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Electrochemical identification of hazardous phenols and their complex mixtures in real samples using unmodified screen-printed electrodes

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- 1 Electrochemical identification of hazardous phenols and their
- 2 complex mixtures in real samples using unmodified screen-printed
- 3 electrodes
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11 Abstract

The electrochemical behavior of some of the most relevant endocrine-disrupting 12 phenols using unmodified carbon screen-printed electrodes (SPEs) is described for 13 the first time. Experiments were made to assess the electrochemical behavior of 14 phenol (PHOH), pentachlorophenol (PCP), 4-tert octylphenol (OP) and bisphenol A 15 (BPA) and their determination in the most favorable conditions, using voltammetric 16 methods such as cyclic voltammetry (CV), linear sweep voltammetry (LSV) and square 17 wave voltammetry (SWV) in Britton Robinson (BR) buffer. Further, the usefulness of 18 19 the electrochemical approach was validated with real samples from a local river and was compared to commercial Phenols Test Kit, which is commonly used for on-site 20 screening in industrial streams and wastewaters. Finally, the approach was compared 21 with a lab-bench standard method using real samples, i.e., high-performance liquid 22 23 chromatography with a photodiode array detector (HPLC-DAD). Keywords: endocrine-disrupting phenolic compounds, simultaneous voltammetric 24

detection, anodic pretreatment, spiked river samples, HPLC-DAD accuracy evaluation.

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28 **1. Introduction**

Phenols are organic compounds classified as priority pollutants due to their impact on 29 the ecosystem, e.g. chlorophenols, alkylphenols and bisphenols [1,2]. Phenolic 30 compounds are commonly found in the environment from either natural [3-5] or 31 synthetic sources [6,7]. Most hazardous synthetic phenols penetrate the ecosystem 32 due to their wide use in disinfectants, dyes, polymers, drugs, explosives, pesticides, 33 and other organic substances [8]. For instance, the European production of phenol 34 35 (PHOH) reached 1.8M tons in 2020, almost half of which was converted into phenolic resin and quart of which was converted into plastic precursor bisphenol A (BPA), 36 accounting for over a quarter of the global phenol market [9]. Moreover, the continuous 37 release of these chemicals can lead to a prominent accumulation in the environment 38 (such as in live organisms, i.e. fat tissue) [10]. Hence, drainage of municipal and 39 industrial sewage to surface water has become a serious environmental issue [11,12]. 40 Phenol concentration levels fluctuate from one place and/or country to another. The 41 highest concentrations of phenols are observed near the outlets of industrial streams 42 and wastewaters. As an example, the concentration of BPA [13], pentachlorophenol 43 (PCP) [14] and octylphenol (OP) [15] detected in European rivers is between 4 – 92 44 nM, 0 – 4 nM and 0.02 – 63.01 nM, respectively. The cytotoxicity of phenols is 45 determined by their hydrophobicity and the formation of phenoxyl radicals [16], with 46 higher values upon the increasing degree of chlorination [17]. Some phenols are 47 categorized as endocrine-disrupting chemicals (EDCs) exhibiting estrogenic properties 48 such as BPA, OP, or nonylphenol [18-20]. Several studies have verified how the 49 phenolic EDCs affect and damage the endocrine, developmental, reproductive, 50 neurological, cardiovascular, metabolic and/or immune systems [21,22]. Hence, 51 exposure to these chemicals in an early life stage leads to an increased prevalence of 52 numerous diseases including asthma, learning and behavior problems, early puberty, 53 infertility, cancer, and obesity [23-25]. Surprisingly, to date, no strict agreements 54 neither legal concentration limits exist for the control and executive regulation of EDCs 55 [12,26,27]. Therefore, there is an undoubted need to assess the concentration levels 56 of phenolic EDCs in wastewaters in order to control, better understand and minimize 57 the impact of EDCs on ecosystems and human health [28]. 58

59 Traditionally, phenols have been quantified with high-performance liquid 60 chromatography (HPLC) and gas chromatography (GC) coupled with detection

techniques such as ultraviolet-visible spectroscopy (UV/VIS), photodiode array 61 detector (DAD) or mass spectrometry (MS) among others [29–31]. These techniques 62 have important disadvantages being expensive, time-consuming (hours) and requiring 63 derivatization steps (e.g., GC), preconcentration steps (e.g. solid-phase or liquid-liquid 64 extraction) and trained personnel, being not suitable for on-site testing. On the other 65 hand, commercially available tests (e.g. phenols test kit of Hanna Instruments[®], 66 HACH[®] or CHEMetricsTM) can quantify phenols in water based on colorimetric or 67 spectrophotometric readout [32–34]. Albeit the kits are easy to use, fast, inexpensive, 68 and portable, they still exhibit some drawbacks in terms of selectivity (determining only 69 the total phenol amount) and sensitivity (i.e., 0.02 mg L⁻¹ Hanna Instruments® 70 https://www.hannainstruments.be/nl/). 71

