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1 **Solid-state polymer membranes for simple, sensitive, and low-cost**
2 **monitoring of mercury in water**

3

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16

17 **Abstract**

18 Solid-state Hg(II) selective membranes were produced and assessed by means
19 of X-ray absorption near edge structure in the total reflection X-ray
20 fluorescence (XANES -TXRF) setup and by the energy dispersive X-ray
21 fluorescence (EDXRF) technique. Membranes were functionalized using four
22 promising ligands for mercury complexation, i.e.: i) 4-(2-Pyridylazo) resorcinol
23 (PAR), ii) thiourea, iii) calconcarboxylic acid (CCS), and iv) dithizone. A
24 simple analytical procedure was followed, using miniscule reagent quantities,
25 thus suggesting the process is also cost-effective. XANES -TXRF revealed that
26 mercury complexes with the ligands, and not simply adsorbed onto the PVC
27 matrix, while the complexation was not affected by the matrix existence.
28 Mercury exhibited an increased oxidation grade and was covalently bound to

29 the ligand functional groups, via a strong chemical bond. EDXRF revealed that
30 the solid-state membranes can be used for mercury speciation and trace analysis
31 from environmental relevant matrices, such as tap water. The membranes could
32 be a promising alternative to polymer inclusion membranes (PIMs), due to their
33 simple configuration and high Hg (II) selectivity in aqueous media, but more
34 research is needed. PAR appears to be the most promising ligand, followed by
35 dithizone and thiourea. CCS had a minuscule preconcentration efficiency since
36 it was preferably bound with Cu in tap water, indicating limited usefulness for
37 mercury preconcentration. Therefore, it is suggested that, depending on the
38 ligand, the solid-state membranes could also possibly used for multi-elemental
39 heavy metals analysis in water.

40

41 **Keywords:** Divalent Mercury; mercury complexation; heavy metal pollution;
42 The International Atomic Energy Agency (IAEA); Elettra Sinchrotron Trieste
43 (EST); Synchrotron radiation-induced XANES

44 **Introduction**

45 The presence of mercury in natural water bodies is a growing
46 environmental problem of emerging concern, since mercury is a toxic and
47 hazardous heavy metal (Cooke-Andrews, 2006; European Environment
48 Agency, 2018; Kallithrakas-Kontos and Foteinis, 2016). Mercury can be found
49 hidden on numerous products, such as in mercury-containing skin creams and

50 soaps, dental amalgam, ethyl-mercury-containing vaccines, and latex paint
51 additives. It is also released, on a large-scale, from power plants, e-
52 waste/fluorescent lamps, wildfire emissions, and artisanal and small-scale gold
53 mining (Budnik and Casteleyn, 2019). Exposure, even at trace levels (ug L^{-1}), is
54 deemed a health hazard, since mercury bio-accumulates and can cause severe
55 biological toxicity. As a result, the World Health Organization (WHO) has set
56 the limit for water intended for human consumption at $1 \text{ ug L}^{-1} \text{ Hg}$, while
57 mercury has also been classified as one of the 33 “Priority pollutants” in the
58 European Water Framework Directive (2000/60/EC) (Marguí et al., 2018).

59 Various analytical methods are available for the environmental
60 monitoring of mercury, including voltammetry, mass spectrometry, atomic
61 absorption or emission spectrometry, and chromatography, but most of them
62 require a tedious sample pre-treatment, sophisticated performance, and/or
63 expensive equipment (Ensafi and Fouladgar, 2006; Kallithrakas-Kontos and
64 Foteinis, 2016). This implies the need for introducing fast, efficient, and low-
65 cost methods for the determination of mercury in water matrices and at trace
66 level concentration.

67 One such method for aqueous mercury preconcentration is the use of
68 polymer-based membranes, functionalized with a promising ligand for aqueous
69 mercury preconcentration. Currently, research is mainly focused on polymer
70 inclusion membranes (PIMs), which are polymer-based liquid membranes that

71 were first introduced around 50 years ago as the sensing membrane in ion-
72 selective electrodes and optodes and more recently have been used for aqueous
73 mercury preconcentration (Almeida et al., 2017). However, these membranes
74 could suffer from interferences from other ions, thus affecting their selectivity
75 and sensitivity in aqueous Hg(II) preconcentration. To overcome such concerns
76 we propose here the use of solid-state membranes for mercury preconcentration.
77 Specifically, solid-state polymer-based membranes have been found versatile,
78 selective, and easy to apply, since detection limits lower than $\mu\text{g}\cdot\text{L}^{-1}$ can be
79 achieved with an energy dispersive X-ray fluorescence (EDXRF) (Hatzistavros
80 and Kallithrakas-Kontos, 2014), a total reflection X-ray fluorescence (TXRF)
81 technique (Aretaki et al., 2006; Koulouridakis and Kallithrakas-Kontos, 2004)
82 or even with a benchtop TXRF system (Marguí et al., 2018).

