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# Novel (Photo)electrochemical Analysis of Aqueous Industrial Samples Containing Phenols

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# Abstract

Phenols are considered as toxic pollutants and their discharge into the environment by industries is regulated by a concentration limit. As these limits are in the low mg $L^{-1}$ to µg $L^{-1}$-range, sensitive methods are necessary to detect these phenols. Here, aqueous industrial phenolic samples throughout a cleaning process were analyzed by two novel electrochemical sensors. Both the photoelectrochemical (PEC) sensor and the square wave voltammetric (SWV) sensors could successfully follow the decrease of the concentration of phenols along the industrial cleaning process. The discharge sample (µg $L^{-1}$) could only be analyzed by the PEC sensor and not by the SWV sensor, as the phenolic concentration was close to the LOD of the latter. With HPLC-diode array detector (DAD) measurements, classical phenols such as phenol (PHOH), hydroquinone, resorcinol and *o*-cresol could be identified in the industrial samples, and their presence could be linked to the electrochemical responses. At last, the performance of the PEC and SWV sensors were compared with commercial colorimetric and chemical oxygen demand (COD) test kits. This comparison demonstrated the high sensitivity of the PEC sensor in the µg $L^{-1}$-concentrated phenolic samples. Together with the identification of the redox peaks through HPLC-DAD analysis, the SWV sensor can be a powerful tool in the qualitative analysis of mg $L^{-1}$-concentrated phenolic samples due to its speed, simplicity and absence of laborious sample pre-treatment steps.



**Keywords:** Photoelectrochemistry, Square Wave Voltammetry, Test Kits, HPLC-DAD, Industrial Samples, Phenol

# 1. Introduction

Phenols are recognized as priority pollutants by the European Commission (EC) and Environmental Protection Agency of the United States (USEPA) due to their high toxicity, potential accumulation, poor biodegradability and endocrine disrupting effects.[1-4] Different sources of phenols released into the environment include natural, agricultural and domestic streams next to industrial activities, such as the production of dyes, resins and oil refineries.[2-5] To minimize the detrimental environmental and health effects, a maximum concentration limit for the industrial discharge of phenols has been implemented.[6] These limits are situated in the low mg $L^{-1}$ to µg $L^{-1}$-level, depending on where it is discharged and the flow of the river or canal.[7-10]

To reach these low limits, sensitive detection strategies are needed to evaluate the level of the phenolic compounds in the effluent. High pressure liquid chromatography (HPLC) or gas chromatography (GC) coupled with detectors as mass spectrometry (MS) or diode array detector (DAD) are often performed methods.[11-15] They have the advantage that they can be applied in a wide variety of matrices, providing accurate results.[10, 15] Nonetheless, these measurements are time-consuming, contain expensive equipment and laborious sample pre-treatment and extraction steps. Additionally, these analyses can only be performed by trained technical personnel and do not allow on-site screening or real-time analysis.[12, 13, 16]

As a result, test kits were developed. Some of these test kits are based on a colorimetric detection which uses the coloring reagent 4-aminoantipyrine (4-AAP). The reaction of phenols with 4-AAP in the presence of an oxidizing agent such as $K_3Fe(CN)_6$ or $K_2S_2O_8$ leads to the generation of a *p*-quinoneimide product, according to the Emerson reaction (Figure S1).[17-19] This method is commonly used due to its high speed, low price and easy-to-use feature without the need of many sample pre-treatment steps.[20] Nonetheless, not all phenols can be measured with this method, especially, some *p*-substituted phenols do not provide a colored product.[18, 19]

Next to these color test kits, chemical oxygen demand (COD) test kit has been applied for the determination of organic pollutants in various water streams, including industrial ones. The COD method is commonly used by regulatory entities to evaluate the pollution degree of a specific sample or stream.[21, 22] It is based on the oxidation of organic pollutants, towards $CO_2$ and $H_2O$, by $K_2Cr_2O_7$ in an acidic environment and in the presence of a $Ag^+$ catalyst. The amount of consumed $Cr_2O_7^{2-}$, which gives an indication on the amount of pollutants, can be measured spectrophotometrically by the increase or decrease of the absorbance bands of respectively $Cr^{3+}$

and $Cr_2O_7^{2-}$ or via titration experiments. Despite that this method does not allow real-time analysis due to its long reaction time (up to 2 hours) and is not selective towards phenols, it is still widely used due to its applicability to a wide variety of samples.[21-23] However, the use of toxic and expensive chemicals during the COD measurements, has motivated the search towards other more environmental-friendly detection methods.[21, 22]