In the last years, electrochemical detection methods have been used to identify harmful 72 phenols in aqueous solutions (see Table 1) mainly because of their outstanding 73 advantages such as multiplex and miniaturization options, selectivity, sensitivity, cost-74 effectiveness, rapid response, and portability [35]. The specific electrochemical 75 fingerprint (EF) of the electroactive phenolic compounds allows their selective 76 detection [36]. Thus, the feasibility of the voltammetric identification has been 77 78 demonstrated by using modified glassy carbon electrodes (GCE), which results in nanomolar range limits of detection (LOD) for BPA, catechol, p-cresol and p-79 80 nitrophenol [37,38]. However, this type of GCE cannot be integrated into a portable configuration. Notably, in the last decade, several modified screen-printed electrodes 81 (SPEs) have been reported for BPA detection (one of the most common phenolic 82 EDCs) exhibiting higher sensitivity, reproducibility and stability. Nevertheless, these 83 approaches have a common drawback caused by the electro-polymerization of 84 phenols into the electrode surface, whereby polymeric non-soluble substances are 85 formed due to the coupling of phenoxyl radicals [39,40]. This causes electrode fouling 86 or passivation by adsorption of these substances, which blocks and deactivates the 87 electrode surface of the SPE. This issue could be avoided by single-use of SPEs as 88 the example recently reported by Wang et al. for BPA detection based on an 89 electrochemical miniaturized device [41], or modifying the SPEs with carbonaceous 90 nanomaterials [42-45]. At the same time, several enzymatic biosensors have also 91 been proposed to detect phenolic compounds at lower LOD (nM range) [46-49]. 92 Nonetheless, in the case of enzymes different factors must be considered such as their 93

chemical and thermal instability, reproducibility and the immobilization process, 94 especially when dealing with industrial wastewater samples. To overcome these 95 drawbacks, a novel bio-inspired photoelectrochemical sensor for phenol detection was 96 recently developed by this group [50]. The detection mechanism is based on a robust. 97 perfluorinated molecular photosensitizer, that mimics the enzymatic reaction providing 98 outstanding sensitivity and limit of detections in the nM to pM level [51]. Despite the 99 last advances, the literature lacks an in-depth understanding of the EFs of a broad 100 101 range of phenolic compounds.

102 The electrochemical behavior of PHOH and three different hazardous derivatives (i.e., pentachlorophenol (PCP), OP and BPA) using carbon SPEs is presented. The 103 chemical structure and main features of the selected phenols are specified in Table 104 **S1** in the Supplementary Material (SM). Firstly, the electrochemical reversibility and 105 mass-transport mechanism were investigated by CV and LSV, respectively, and the 106 EFs of four phenols were studied in Britton Robinson buffer by SWV in the entire pH 107 108 range (2 - 12). Secondly, the stability of the phenols at pH 12 over time (up to 5 hours) was measured under different storage conditions of the samples: i) in ice and dark, ii) 109 at room temperature and in dark, and iii) at room temperature and daylight. 110 Subsequently, calibration curves of all phenols were carried out (pH 12 BR buffer) in 111 the concentration range from 1 to 50 µM, N=3. Afterward, the electrochemical oxidation 112 of binary and complex mixtures of the four phenols was studied. Furthermore, the 113 electrochemical approach is compared to commercial phenols tests which are difficult 114 to interpret (i.e., colorimetric) and lack selectivity (without being able to distinguish 115 different phenols). Finally, the accuracy of the optimized approach was successfully 116 117 evaluated for the PHOH, OP, PCP and BPA identification in real samples from a local river (Scheldt, Belgium) against a lab-bench standard method (HPLC-DAD). 118 Altogether, the insights gained from this study will be of assistance towards the 119 development of a fast accurate, selective and sensitive electrochemical sensing 120 approach for the detection of phenolic EDCs in industrial wastewaters and process 121 122 streams.

Table 1. Summary of the electrochemical sensors for hazardous phenols present in aqueous solutionsover the past five years.

Detection method	Phenol type	Working electrode	Linear range (µM)	Sensitivity (µA µM⁻¹)	LOD (nM)	Real sample	Ref	
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CV, LSV, DPV	2,4,6-trichlorophenol PCP	PRhB/GO/MW CNTs/GCE	0.004 - 0.1 & 0.1 - 100 0.002 - 0.1 & 0.1 - 90	26.26 & 0.22 36.25 & 0.23	0.8 0.5	-	[52]
CV	PCP, 2,3,7,8- tetrachlorodibenzo- p-dioxin	Pt/ZnO/AChE/ chitosan bioelectrode	0.001 - 0.02	_	0.5 0.8	guar gum samples	[53]
CV	BPA	Lac/Ag– ZnONPs/MWC NTs/C-SPE	0.5 – 2.99	-	6.0	disposal water	[54]
DPV	OP	nanocomposit es modified electrode	0.01 – 1 & 1 – 50	0.20 & 0.03	3.3	lake water	[55]
CV, DPV	catechol, p-cresol, p-nitrophenol	SWCN-GCE	0.1 – 2	135.08 94.90 110.38	2.3 3.7 7.7	tap water	[37]
CV, AMP	BPA	MWCNT-GCE	0.004 – 0.1	3.5	3.5	water contained in plastic and baby bottles	[38]
CV, SWV	BPA	CoF- MWCNTs- SPE	0.5 – 50 & 0.02 – 1.5	0.005	200.0 10.0	tap water, drinking water, mineral water	[44]
CV, LSV	BPA	Disposable Au-film electrode	50 – 1000	-	131.4	lake and plastic water	[41]
AMP	catechol, dopamine, octopamine, pyrogallol, 3,4-dihydroxy- L-phenylalanine	HRP-SPCE, HRP-MWCNT- SPCE, HRP-SWCNT- SPCE	0.5–500 0.5–250 1–250	5.1* 4.5* 1.6*	110.2 640.2 3341 50.10 980.7	-	[46]
CV, SWV	PHOH, PCP, OP, BPA	Unmodified SPE	5 – 50	0.034 0.052 0.036 0.053	930 915 331 176	Scheldt river	This work

125 * Sensitivity in $\mu A \mu M^{-1} \text{ cm}^{-2}$.