83 Herein we comprehensively examine four promising ligands for Hg(II)
84 complexation, i.e. 4-(2-Pyridylazo)resorcinol (PAR), thiourea, calconcarboxylic
85 acid (CCS), and dithizone, which were successfully immobilized on the solid-
86 state membrane matrix (i.e. PVC). Hg(II) is a soft Lewis acid, which
87 preferentially bonds with soft Lewis bases, and therefore sulfur-containing
88 chemicals, such as, thiourea, CCS, and dithizone, have been found effective in
89 Hg adsorption from water matrices, since the thiol functional group is a soft
90 base (Sun et al., 2018). Specifically, PAR, thiourea and dithizone are well-
91 known ligands for mercury adsorption (Elly, 1973; Eshwar and Nagarkar,

92 1972; Litman et al., 1977; Zuo and Muhammed, 1995). Our group has also
93 preliminary examined them for Hg(II) preconcentration, but only by means of
94 TXRF (Aretaki et al., 2006; Koulouridakis and Kallithrakas-Kontos, 2004).
95 Furthermore, CCS is a sulfur-containing chemical that we had successfully
96 immobilized in selective membranes for aqueous ^{238}U and ^{234}U complexation
97 (Kallithrakas-Kontos et al., 2018). Here we examine its sensitivity in aqueous
98 Hg(II) preconcentration.

99 To study the chemical binding of aqueous Hg(II) ions in the solid-state
100 functionalized membranes, TXRF-XANES was employed. Furthermore,
101 EDXRF was used to quantitatively assess the membranes' Hg(II)
102 preconcentration selectivity. Even though there are many works dealing with
103 aqueous Hg(II) preconcentration approaches (Kallithrakas-Kontos and Foteinis,
104 2016; Pokhrel et al., 2017; Sun et al., 2018), a comprehensive chemical
105 speciation study that could shed light on the nature of the chemical binding that
106 it is formed between the aqueous Hg(II) ions and specific ligands immobilized
107 on solid-state membranes is missing from the literature.

108 **2. Materials and methods**

109 **2.1 Reagents and solvents**

110 The membrane solution was prepared by mixing the following, high
111 quality, analytical reagents. High molecular weight Polyvinyl chloride, popular
112 known as PVC, was sourced from Fluka™ (no. 81387) and used as the

113 membrane matrix. PVC was mixed with: i) dibutyl phthalate (DBP), i.e. the
114 plasticizer, which was sourced from Riedel-de Haën (no. 36736, Pestanal®); ii)
115 Elman's reagent (5,5'-dithiobis-(2-nitrobenzoic acid), popular known as DTNB,
116 i.e. the ionophore, which was used to enhance anions binding properties on the
117 membrane surface and was sourced from Fluka™ (no. 43760); and finally iii)
118 the complexing agent (ligand), which was one of the following: a) 4-(2-
119 Pyridylazo)resorcinol (PAR), sourced from Fluka™ (no. 82970); b) thiourea,
120 sourced from Riedel-de-Haën™ (no. 33717); c) calconcarboxylic acid (CCS),
121 both anion and cation sourced from Merck (no 4595); and d) dithizone, sourced
122 from Sigma–Aldrich® (No. 43820). All chemical reagents were in solid form
123 and were diluted in tetrahydrofuran (THF), sourced from Sigma–Aldrich® (No.
124 401757). Ultrapure water (ASTM Type I) was used throughout the work, while
125 Fluka Mercury Standard for Atomic Absorption Spectroscopy AAS (Cat. No.
126 16482) was used for Hg(II) spiking.

127 **2.2 Membrane preparation procedure**

128 The functionalized membranes were prepared as a 10 uL solvent
129 containing 52% PVC, 32% DBP, 9.5% ligand and 6.5% DTNB, all diluted in
130 tetrahydrofuran (Hatzistavros and Kallithrakas-Kontos, 2014). For the EDXRF
131 analysis, each solvent was directly applied on thin-film substrates (Mylar® 2.5
132 µm). For solvent evaporation and membrane solidification, the film substrate
133 was left to dry in room temperature for 24 hours (alternatively an IR lamp can

134 be used for reduced drying time, but this was not required herein). Once
135 prepared, the membranes were immersed on ultrapure water containing 50 ug
136 L⁻¹ Hg(II) for 24 hours. During this time the Hg(II) - ultrapure water solution
137 was kept stirred, as673 to enhance mercury ions mobility. After Hg(II)
138 collection, the membranes were rinsed with high ultrapure and kept for analysis.
139 All experiments were carried out at room temperature.

140 For the TXRF-XANES measurements, membrane solutions were
141 prepared as described above. Then, 10 µL of each membrane solution was
142 directly placed in the center of quartz reflectors, instead of the Mylar® 2.5 µm
143 film, producing a 10-mm diameter spot. The reflectors containing the
144 membranes were left to dry at room temperature and then immersed in the
145 stirred Hg(II) - ultrapure water solution. The Hg(II) XANES spectrum was also
146 obtained, to be used as a reference, by directly pipetting 10 uL of Hg(II) nitrate
147 solution on a quartz reflector and left to dry at room temperature.