In this regard, electrochemical sensors have emerged as a suitable alternative for these test kits. They have the advantage of high simplicity of operation and instrumentation, fast response, low cost and sample volume, and ability to perform real-time analysis and on-site measurements.[16, 24-30] Recently, novel electrochemical sensors for phenols have been described by our group in literature.[31-33] In this work, we focus on the use of a photoelectrochemical (PEC) and a square wave voltammetric (SWV) sensor for detection of phenols in an industrial process stream. The former uses a singlet oxygen ($^1O_2$) producing photosensitizer (PS) and a laser for the detection of phenolic compounds.[31, 32] Upon illumination of the PS-coated electrode, $^1O_2$ is produced which oxidizes phenolics present in the sample. By applying a reductive potential during the amperometric measurement, these oxidized compounds are reduced at the electrode surface. The generated phenolic compounds can be oxidized again by $^1O_2$ leading to a redox cycle. The PEC sensor demonstrates a high sensitivity with detection limits (LOD) in the nmol $L^{-1}$-range and is thus a useful candidate for measuring phenols in effluent streams.[31, 32] A SWV analysis with the second sensor will allow to identify the nature of the phenolic compounds based on their voltammetric fingerprints.[33-35]

Up till now, these sensors have only been applied for the detection of phenols in buffer solutions. Therefore, no information is yet obtained on the applicability of the sensors in industrial processes. As a result, in this research, the two sensors will be applied for the detection of phenolics in industrial samples from Sumitomo Bakelite, a phenolic resins producer in Belgium. Different samples throughout their cleaning process were obtained and analyzed. The sensors will be assessed 1) if they can follow the removal of (phenolic) contaminants during the cleaning process and 2) if sample pre-treatment is necessary for their electrochemical measurements. The samples will be measured by HPLC-DAD in order to identify single phenols present in the samples. Finally, the performance of the sensors will be compared with two commercially available colorimetric phenols test kits and one COD kit, demonstrating the added value of these electrochemical sensors

compared to the current market offer. The used methodologies will also contribute to the current knowledge in the electrochemical analysis of industrial samples in general.

# 2. Experimental

## 2.1. Reagents

The photosensitizer, $F_{52}PcZn$ (Figure S2.A), was deposited on a $TiO_2$ (P25) carrier matrix, abbreviated by $F_{52}PcZn|TiO_2$, with loadings of 3 wt%. The powder was obtained from the lab of S. Gorun at Seton Hall University (USA).

Phenol (PHOH) (99% purity), *o*-cresol, *m*-cresol, *p*-cresol, 4-cumylphenol, 4-*tert* octylphenol, catechol and resorcinol were purchased from J&K Scientific. 2,4-dimethylphenol and 3,4-dimethylphenol were obtained from TCI. 2,6-dimethylphenol and hydroquinone were purchased from Acros Organics. Bisphenol A was acquired from Sigma-Aldrich. 4-Nonylphenol and 1,2,4-trihydroxybenzene were obtained from Alfa Aesar.

The following components were used for the buffer solutions: borax ($Na_2B_4O_7 \cdot 10\ H_2O$) obtained from Merck, sodium carbonates acquired from VWR, KCl purchased from Acros Organics and potassium phosphate from Sigma-Aldrich.

For the HPLC-DAD eluents, phosphoric acid (>85% purity) and acetonitrile (99.9% purity) were purchased from Acros Organics.

## 2.2. Industrial samples: sampling positions and scheme

Samples were obtained from Sumitomo Bakelite (Genk, Belgium), a phenolic resins producer. To discharge their industrial wastewater, according to their environmental permit, the company needs a wastewater treatment (WWT) plant to purify the streams from chemicals that could be harmful for the environment. A flow chart of the WWT plant is presented in Figure 1.