AMP: Amperometry CV: cyclic voltammetry, LSV: linear sweep voltammetry, DPV: differential pulse voltammetry, PCP:
 pentachlorophenol, PRhB: poly(Rhodamine B), GO: graphene oxide, MWCNTs: Multiwall carbon nanotubes, GCE: glassy carbon
 electrode, Pt: platinum, ZnO: zinc oxide, AChE: acetylcholinesterase, BPA: bisphenol A, Lac: Laccase, Ag– ZnONPs: silver doped
 zinc oxide nanoparticles, C-SPE: carbon-screen-printed electrodes, OP: octylphenol, NiO-Ni-GCN: Nickel Oxide and Nickel Co doped Graphitic Carbon Nitride, SWCN-GCE: single-wall carbon nanotube-glassy carbon electrode, CoF: cobalt ferrites, Au-film:
 gold-film, HRP-SPCE: horseradish peroxidase screen-printed carbon electrode, PHOH: phenol.

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133 2. Experimental

134 2.1. Reagents

Phenol and 4-*tert* octylphenol both with purity 99% were obtained from J&K Scientific
GmbH (Germany). Pentachlorophenol and bisphenol A with purity 97% and 99%
respectively, were acquired from Sigma-Aldrich-Chemie GmbH & Co KG (Germany).

Ethanol with a purity of 99.8% was purchased from Acros Organics[™] (Geel, Belgium). 138 All analytical grade salts of potassium chloride, sodium phosphate, sodium acetate, 139 sodium borate and potassium hydroxide were obtained from Sigma-Aldrich (Overijse, 140 Belgium). All phenols stocks were prepared in ethanol, in a concentration of 1 mM (for 141 the electrochemical analysis) and 10 mM (for the Scheldt spiked analysis). 142 Electrochemical measurements were performed in Britton Robinson buffer at 20 mM 143 ionic strength with supporting electrolyte 100 mM KCl, by applying 80 µL of the buffer 144 onto the SPE. All aqueous solutions were prepared in ultrapure water obtained from 145 18.2 M Ω cm⁻¹ doubly deionized water (Sartorius, Arium® Ultrapure Water Systems). 146 Adjustment of the pH was performed using a 100 mM KOH solution. 147

148 **2.2. Instrumentation and apparatus**

All CV, LSV and SWV measurements were performed using a MultiPalmSens4 or 149 EmStat Blue potentiostats (PalmSens, The Netherlands) with PSTrace/MultiTrace or 150 PStouch software, respectively. Disposable ItalSens IS-C graphite screen-printed 151 electrodes (SPE) (provided by PalmSens, Utrecht, the Netherlands), containing a 152 graphite working electrode (\emptyset = 3 mm), a carbon counter electrode, and a silver 153 reference electrode were used for all measurements. The CV parameters used were 154 a potential range of -0.5 V to 1.1 V (3 scans), 5 mV step potential and 50 mV s⁻¹ scan-155 rate. The LSV parameters used were potential range of 0 V to 1 V, 5 mV step potential 156 and scan-rate range from 5 to 500 mV s⁻¹. The optimal SWV parameters used were a 157 potential range of -0.3 V to 1.1 V, frequency 10 Hz, 25 mV amplitude and 5 mV step 158 potential. All the voltammograms are background corrected using the "moving average 159 iterative background correction" (peak width = 1) tool in the PSTrace software. During 160 the anodic pretreatment (for the degradation of phenol over time) the applied potential 161 was 0.9 V. The LOD of the phenols was determined by the ratio of 3 times the standard 162 deviation of the blank over the slope of the calibration curve. Whereas the limit of 163 quantification (LOQ) was calculated by the ratio of 10 times the standard deviation over 164 the slope of the calibration curve. 165

The pH was measured using a Metrohm 913 pH-meter from Metrohm AG (Herisau,
Switzerland) connected to a HI-1131 glass bodied pH electrode from Hanna
Instruments[™] (Bedfordshire, United Kingdom). HI3864 Phenols Test Kit was
purchased from Hanna Instruments[™] (Temse, Belgium).

The HPLC-DAD experiments were performed with a Shimadzu HPLC system ('s-170 Hertogenbosch, The Netherlands) equipped with a Prominence LC-20AT connected 171 to a DGU-20A5R degassing unit with a CBM-20A integrator, a SIL-20AC HT cooled 172 autosampler (with a 0.1 - 100 µL injection volume range and up to 35 MPa operating 173 pressure) and a SPD-M20A photodiode array detector with temperature-controlled flow 174 cell, wavelength range 190-800 nm, W-halogen- and D2-lamp, 4 channel analogue 175 outlet, includes standard cell, 10 mm path, 10 µL. Phenol samples (25 µL injection 176 volume and 1 mL min⁻¹ flow rate) were separated by reversed phase HPLC-DAD on a 177 100 x 4.6 mm id, 2.6 µm particle size, 100 Å, Kinetex C-18 LC column from 178 Phenomenex (Utrecht, The Netherlands) and eluted with mobile phase A consisted of 179 0.1% phosphoric acid in ultrapure water (v/v) and mobile phase B consisted of 0.1% 180 phosphoric acid in acetonitrile/ultrapure water (95/5, v/v). The gradient started at 0 min 181 at 20% B, from 0 to 3 min: 20% B to 100% B, from 3 to 5 min: 100% B, from 5 to 5.1 182 min: 20% B and from 5.1 until 12 min 20% B to re-equilibrate the column for the next 183 184 analysis. The phenols were detected at selected wavelength of 220 nm. All measurements were done in triplicate. All data analysis were done mathematically with 185 the software LabSolutions. 186

187 **3. Results and Discussion**

188 3.1. Exploring the electrochemical behavior of phenols: reversibility study and 189 mass-transfer mechanism