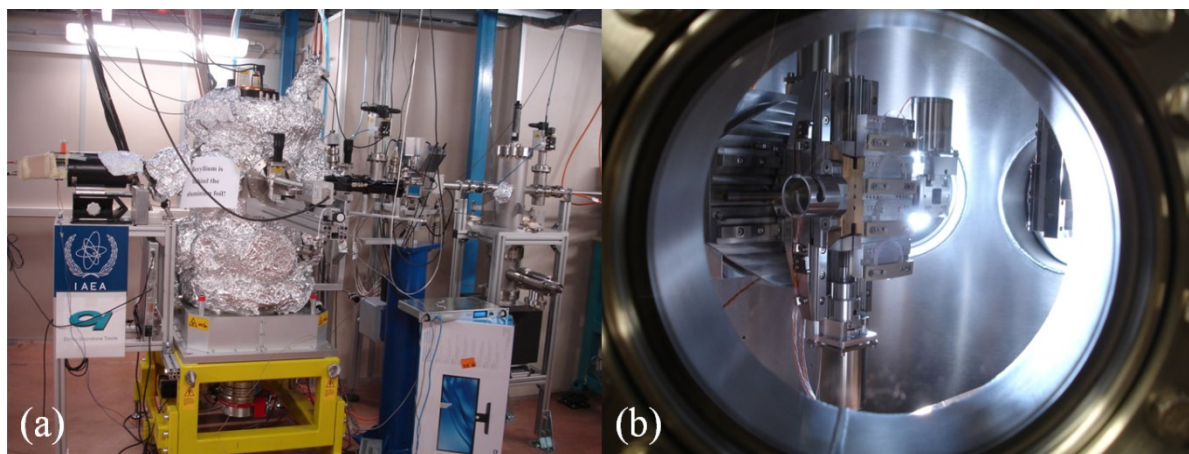
148 **2.3 EDXRF analysis**

149 For EDXRF measurements an AMETEK® SPECTRO XEPOS unit,
150 which is widely used in environmental monitoring and assessment applications,
151 was employed. A description of the unit can be found elsewhere (Foteinis et al.,
152 2013; Hatzistavros and Kallithrakas-Kontos, 2014). In the context of this work
153 the SPECTRO XEPOS Compton secondary/molybdenum mode (at 40 kV and
154 0.9 mA) was used under helium gas flushing, instead of in air atmosphere. Each

155 sample was irradiated for 5 min (300 s) and the measured raw data were
156 processed with X-Lab Pro 4.0 quantitation software, using the TurboQuant
157 screening method.

158 **2.4 TXRF-XANES experiments**

159 TXRF-XANES was employed to investigate whether i) mercury was
160 simply adsorbed or was complexed with the ligand in the membrane and ii) the
161 presence of the membrane matrix affected this complexation. Measurements
162 were carried out at the X-ray Fluorescence beamline (10.1L) of Elettra
163 Sincrotrone Trieste (EST), using the multi-technique X-ray spectrometry
164 instrument developed by the International Atomic Energy Agency (IAEA Xspe)
165 (Fig 1).



166
167 Fig 1: Picture of the: (a) IAEA Xspe instrument positioned at the 10.1L XRF beamline of
168 Elettra Sincrotrone Trieste, and (b) Ultra High Vacuum chamber.

169 All the measurements were carried out in vacuum conditions, using a
170 multi-axis motorized sample manipulator (Fig 1). More information concerning

171 the IAEA Xspe instrument hardware components and setup can be found
172 elsewhere (Karydas et al., 2018; Marguí et al., 2018).

173 The XANES spectra were collected at the energy range of -50 to +200 eV
174 around the Hg L₃ edge (12284 eV), in steps of 0.5 eV in the edge region and in
175 steps of 2 and 1 eV in the pre- and post-edge regions, respectively. The spectra
176 were collected in the TXRF detection mode. Raw data were processed using
177 ATHENA software (Newville, 2001; Ravel and Newville, 2005). The pre-edge
178 background of each spectra was subtracted, and the absorption coefficient was
179 normalized to a unit-edge step. The low mercury concentration in the samples
180 (the membranes were immersed in a solution containing 50 ug L⁻¹ mercury) and
181 their limited thickness (thin films onto the TXRF sample supports), suggests
182 that self-absorption correction for the XANES spectra could be omitted.

