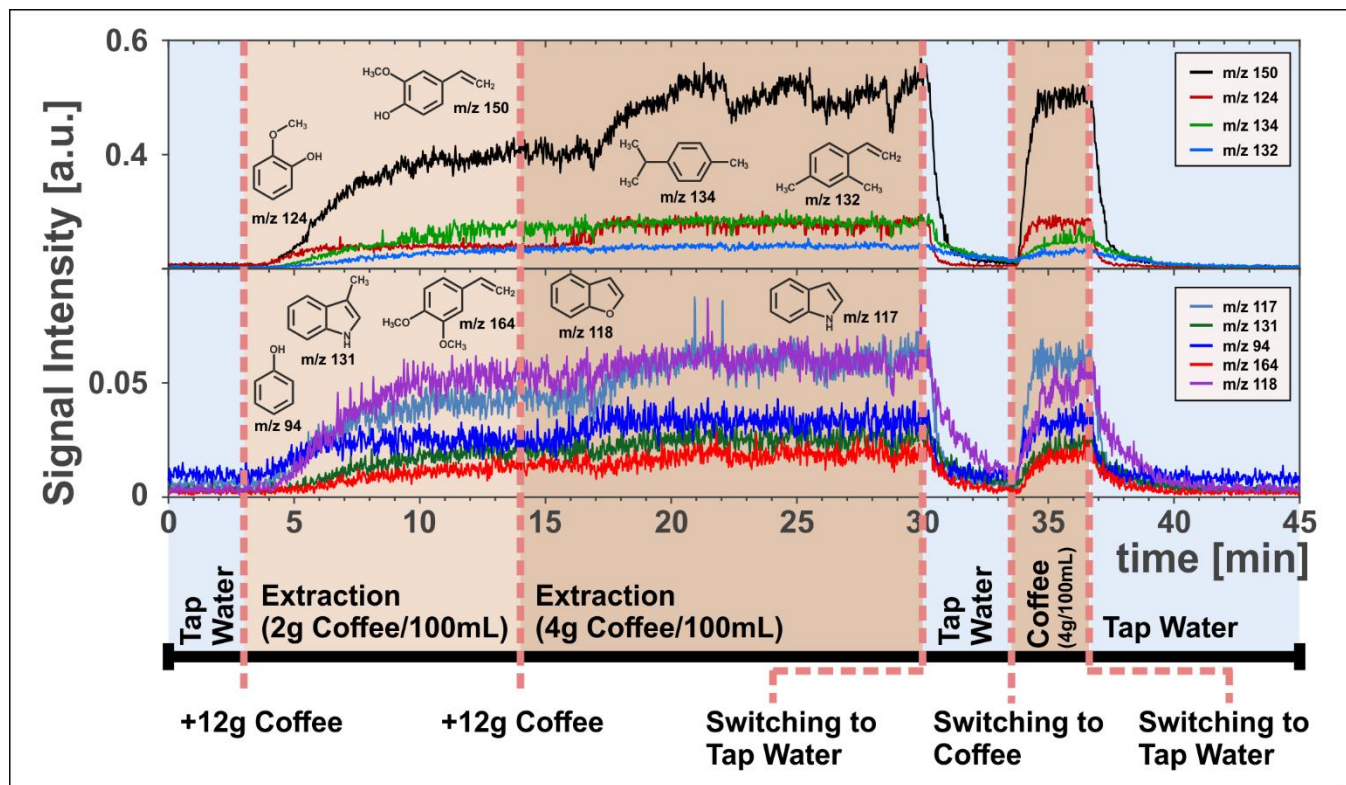


Figure 7. Traces of selected ions for the online extraction monitoring of coffee. In a closed-loop, tap water was circulating through the membrane probe and a filter setup. Coffee powder was sequentially added to the filter. After the final addition the liquid was changed to tap water. For determination of the response times of the individual substances, the liquid was changed back to coffee.

418 After 3 min, 12 g of freshly grinded coffee was added to the
 419 filter. Based on the ion traces, approx. 1 min after the addition
 420 of coffee powder the signal began to rise slowly up to steady-
 421 state conditions. At 14 min another 12 g of freshly grinded cof-
 422 fee was added to the filter. For most compounds, signal intensi-
 423 ties slowly increase ~2 min after coffee addition. In steady-state
 424 conditions at 30 min the circulating liquid was switched to tap
 425 water, which results in a fast decrease of all signals almost down
 426 to baseline levels. For the comparison of the actual eMIMS re-
 427 sponse times of analytes and their corresponding extraction behav-
 428 ior, the liquid was switched back to 4g/100mL coffee. It can
 429 be clearly seen that the response time of the membrane process
 430 is much shorter compared to the extraction process. In addition,
 431 this illustrates that the signal intensities of the I_{SS} are well re-
 432 producible with this setup. The corresponding mass spectra of
 433 both concentration steps are drawn in Figure A4 (SI). Here, only
 434 slight differences regarding the relative intensities are detecta-
 435 ble. The base peak is formed by m/z 150, which we assign as
 436 vinyl guaiacol. Caffeine as a very abundant species in coffee
 437 was not detected in our measurements, which can be attributed
 438 to low pervaporation rates.

439 The range of detectable analytes could be extended by the
 440 utilization of polar membrane materials or microporous mem-
 441 branes. It is expected that the increasing permeation of water
 442 will not affect the REMPI response.

443 CONCLUSION

444 An external membrane probe using a sheet membrane for
 445 photo ionization mass spectrometry was developed. The focus
 446 was laid on the detection of aromatic pollutants which suggest

447 the application of REMPI. Unlike the direct membrane inlet ap-
 448 proach, where a direct transfer of the analytes in the ion source
 449 allows straight forward low limits-of-detection but cause sub-
 450 stantial memory effects, the external-membrane inlet MS ap-
 451 proach (eMIMS) separated the membrane extraction from the ion
 452 source. Thus, different external membrane units can be set
 453 up and coupled via a standard capillary gas connector in a
 454 heated transfer line to the REMPI-MS System. This allows to
 455 perform trace- as well as process control applications in the
 456 same instrument.

457 With the developed prototype, detection of (polycyclic)aroma-
 458 tic species in water samples is accessible within minutes and
 459 without any sample preparation down to ng/L levels. The per-
 460 formance of the presented setup may be improved by introduc-
 461 ing additional heating strategies of the membrane, thus determi-
 462 nation of PAHs on board of sea going vessels should become
 463 possible at least for scientific purposes. Additionally, this sys-
 464 tem can be used for fast detection of different highly abundant
 465 aromatic species in processes waters for monitoring applica-
 466 tions. This can be useful especially for pilot plants or process
 467 optimization under research-oriented questions.

468 ASSOCIATED CONTENT

469 Supporting Information

470 The Supporting Information is available free of charge on the ACS
 471 Publications website.

472 Figures of Calibration curves, REMPI-eMIMS at 248 nm (cold in-
 473 let), extracted mass spectra for online extraction, comparison of
 474 REMPI-eMIMS with TG-REMPI and GC-MS data for HFO and
 475 DF; (PDF)

476 AUTHOR INFORMATION

477 Corresponding Author

478 * E-Mail: thorsten.streibel@uni-rostock.de, Phone: +49-381-498-
479 6527

480 Author Contributions

481 The manuscript was written through contributions of all authors. /
482 All authors have given approval to the final version of the manu-
483 script. /

484 Notes

485 The author declares no competing financial interest.

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