The electrochemical reversibility of redox processes of PHOH, PCP, OP and BPA was 190 explored using CV. The cyclic voltammograms (three scans) at 100 µM concentration 191 of all phenols in pH 12 BR buffer on SPEs are shown in Fig. 1. Blank results are 192 displayed in the SM (Fig. S1). A sharp single anodic peak was noted for all phenols 193 after the first CV scan, which is consistent with the oxidation peak of the corresponding 194 phenol. The oxidation peak potentials (E_p) observed (PHOH at 0.44 V, PCP at 0.60 V, 195 OP at 0.18 V and BPA at 0.26 V) are characteristic of the analyte at the specific pH 12. 196 197 None of the phenols displayed a cathodic/reduction peak in the reverse potential scan, which reveals the irreversible nature of the ongoing processes at the bare SPE. 198 199 Moreover, fouling of the generated phenoxyl radicals in the first oxidation step influences the electrochemical signal of the next cycle scans as expected [39,40]. 200 Therefore, the oxidation peak decreases in subsequent scans since less electrode 201 surface area is available due to the adsorption of phenoxyl radicals and/or oxidation 202

products on the electrode surface, as can be seen in Fig. 1. To reveal the irreversibility 203 of the adsorption process, the same experiment was performed rinsing the SPE and 204 drop-casting a fresh phenol before each scan, results shown in Fig. S2A-D. A small 205 decrease in current intensity of the second and third scans are displayed for PHOH 206 (Fig. S2A) and PCP (Fig. S2B), this indicates the irreversibility of the phenoxyl radicals 207 and/or oxidation products after rinsing the SPE. Besides, a clear decrease in the 208 second and third scans is observed for BPA (Fig. S2D), probably due to the fouling, 209 as previously described in section 1. On the other hand, an increase of the signal 210 during the second and third scans is shown for OP (Fig. S2C), being in concordance 211 with the adsorption mechanism observed during the mass-transfer study (see below). 212



213

Fig. 1. Cyclic voltammograms of A) PHOH, B) PCP, C) OP and D) BPA using 100 µM concentration in
 pH 12 Britton Robinson buffer at Italsens SPE. First scan (black line), second scan (red dotted line) and
 third scan (green dotted line). Three consecutive scans were performed within the same phenol droplet.

217 Besides the electrochemical irreversibility of all phenols, the nature of the masstransport mechanisms at the electrode surface was revealed from the scan-rate 218 experiments. Therefore, solutions containing PHOH, PCP, OP or BPA at 500 µM 219 concentration in pH 12 BR buffer were evaluated by LSV on bare SPEs varying the 220 scan-rate (5, 10, 25, 50, 75, 100, 200, 300 and 500 mV s⁻¹), results shown in Fig. S3A-221 **D**. According to the LSV results, a non-linear relationship was obtained between the 222 I_p and the scan-rate (v), suggesting that the electrochemical reaction is governed 223 by a diffusion-controlled process in PHOH, PCP and BPA (**Fig. S3E** for PHOH, I_{p} (μ A) 224 = 2.26 v (mV s⁻¹) + 0.58, R² = 0.99; Fig. S3F for PCP, I_p (µA) = 1.44 v (mV s⁻¹) + 225 1.05, $R^2 = 0.99$; Fig. S3H for BPA, I_p (µA) = 2.09 v (mV s⁻¹) + 2.25, $R^2 = 0.99$). On the 226

other hand, a linear relationship was observed in OP, which means an adsorption-227 controlled process (**Fig. S3G** for OP, I_p (μ A) = 0.25 v (mV s⁻¹) + 1.03, R² = 0.99), in 228 harmony with the aforementioned Fig. S2C. To confirm these findings, the Ip was 229 plotted against the square root of the scan-rate (Fig. S3I-L). In this case, a linear 230 relationship should be presented for a diffusion-controlled process, which was the case 231 for PHOH, PCP and BPA as it was previously confirmed. Besides, the logarithm of Ip 232 and the logarithm of the scan-rate were plotted. Herein, a slope close to the theoretical 233 value of charge transfer coefficient ($\alpha = 0.50$, corresponding to diffusion-controlled 234 process) is expected for PHOH, PCP and BPA meanwhile a slope higher to the 235 theoretical value ($\alpha > 0.50$, corresponding to an adsorption-controlled process) is 236 expected for OP. Thus, the theoretical values were consistent for most of the phenols 237 where Fig. S3M-P shows a slope of 0.49 for PHOH, 0.46 for PCP, 0.83 for OP and 238 239 0.62 for BPA, respectively.

3.2. Influence of the pH in the electrochemical behavior of the different phenols

The EF of each phenol was analyzed on SPE in the entire pH range (2 - 12) using 241 242 SWV (Fig. 2). An improved resolution of the irreversible oxidation process provided by SWV, making the identification of the four phenols easier. A single oxidation peak was 243 observed for PHOH, PCP and OP since all of them contain one phenolic substituent. 244 245 On the other hand, a major peak with a shoulder at lower pHs (2-4) is shown for BPA, Fig. 2D, previously reported by Kuramitz et al. [56]. In general, at lower pH values 246 247 (from pH 2 to pH 5) the oxidation peaks for all phenols were in the same potential range (0.7 V - 0.9 V). Notably, these values shift to less positive potentials when increasing 248 the pH, facilitating the identification of the four different phenols at higher pHs. Given 249 the existing similarity between E_p at acidic pHs, the broader peak separation was 250 reached at pH 12 (Fig. 2), where the four phenols have different oxidation potentials 251 (0.42 V for PHOH, 0.59 V for PCP, 0.19 V for OP and 0.25 V for BPA). Therefore, pH 252 12 was chosen as optimal pH, which simplifies the simultaneous determination of the 253 different phenols without any overlap between peaks. 254



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Fig. 2. Baseline corrected square wave voltammograms of 10 μM concentration of phenols: A) PHOH,
B) PCP, C) OP and D) BPA; obtained during pH screening in Britton Robinson buffer (20mM and 0.1 mM KCl, in the pH range 2 to 12) on Italsens SPE.