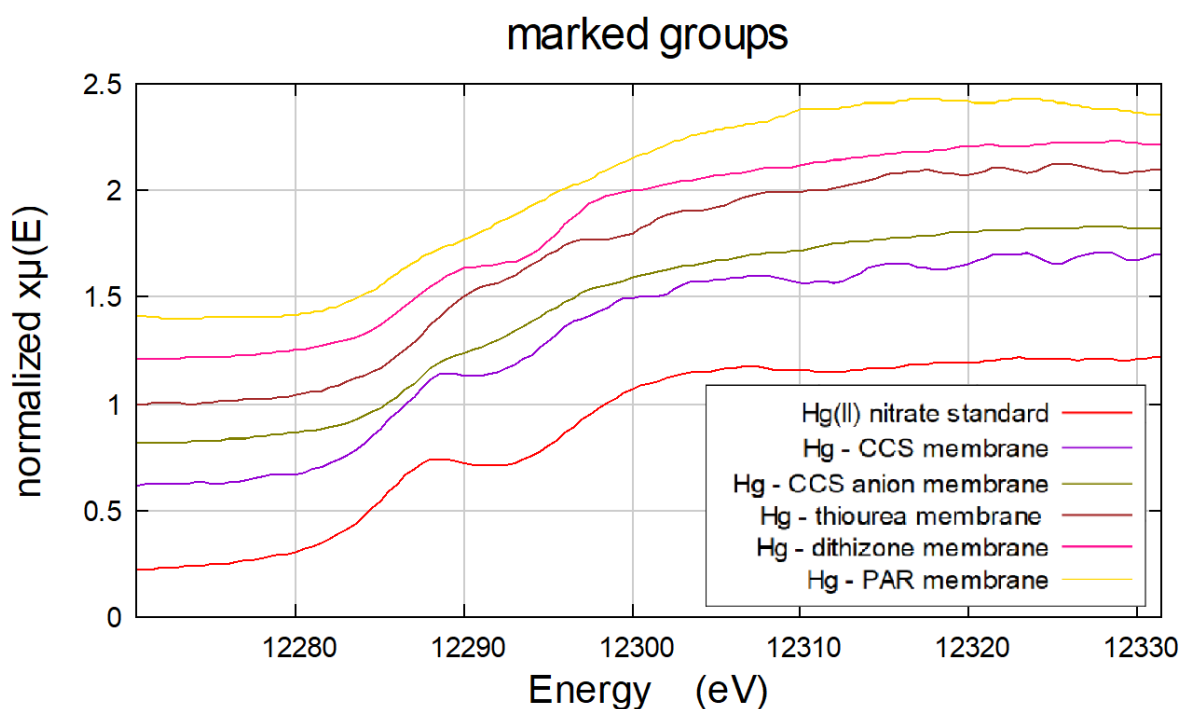
183 **3. Results and Discussion**

184 First XANES measurements are presented, as to identify the chemical
185 environment of Hg(II) – ligand complexation. Thence, a comparative analysis
186 between the solid-state membranes, in terms of Hg(II) preconcentration, is
187 carried out by means of the EDXRF technique.

188 **3.1 XANES results**

189 TXRF-XANES was employed to investigate whether mercury is simply
190 adsorbed in the membrane or complexes with the ligand and whether the
191 presence of the membrane affects this complexation.

192 In order to answer the first question, the XANES spectra of the solid-state
193 membranes were compared with the reference spectrum of Hg(II) nitrate. The
194 normalized XANES spectra are shown in Fig. 2.

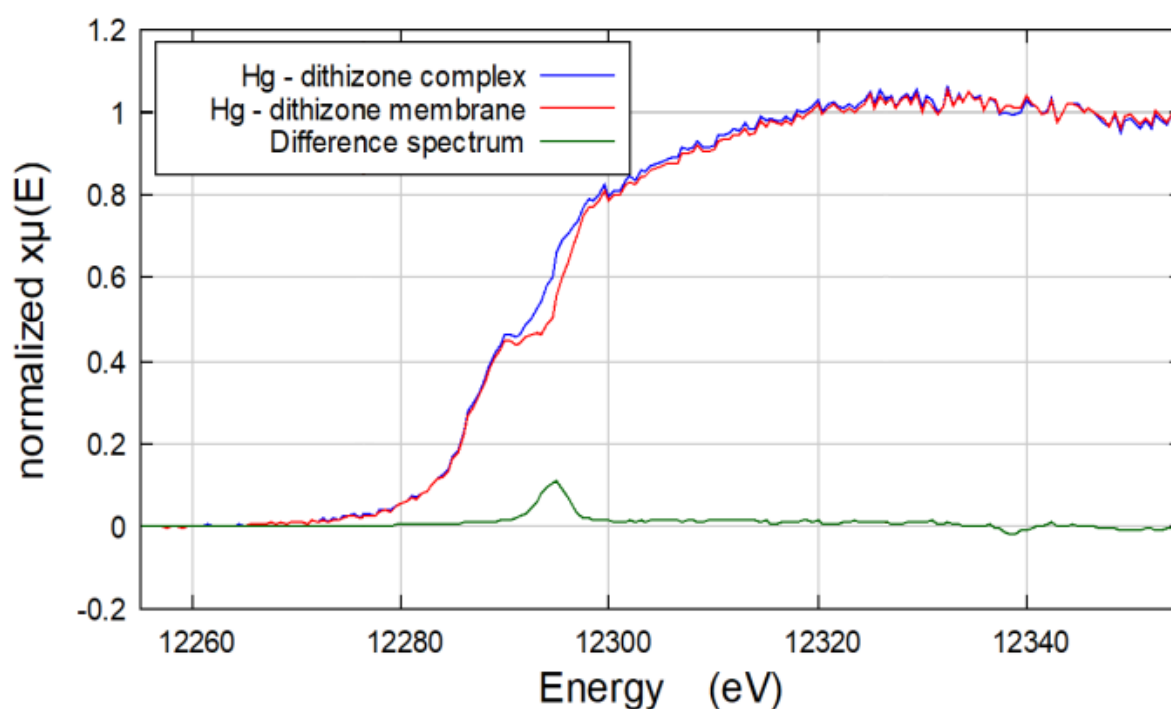


195
196 Fig. 2: Normalized Hg-L₃ TXRF-XANES spectra of the solid state membranes along with
197 the reference spectrum of Hg(II) nitrate spectrum.

198 The spectra of Hg-CCS anion membrane presented a pronounced XANES
199 feature (shoulder), which is also characteristic for the Hg(II) nitrate standard
200 (Fig. 2). On the other hand, the absence of this feature at the spectra of Hg on
201 the cation membranes (i.e. CCS cation, thiourea, dithizone and PAR), suggests

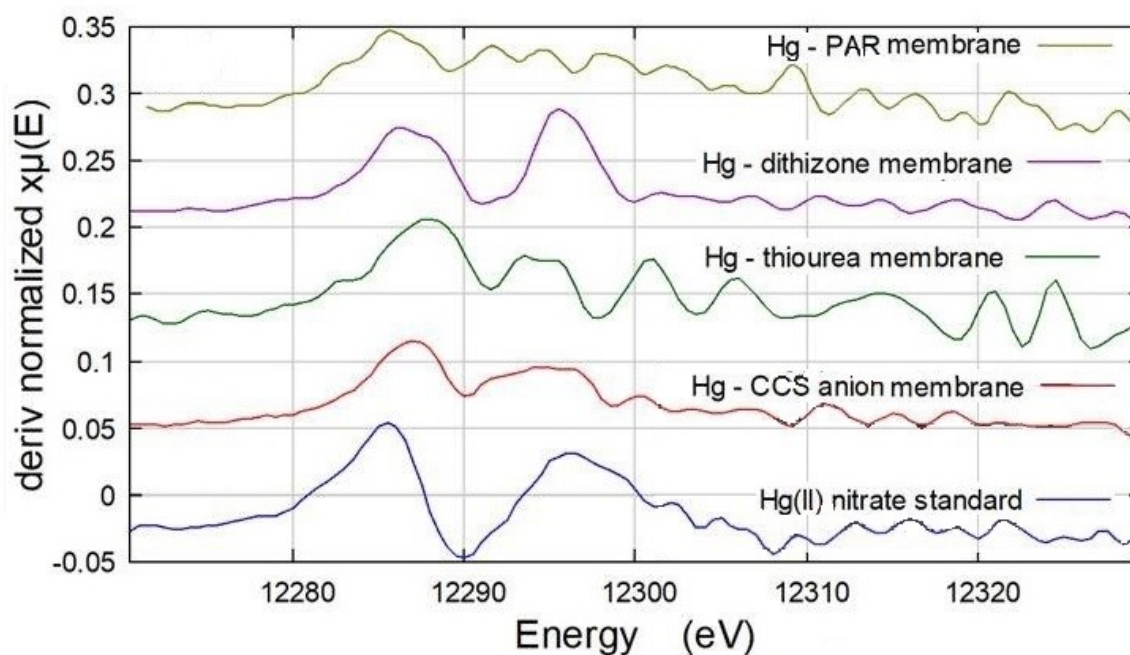
202 that Hg(II) is complexed with each ligand's functional groups into the PVC
203 membrane, and not simply adsorbed.

204 To evaluate the possible PVC contribution forward the complexation procedure,
205 the XANES spectrum of the Hg-dithizone was collected to be used as a
206 reference and thence it was compared with the XANES spectrum of the
207 dithizone functionalized membrane, which is PVC based (Fig. 3). The similarity
208 between the Hg-dithizone reference spectrum and the one of the dithizone-
209 functionalized PVC membrane permits the consideration that the presence of
210 the membrane matrix (PVC) does not affect the complexation itself and seems
211 to play a very small role during this procedure.



212
213 Fig. 3: Normalized TXRF-XANES spectra of Hg(II)-dithizone and the dithizone-
214 functionalized PVC membrane and their difference

215 In order to get insight into the chemical state of mercury after its complexation
216 with each ligand, the first derivative of each collected spectrum was calculated.
217 The energy position of the first inflection point of normalized $x\mu(E)$ is
218 considered as an indicator of the Hg oxidation state (Mishra et al., 2011; Rajan
219 et al., 2008). Here, the position of the Hg L_3 edge in the membrane XANES
220 spectra indicated by the maximum of the derivative (Fig. 4), is shifted towards
221 higher energy, in an obvious manner, relative to that of the Hg(II) nitrate
222 standard.



223
224 Fig. 4: First derivative of the Hg L_3 edge TXRF-XANES of anion and cation selective
225 membranes, along with Hg(II) nitrate standard sample.

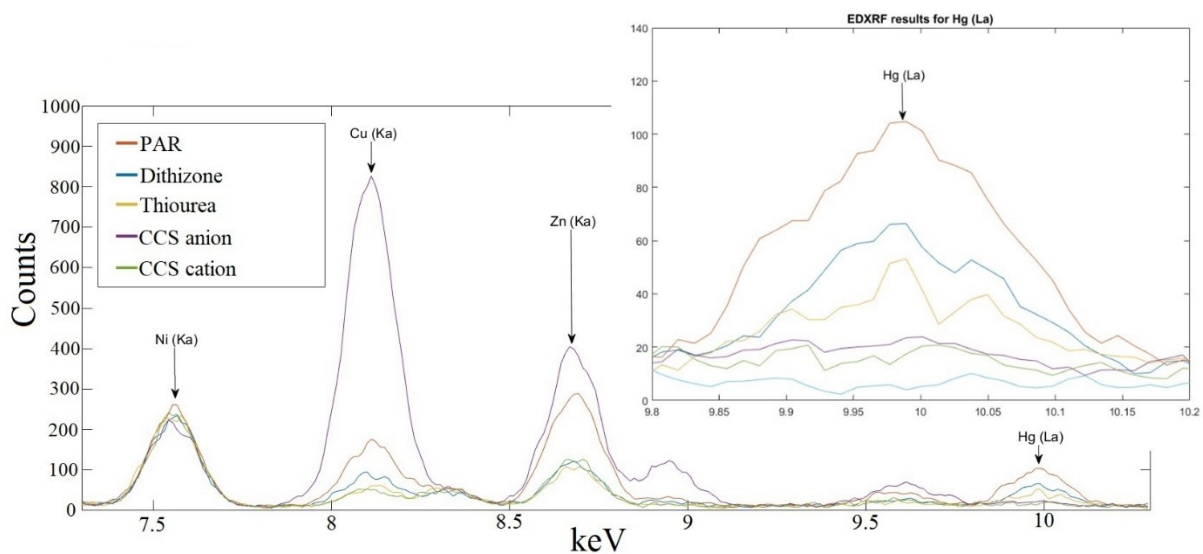
226
227 It can be observed that two main peaks exist in the Hg(II) nitrate and Hg
228 dithizone membrane spectra, while in the remaining spectra the second main
229 peak is subtle (Fig. 4). The energy difference between them (ΔE) has been