The linear relationship between the oxidation E_p of the four phenols in function of the 259 pH is displayed in Fig. S4. Thus, a linear behavior is shown for PHOH, PCP, OP and 260 BPA until pH 11, pH 7, pH 12 and pH 11, respectively, with Nernstian slopes (60 ± 2 261 mV decade⁻¹, average of four phenols) indicating that the number of protons is equal 262 to the number of electrons transferred during the electrochemical oxidation process at 263 the bare SPE. These results are supported by the literature which reports that one 264 electron and one proton are transferred in the process of PHOH [57] and two electrons 265 and two protons are exchanged in the processes of PCP, OP and BPA [42,58,59]. At 266 these pHs, far above the pKa value (9.99, 4.98, 10.23 and 9.6, respectively), the 267 phenols are all deprotonated and can be found in their phenolate anions form, where 268 proton exchange cannot take place during the electrochemical process. 269

270 **3.3. Stability and degradation studies of phenols over time**

Many published studies have prepared and stored the stock solutions of phenols in 271 different ways such as in absolute ethanol[38,60,61] or ultrapure water[57], at 272 low[38,57,61] or room temperatures[53], in daylight or darkness[34], and freshly 273 prepared. Therefore, the next step to take into consideration was the stability of the 274 phenol's stocks. Hence, the possible degradation of the four phenols over time (0, 30, 275 120 and 300 min) was evaluated by performing a stability study at pH 12 in BR buffer 276 using different types of storage conditions: *i*) ice and dark; *ii*) room temperature (RT) 277 and dark; and iii) room temperature and daylight. A remarkable stability of BPA, PHOH 278

and PCP solutions overtime under the different storage conditions (10 μ M concentration) is shown in **Fig. 3**. On the other hand, OP appears to be the most unstable compound throughout time, showing fluctuations in the peak oxidation intensity (**Fig. 3C**) probably due to the adsorption-controlled mechanism involved in this specific case. The relative standard deviation (RSD) of the I_p and E_p of the four phenols is summarized in **Table 2**. Excellent RSDs of E_p (< 3%) over time at pH 12 for all storage conditions is shown for all four phenols.



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Fig. 3. Baseline corrected square wave voltammograms of 10 µM phenols in pH 12 BR, A) PHOH, B)
PCP, C) OP and D) BPA. Stability of different stocks over the time (from 0 to 5 hours) stored in ice and
dark; at room temperature and dark; and at room temperature and daylight.

Table 2. Relative Standard Deviation (RSD) of peak current (I_p) and peak potential (E_p) obtained from

the stability study over time (0, 30, 120 and 300 min) of all phenols (PHOH, PCP, OP and BPA) at 10 μ

292	µivi concentration ir	1 pH 12 BR usir	ig three different	t storage conditions	(N=4).

	Storage	PHOH	PCP	OP	BPA
	ice & dark	9.80	5.94	7.66	4.59
RSD (%) of I _p over time	RT & dark	3.36	8.34	12.86	1.82
	RT & light	2.01	5.06	12.06	1.97
$PSD(\mathbb{Q})$ of E over time	ice & dark	2.59	0.42	1.47	0.98
K_{OD} (%) of E_p over time	RT & dark	1.64	0.48	1.39	1.00

Due to the high toxicity that these hazardous phenolic compounds promote into the 294 environment, a simple way for their elimination from (industrial) wastewaters is highly 295 needed. The voltammetric curves obtained after an anodic pretreatment of the samples 296 are summarized in Fig. 4a. The anodic pretreatment was selected as the easiest way 297 of degradation of phenol within the sample drop. As it can be seen in Fig. 4b, after 180 298 minutes of anodic pretreatment, 64% of the phenol is oxidized. Moreover, to eliminate 299 not only the phenol but also the hazardous byproducts[57] such as catechol and/or 300 hydroquinone, the selected applied potential was 0.9 V, which is far above the peak 301 potentials observed during the entire electrochemical study. It is important to highlight 302 herein the evaporation that takes place within the drop of the sample throughout time. 303 304 To control this issue, the setup of this specific experiment was designed to close and preserve humidity inside a reduced space. However, the total evaporation rate cannot 305 306 be avoided and considering this fact, the final degradation could be likely lower than the represented in Fig.4. Hence, with this straightforward anodic pretreatment, the 307 308 phenol concentration present in the sample can be decreased up to two-thirds promoting two major advantages for future applications: i) on-site detection and ii) 309 310 environmental removal.



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Fig. 4. Baseline corrected square wave voltammograms of A) 100 µM PHOH in pH 12 BR after anodic
pretreatment at 0.9 V over time (from 0 to 3 hours). Corresponding degradation plot of B) PHOH over
time (N=3).

315 3.4. Analytical performance of the SPE during calibration curves

³¹⁶ Under the optimized parameters and conditions, the analytical performance of the bare ³¹⁷ SPE was evaluated to determine different concentrations of phenols (N=3). Square ³¹⁸ wave voltammograms upon increasing concentrations of PHOH, PCP, OP and BPA (1 ³¹⁹ - 50 µM) are exhibited in **Fig. 5A-D** with the corresponding linear relationships for the ³²⁰ oxidation peaks (**Fig. 5E-H**). The analytical parameters have been collected in **Table**

- 321 **3** and show outstanding reproducibility among the triplicates for each phenol (with RSD
- of $I_p < 10\%$ and RSD of $E_p < 2\%$), sensitivity and limit of detection.