230 correlated with the bonding environment of the probed element (Colombo et al.,
231 2014; Powers, 1982). From Fig. 4 it can be observed that the ΔE for Hg(II)
232 nitrate standard 11.0 eV, while the ΔE for the dithizone, PAR, CCS anion,
233 thiourea 9.0, 7.2, 8.4 eV, respectively. In general, large ΔE values correspond to
234 Hg-ligand complexes with ionic character, while a small ΔE values are
235 correlated with complexes having a more covalent character (Colombo et al.,
236 2014; Powers, 1982). Therefore, results imply that Hg(II) was covalently bound
237 to all ligands functional groups via a strong chemical bond. Finally, the
238 differences between the Hg(II) nitrate standard and the solid-state membranes
239 mainly lie to the different position of the main peak and the ΔE between the two
240 main peaks, which reveal the slightly different oxidation state of the Hg.

241 **3.2 EDXRF results**

242 In our previous works, solid-state PVC-based functionalized membranes
243 were studied in terms of mercury preconcentration efficiency and were found
244 promising (Aretaki et al., 2006; Hatzistavros and Kallithrakas-Kontos, 2014;
245 Koulouridakis and Kallithrakas-Kontos, 2004; Marguí et al., 2018). Here, four
246 different functionalized membranes, i.e. dithizone, PAR, thiourea, and CCS (both
247 anion and cation) were examined by EDXRF. In order to comprehensively
248 examine and acquire an in-depth understanding of each functionalized
249 membrane efficiency in environmental relevant water matrices, mercury
250 preconcentration took place in tap water instead of ultrapure water.

251 The reason that tap water was chosen over ultrapure water is twofold.
252 Firstly, mercury monitoring and assessment in tap water comprise a common
253 environmental problem. Secondly, apart from the spiked mercury content, tap
254 water contains a wide array of other (heavy) metals and elements, which could
255 have different affinities which each ligand, thus possibly affecting the selective
256 preconcentration of mercury. Specifically, as mentioned above the ligands
257 under study are sensitive to a vast spectrum of heavy metals, apart from
258 mercury, as well as other metals and elements typically found in environmental
259 relevant samples. Therefore, when the membranes are exposed to environmental
260 relevant matrices each ligand could have a strong affinity towards other (heavy)
261 metals, thus reducing the selectivity in preconcentrating mercury. Fig. 5 shows
262 the comparison of EDXRF spectra for functionalized membranes, highlighting
263 mercury preconcentration efficiency, as well as their affinity towards Ni, Cu,
264 and Zn, which were present in the tap water used.



265

266 Figure 5: Section of EDXRF spectra for the non-functionalized membrane (light blue colour)
267 compare to the membrane functionalized with a) PAR (red colour)), thiourea (yellow colour),
268 CCS anion (purple colour), CCS cation (green colour), and dithizone (blue colour). Inset:
269 Zoom on the EDXRF results for mercury, i.e. Hg(La).

270 As observed in Fig. 5, membrane functionalization has a profound effect in
271 aqueous Hg(II) sorption. It was found that the PAR functionalized membrane
272 yielded, by and large, the higher sensitivity in aqueous Hg(II) preconcentration,
273 followed by dithizone and thiourea. Specifically, we have established that for the
274 dithizone-functionalized membrane the aqueous mercury detection limit is and
275 0.069 ng mL⁻¹ for doped ASTM Type I water and seawater, respectively (1000
276 mL sample volume, with 24 h equilibration time and 300 s irradiation time).
277 The obtained results (Fig. 5) suggest that PAR could achieve a 66 % lower, i.e.
278 better, detection limit, while thiourea appears to have about 25% higher, i.e.
279 worse, detection limit. However, the exact performance and detection limits of
280 each membrane will be further examined in our future works. Finally, results
281 are suggestive that both the anion and cation CCS membranes had very low
282 efficiency in preconcentrating aqueous Hg(II). Nonetheless, it was identified that
283 the CCS cation membrane has a very high affinity towards Cu, and to a smaller
284 degree towards Zn, both abundant in the tap water used in the present study.
285 This possibly grossly affects the selectivity of the CCS cation membrane in
286 Hg(II) selective preconcentration. The above suggests that CCS usefulness for
287 mercury monitoring and assessment in natural water bodies is limited. However,

288 it could be an excellent indicator for other (heavy) metals found in
289 environmental relevant matrices.