Fig. 5. Baseline corrected square wave voltammograms for A) PHOH, B) PCP, C) OP and D) BPA in
pH 12 Britton Robinson buffer in a concentration range from 1 to 50 µM using Italsens SPE (N=3).
Corresponding calibration curves of all phenols E) PHOH, F) PCP, G) OP and H) BPA showing the
average of the peak current upon increasing concentrations of each phenol (N=3).

Table 3. Analytical parameters for the electrochemical approach, obtained from calibrations curves of
 all phenols (PHOH, PCP, OP and BPA) in a range from 1 to 50 µM concentration and RSDs obtained
 from the reproducibility study (N=3).

	РНОН	PCP	OP	BPA
Peak potential (V)	0.420 ± 0.003	0.593 ± 0.003	0.188 ± 0.003	0.251 ± 0.003
Sensitivity (µA µM ⁻¹)	0.033 ± 0.001	0.047 ± 0.005	0.038 ± 0.003	0.054 ± 0.002
R-squared Linear range (μM)	0.998 5 — 50	0.998 5 — 50	0.997 5 — 50	0.994 5 — 50
Limit of detection (µM)	0.930 ± 0.015	0.915 ± 0.086	0.331 ± 0.031	0.176 ± 0.007
Limit of quantification (µM)	3.099 ± 0.003	3.049 ± 0.015	1.104 ± 0.003	0.586 ± 0.004
RSD of I _p (%) at 10 μ M, N=3	2.36	4.14	8.38	0.31
RSD of E_p (%) at 10 μ M, N=3	0.69	0.49	1.55	1.15

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332 3.5. Selective identification of all phenols in complex mixtures and validation 333 with the commercial Phenols Test Kit.

To achieve the main goal of this work and present an accurate, rapid and user-friendly method to distinguish and identify these four hazardous phenols in real (industrial) wastewaters, a pH screening (2 - 12) of the complex mixture containing all phenols in an equimolar concentration of 10 µM was performed. Thus, the possible interference

caused by the different phenols present in the complex mixture on each other's EF 338 was investigated. The entire pH screening where the optimal peak separation was 339 achieved at pH 12 is shown in Fig. 6A, proving that the four phenols can be easily and 340 simultaneously distinguished at this pH ($E_{PPHOH} = 0.39 \text{ V}$, $E_{PPCP} = 0.61 \text{ V}$, $E_{pOP} = 0.21$ 341 V and $E_{pBPA} = 0.25$ V). A negligible overlapping of the electrochemical response of OP 342 and BPA was witnessed although it does not interfere with the final identification of the 343 four different phenols present in the sample. Besides, suppression of the PCP peak 344 was observed in all the complex mixtures (Fig. 6A). To thoroughly evaluate possible 345 shifts in the peak potential as well as suppression effects, the electrochemical 346 performance of binary mixtures was subsequently carried out (Fig. 6B). The results 347 exhibited suppression of the PCP peak only when PHOH is present, and total 348 suppression of PCP was observed at higher PHOH ratios (i.e. 70:30 and 90:10 349 350 PHOH:PCP) as displayed in Fig. S5. Moreover, this suppression could be likely due to the reaction rate of oxidation of each phenol where probably the by-products 351 352 generated after oxidation of PHOH (faster reaction) would attach to the surface of the electrode preventing the oxidation peak of PCP to be seen [51,57]. Another possible 353 354 explanation lies in the formation of a complex between PCP and PHOH [62]. Further exploration and clarification of the suppression mechanism involved need to be 355 achieved, however, it is not the main focus of the present work. Besides, despite the 356 suppression observed and based on the acquired results, the simultaneous 357 differentiation of all the phenols (in binary and complex mixtures) is successfully 358 allowed by the proposed electrochemical approach. Remarkably, and considered for 359 future steps, a tailor-made Matlab script, previously developed by this group [63,64], 360 could be used to enhance peak separation and identification of the SWV-data of phenol 361 362 mixtures samples.

363



364

Fig. 6. Baseline corrected square wave voltammograms obtained after A) pH screening (pH 2 to 12) in
Britton Robinson buffer of the complex mixture (black line) using 10 μM concentration of each phenol
(1:1:1:1 ratio) and B) binary mixture of phenols (black line) of 10 μM concentration of each phenol (1:1
ratio) in pH 12. Single phenol solutions of PHOH (blue line), PCP (red line), OP (green line) and BPA
(orange line) were also provided.

Nowadays, on-site analysis in industrial streams and wastewaters is performed 370 employing test kits allowing quantification of total phenol amount although lacking 371 selectivity. Therefore, a comparison of the current approach based on SWV detection 372 and the Phenol Test Kit (Fig. S6) analysis was performed whereby Scheldt river water 373 was spiked with all phenols (PHOH, PCP, OP and BPA) at three different equimolar 374 concentrations (50, 100 and 200 µM). Subsequently, these samples were diluted 50 375 times for the Phenols Test Kit analysis and 10 times in pH 12 BR buffer for the 376 electrochemical measurements. Table 4 summarizes the analytical parameters of the 377 electrochemical approach and Phenols Test Kit validation results. However, the 378 379 Phenols Test Kit analysis allows to determine the total phenol amount in samples sensitively but lacks selectivity. An underestimation of the total phenol amount in all 380 the mixtures is shown by the Phenols Test Kit analysis. In fact, most *para*-substituted 381 phenols do not produce color with the 4-aminoantipyrine reagent.[65] The reaction with 382 4-aminoantipyrine occurs in the para position to the phenolic group. This reaction 383 happens either in unsubstituted para position (as PHOH) or phenols which are para-384 substituted by halogen (as PCP), carboxyl, sulfonic acid, hydroxyl, or methoxyl in which 385 this group is expelled during the reaction. But in the cases in which this position is 386 substituted by an alkyl (such as OP and BPA), aryl or others, the reaction is blocked, 387 and no color change can be observed, resulting in underestimated total phenol 388 amount. Because of that, and due to the visual error inherent in the colorimetric read-389

out (which can be also influenced by the daylight intensity), the concentration of phenols is very difficult to be accurately predicted by using these commercially available Test Kits. The current electrochemical approach based on SWV detection offers faster results (< 5 minutes) and requires a small amount of sample, without additional harmful reagents, allowing to quickly screen mixtures with sensitivity in submicromolar levels and high selectivity between the four phenols (**Table 4**).