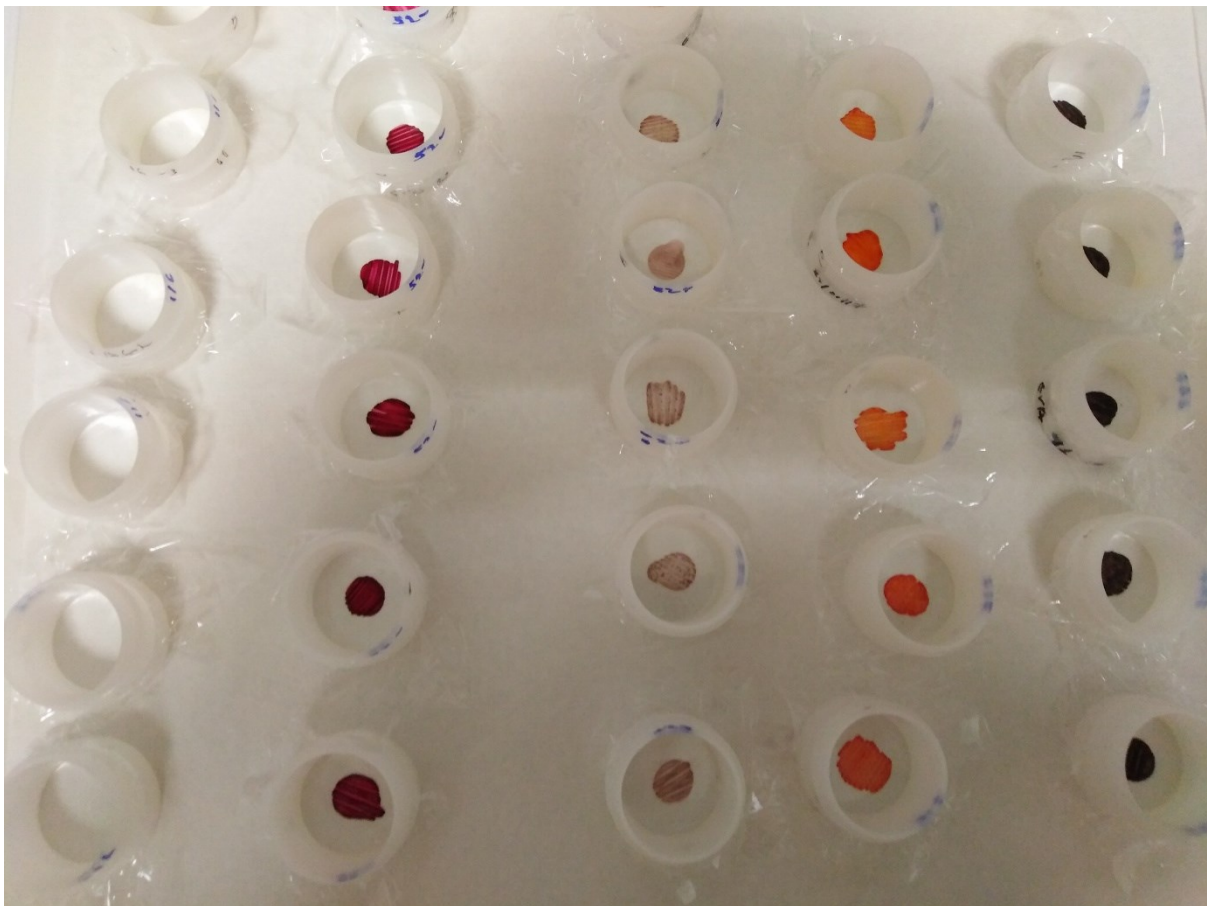
290 Therefore, results indicate that the most promising, by and large, ligand for
291 aqueous Hg(II) preconcentration is PAR. Dithizone performed better than
292 thiourea, which exhibited around ~ 29 % lower Hg (II) preconcentration
293 efficiency compared to dithizone. Results for CCS (both anion and cation)
294 were not encouraging for its use for aqueous Hg(II) preconcentration, however,
295 it appears that it could act as a promising indicator for other (heavy) metals
296 typically found in natural water matrices.

297 **3.3 Interferences with other ions and environmentally relevant applications** 298 **of the functionalized membranes**

299 The solid-state membranes were proved to be a relatively simple medium
300 for aqueous Hg(II) monitoring and assessment. Furthermore, once the
301 membranes are prepared, they can be used both in the laboratory but also on
302 the field by non-specialized personnel, due to their small size and simple
303 configuration with no moving parts (Fig. 6). This assumption was tested by
304 using the solid-state membranes at the easiest possible level. Specifically, in
305 this scenario analytical accuracy was set in second place in order to examine
306 the selectivity and Hg(II) detection limit when the membranes are used by
307 non-specialized personnel. As such, each membrane was simply submerged
308 for 24 h in 1 L of bottled water, containing 100 ug L^{-1} Hg(II). The water was

309 not stirred, which enhances mercury ions mobility and thus lowering Hg (II)
310 detection limit, to account for cases where the membranes are used directly on
311 the field with limited means.

312 Furthermore, bottled water was examined, which is an environmentally
313 relevant water matrix rich in ions that could hamper membrane selectivity in
314 Hg(II). Specifically the bottle water main characteristics were pH 8.0, 290 μS
315 cm^{-1} , 134 mg L^{-1} (CaCO_3), 31 mg L^{-1} Ca^{+2} , 14 mg L^{-1} Mg^{+2} , 7 mg L^{-1} Na^+ , 160
316 mg L^{-1} HCO_3^- , 13 mg L^{-1} Cl^- .



317

318 Figure 6: The prepared solid-state membranes.

319 Table 1 list the identified detection limits (DL) when using the simplest
320 membrane configuration. DL was estimated by dividing the net intensity with
321 the sensitivity in counts per second per percent (Van Grieken and Markowicz,
322 2001). It can be observed that even though bottled water contained a large
323 number of ions, which could interfere with Hg(II) selectivity, the solid-state
324 membranes yielded very low detection limits using the simplest configuration,
325 i.e. just submerging the membranes in the water without stirring.

326 It was found that in the case of bottled water PAR gave the lowest DL,
327 by and large, followed by dithizone, thiourea, CCS anion, and finally CCS
328 cation. Results are in agreement with those obtained in tap water, which was
329 expected since both water matrices are quite similar. However, the most
330 important fact is that even when using the solid-state membranes at the
331 possible simplest configuration, very low DL are achieved, which are on par or
332 even lower than the 1 ug L^{-1} limit set by the World Health organization (WHO)
333 for water intended for human consumption (Marguí et al., 2018). Therefore, it is
334 possible to use the solid-state membranes on the field and thence just mail them
335 to the laboratory for the EDXRF measurements, especially when taking into
336 account their small size (Fig. 6). Overall, results suggest that the produced
337 solid-state membranes could be promising for real-world applications and
338 possibly an alternative to liquid membranes, such as the polymer inclusion

339 membranes (PIMs) which are largely employed for mercury monitoring and
340 assessment applications. However, more research is need towards that end.

341 Table 1: The achieved detection limits for bottled water. Irradiation time 4,200
342 sec.

Membrane	Detection limit ($\mu\text{g L}^{-1}$)
Dithizone	1.9
CCS-	5
CCS+	13.3
PAR	0.88
Thiourea	3.25

343

344 Furthermore, the method can be characterized as cost-effective since,
345 compared to other analytical techniques, EDXRF is a relatively low-cost
346 technique, which is also the chemical reagents used for membrane preparation.
347 Specifically, PAR, the most promising ligand, is a well-known and low-cost
348 chemical reagent (Liu et al., 2012). This is also the case for all chemical
349 reagents utilized herein towards producing the functionalized membranes,
350 which are in general characterized by low-cost and are easy to find and
351 purchase.

352 Finally, PAR, apart from being the most promising indicator for aqueous
353 Hg(II), is also an excellent indicator for many other heavy metal ions, such as
354 Co^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Pb^{2+} and Cu^{2+} (Liu et al., 2012). This is the case for
355 thiourea, CCS, and dithizone, which are also sensitive to a vast spectrum of
356 heavy metals. Therefore, it is suggested that the novel functionalized

357 membranes can be used for multi-elemental or selective analyses of (heavy)
358 metals in water matrices, which will be examined in our future works. Given the
359 fast, simple, and low-cost membrane preparation method, it is suggested that the
360 functionalized membranes can act as a fast, efficient, and low-cost indicator for
361 mercury, and possibly other heavy metals, monitoring and assessment in natural
362 water bodies. Future applications could also include the mercury and heavy
363 metal collection, not only from natural waterbodies but also from industrial
364 heavy metal hotspots, provided that the membranes are produced and used in
365 large-scale routine works.

366 **4. Conclusions**

367 Here we introduced, studied, and assessed a simple, sensitive, and low-
368 cost method for Hg(II) monitoring and assessment in water matrices, and even
369 at trace level. Solid-state membranes were successfully functionalized either
370 with i) thiourea, ii) PAR, iii) CCS or iv) dithizone, using as a membrane matrix
371 PVC.

372 TXRF-XANES results revealed that mercury complexes with each of the
373 selected ligands, rather than simply adsorbed in the membrane matrix. Using the
374 EDXRF technique each membrane was quantitatively assessed in terms of
375 Hg(II) preconcentration efficiency. It was found that membrane
376 functionalization has a profound effect in Hg(II) preconcentration, with PAR
377 appearing to have, by and large, the highest efficiency in mercury

378 preconcentration. Thiourea exhibited around 29 % lower preconcentration
379 compared to dithizone, but both had a significantly lower Hg(II)
380 preconcentration efficiency compared to PAR. CCS (both anion, but
381 particularly cation) gave poor efficiencies, suggesting that its use for aqueous
382 Hg(II) preconcentration is limited.

383 When using the membranes at their simple configuration, i.e. just immerse
384 them in a water matrix, very low detection limits are achieved. Furthermore, the
385 solid-state membranes were found to perform very well in environmentally relevant
386 matrices, such as tap and bottled water, even though they contain a large
387 number of anions. Results suggest that the solid-state membranes can act as a
388 simple, sensitive, and low-cost indicator not only for aqueous mercury, but
389 possibly for other (heavy) metals, implying that they could be used for multi-
390 elemental analysis in environmentally relevant water matrices.

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403 PAR is a well-known (Eshwar and Nagarkar, 1972)

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