Table 4. Analytical parameters for the electrochemical approach and Phenols Test Kit, obtained from
 the spiked Scheldt river samples of four phenols (PHOH, PCP, OP and BPA) in three different equimolar
 concentrations.

	e.	N/\ /	HI3864 Pher	HI3864 Phenols Test Kit,		
	51	VV	Hanna Inst	truments™		
Detection method	electrochemical	oxidation by an	colorimetric re	colorimetric reaction with 4-		
Detection method	applied	potential	aminoantipyrine ^a			
Analyze time/sample	< 5 m	inutes	> 12 m	ninutes		
Sample volume needed	< 10	00 µl	20	ml		
Analyte	PHOH+PCP	+OP+BPA mixture	es spiked in Schel	dt river water		
	mixtu	ıre 1: 39.75 mg l ⁻¹	(i.e. 50 µM equin	nolar)		
Real spiked concentration ^b	mixture 2: 79.51 mg l ⁻¹ (i.e. 100 μM equimolar)					
	mixture 3: 159.01 mg l ⁻¹ (i.e. 200µM equimolar)					
Dilution	10 ti	mes	50 times			
Lincer recerb	0.00 0.01 m = 11		0.00 – 1.00 mg l ⁻¹			
Linear range ³	0.99 – 9.	94 mg F	0.5 – 5.0 mg l ⁻¹			
LOD ^b	0.11 mg l⁻¹ (ave	erage sensitivity	0.1 mg l=1			
	of four p	ohenols)	0.1 mg F			
Selective	у	es	no			
	real total	determined	real total	determined		
Samples ^b	concentration	total	concentration	total		
	(10x diluted)	concentration	(50x diluted)	concentration		
Mixture 1	3.98 mg l ⁻¹	4.09 mg l ⁻¹	0.80 mg l ⁻¹	< 0.32 mg l ⁻¹		
Mixture 2	7.95 mg l ⁻¹ 8.09 mg l ⁻¹		1.59 mg l ⁻¹	< 1.20 mg l ⁻¹		
Mixture 3	15.90 mg l ⁻¹	16.36 mg l ⁻¹	3.18 mg l ⁻¹	< 1.70 mg l ⁻¹		

^a Most *para*-substituted phenols do not produce color with the 4-aminoantipyrine.

^b The units of the values are shown in mg L⁻¹ to easily compare with the one provided by the commercial
 kit.

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3.6. Determination of phenols in real samples (Scheldt river water) and accuracy evaluation with HPLC technique

To evaluate the accuracy of the optimized electrochemical detection approach, HPLC-405 DAD was used as a reference technique allowing the identification and quantification 406 407 of the different phenols. In addition, to demonstrate the potential application of this approach in real samples, Scheldt river water was spiked with individual phenols 408 409 (PHOH, PCP, OP and BPA) at three different concentrations (50, 100 and 200 µM). Subsequently, these samples were diluted 10 times in pH 12 buffer for SWV 410 411 measurements or in ultrapure water for HPLC-DAD measurements. External standard calibration method was used for HPLC-DAD analysis to construct the calibration plots 412 413 of PHOH, PCP, OP and BPA using the peak areas of the responses of different concentrations (2, 5, 10, 20 and 50 µM) of phenols (N=3). Analytical parameters such 414 415 as retention times, linear dynamic curves and linear range have been collected in Table S2. The average of the recoveries of both SWV and HPLC-DAD measurements 416 of 12 spiked samples, as well as the accuracy of the electrochemical approach versus 417 the HPLC-DAD are shown in Table 4. Remarkably, PHOH, PCP and BPA indicate that 418 this method has great accuracy compared with HPLC-DAD (values between 99% and 419 112%) with good recoveries for both methods (values between 90% and 117%). While 420 lower accuracy and recovery (SWV) values are shown for OP, as previously observed 421 and described in section 3.3, probably due to the lower solubility of OP in an aqueous 422 medium (Table S1) as well as the adsorption-controlled mechanism determined. 423

Table 4. Recovery values were obtained from the spiked Scheldt river samples of individual phenols (PHOH, PCP, OP and BPA) in three different concentrations (5, 10 and 20 μ M) in pH 12 BR buffer for SWV and ultrapure water for HPLC-DAD, and the accuracy values between the electrochemical approach and the standard technique, HPLC-DAD (all measurements, N=3).

	SV	VV	HPLC		
Sample	Concentration (µM)	Recovery (%)	Concentration (µM)	Recovery (%)	Accuracy (%)
	5.85 ± 0.10	116.96 ± 2.08	5.77 ± 0.44	115.40 ± 8.86	101.35
РНОН	11.03 ± 0.05	110.32 ± 0.45	10.23 ± 0.01	102.29 ± 0.05	107.86
	21.96 ± 0.13	109.80 ± 0.63	20.27 ± 0.04	101.35 ± 0.19	108.33
	4.86 ± 0.15	97.28 ± 2.98	4.54 ± 0.00	90.86 ± 0.01	107.07
PCP	10.32 ± 0.15	103.23 ± 1.54	10.14 ± 0.00	101.42 ± 0.03	101.79
	20.92 ± 0.25	104.61 ± 1.26	20.95 ± 0.01	104.76 ± 0.04	99.86
	5.01 ± 0.53	100.16 ± 10.62	4.98 ± 0.02	99.59 ± 0.34	100.58
OP	8.82 ± 0.48	88.19 ± 4.80	11.02 ± 0.03	110.21 ± 0.30	80.02
	19.30 ± 2.46	96.50 ± 12.29	22.45 ± 1.16	111.45 ± 5.53	86.58
BPA	5.29 ± 0.05	105.86 ± 0.93	4.95 ± 0.01	99.09 ± 0.15	106.84

10.88 ± 0.14	108.76 ± 1.41	10.72 ± 0.01	107.25 ± 0.05	101.41
20.78 ± 0.90	103.91 ± 4.49	18.56 ± 0.01	92.82 ± 0.00	111.95

428

Furthermore, real samples containing different mixtures of phenols were also studied 429 (Table S3). Therefore, Scheldt water was spiked in equimolar ratios with two binary 430 mixtures (PHOH+OP and PCP+BPA), two tertiary mixtures (PHOH+OP+BPA and 431 PCP+OP+BPA) and the complex mixture (PHOH+PCP+OP+BPA) at two different 432 concentrations (50 and 200 µM) and diluted 10 times in pH 12 (for SWV analysis) or 433 ultrapure water (for HPLC-DAD analysis) to reach a final concentration of 5 and 20 µM 434 of each phenol. Due to shifts of the oxidation peaks of some phenols after mixing, the 435 recovery values of the mixtures in SWV were calculated based on the maximum Ip at 436 the corresponding E_p of the anodic oxidation peak of each phenol in the mixture. As it 437 can be seen in Table S3, PHOH can be successfully identified and quantified in all the 438 mixtures, showing the best results in terms of recoveries and accuracy between both 439 440 methods (SWV and HPLC). For the three phenol derivatives, the situation is more controversial. First of all, the lowest SWV recovery and accuracy values are exhibited 441 442 for PCP, more specifically in complex mixtures, likely due to the suppression of the oxidation signal caused by PHOH previously described in section 3.5. Secondly, and 443 probably influenced by the lower solubility as well as the adsorption-controlled 444 mechanism of OP, its quantification is overestimated as can be seen in the recovery 445 values from both, SWV and HPLC-DAD. Last but not least, the highest SWV recovery 446 and accuracy values are shown for BPA as a result of peak overlap, resulting in the 447 peak broadening and the increase of the peak potential. Hence, the recovery values 448 of each phenol derivative in the mixtures (Table S3) are worse than in the case of the 449 single phenols (Table 4) due to the influence among them. It is important to highlight 450 that even though this approach cannot be implemented for the quantification of each 451 phenol in complex mixtures, their identification is completely successful. Moreover, the 452 insights revealed during this study are being already used for the improvement of the 453 envisioned sensor. Current efforts are being carried out in this group towards the 454 455 development of a novel sensor that combines the present electrochemical approach with photoelectrochemical readout to further enhance the sensitivity. This will result in 456 457 a powerful device able to accomplish not only an accurate differentiation (SWV) but also the highly sensitive quantification (photoelectrochemistry) of the total amount of 458 459 phenols in industrial wastewaters and process streams ensuring limits of detection in

the sub-nM range. By this combination, the drawbacks of both techniques (in terms of sensitivity and selectivity), when used separately, will be excluded. Using disposable SPEs and integrating both techniques on wireless potentiostats will allow on-site detection and/or monitoring. Resulting in a first-of-its-kind, more reliable and fast sensing application in the analysis of phenolic samples compared to the currently used commercial Phenols Test Kits.

466 **4. Conclusions**

The electrochemical detection of four highly relevant phenols as EDC on unmodified 467 SPE via rapid voltammetric detection method in complex and real samples has been 468 presented. Importantly, the electrochemical oxidation and behavior of PHOH, PCP, OP 469 and BPA have been unraveled for the first time using BR buffer including reversibility, 470 mass-transfer, pH screening, stability and degradation studies. Moreover, the 471 analytical performance of the SPEs and their capability for the accurate identification 472 of different hazardous phenols in complex mixtures simultaneously are shown by the 473 474 performed calibration curves. A reliable identification and quantification of real samples from spiked Scheldt river water (Belgium) in comparison with the 475 commercially available Phenols Test Kit is offered by the current method based on 476 SWV detection. Finally, the accuracy of the methodology was evaluated using real 477 samples and comparing with the lab-bench standard method (HPLC-DAD). Overall, 478 the potential of the electrochemical approach for providing rapid and reliable screening 479 of the most important phenolic EDCs during on-site testing has been demonstrated. 480 The advances presented in this article will pave the way for the development of a new 481 generation of electrochemical sensors aiming for on-site detection and degradation of 482 483 phenols in industrial processes and/or wastewater.

484 **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

487 **Author contributions**

488 **‡** Hanan Barich and Rocío Cánovas contributed equally to this work.

Hanan Barich: Conceptualization; Data curation; Formal analysis; Investigation; 489 Methodology; Validation; Visualization; Writing - original draft, review & editing. Rocio 490 **Cánovas**: Conceptualization; Formal analysis; Methodology; Supervision; Validation; 491 Visualization; Writing - original draft, review & editing. Karolien De Wael: 492 Conceptualization; Fundina acquisition; Project 493 administration; Resources: Supervision; Validation; Visualization; Writing - review & editing. 494

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