Two waste streams are generated from the production process, i.e. a PHOH-rich stream and a PHOH-poor stream, where the latter is directly transported towards the storage tank of the WWT plant. From the PHOH-rich stream, the raw materials are extracted by methyl isobutyl ketone (MiBK) leading to two novel streams: an aqueous (sample 1) and a PHOH-MiBK stream. The latter stream is transferred back into the production process while the former stream, which should contain a maximum amount of 25 mg $L^{-1}$ PHOH, is carried to the storage tank of the WWT plant. The stream from the storage tank (sample 2) is then filtered over a sand-based filter to remove the solid particles which can potentially block the active carbon (AC) filter(s) (sample 3). A second

filter, namely the plate filter, separates the sludge (sample 7) from the aqueous stream (sample 6). The sludge stream is externally processed (sample 7). After the sand filter, two AC filters are placed in series to remove the chemicals out of the stream before the water can be discharged into a nearby river (samples 4 and 5).

The samples 1-7, collected during the different stages of the cleaning process, were analyzed by the PEC and SWV sensors. Sample 7 is a sludge containing a lot of solid particles. Its measurement by the sensors is useful to assess the performance of the PEC and SWV sensors on these kind of samples. Lastly, sample 1 was taken from the aqueous phase after extraction with MiBK. It contains a high level of PHOH (25 mg $L^{-1}$) and its composition is expected to be different compared to the other samples 2 to 7.

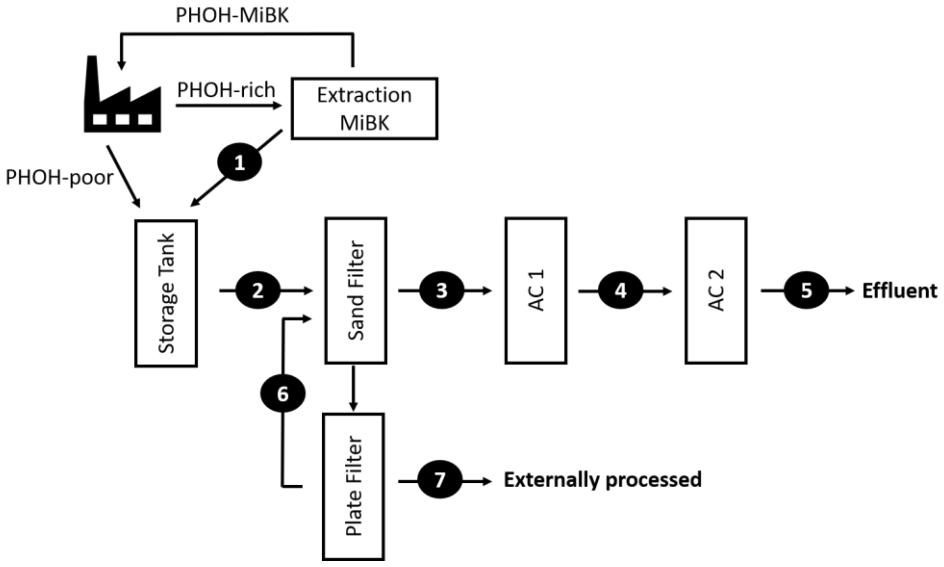


**Figure 1.** Flow chart of the wastewater treatment plant with indication of the different sampling positions (i.e. 1 to 7). Active carbon filters and methyl isobutyl ketone are abbreviated by AC and MiBK, respectively.

The samples were divided into tubes of 40 mL, stored in the freezer at -18 °C to avoid too much degradation of the samples during sampling time and the measurement.[33, 36, 37] Each time when a tube of 40 mL was defrosted, the remaining solution was distributed into aliquots of 1 mL which were stored in the freezer again. This was done to minimize the overall defrosting and freezing times of the 40 mL sample tubes since only small amounts, i.e. < 1 mL, were necessary for the measurements. The pH of these samples were verified via a pH-strip. All samples possessed a pH-level of 6 while sample 1 had an acidic pH-value of 4.

## 2.3. PEC sensing

Metrohm DropSens graphite screen-printed electrodes (SPE) were used for the PEC measurements. These SPEs contained a pseudo-reference electrode (RE) of Ag, and a counter and working electrode (CE and WE, respectively) of graphite. The diameter of the WE was 4 mm and the RE has a potential of +0.05 V *vs.* SCE.

Prior to the PEC measurements, a droplet of 4.27 µL of a 10 mg $mL^{-1}$ aqueous suspension of $F_{52}PcZn|TiO_2$ was casted on the surface of the WE. The droplet was left to dry overnight resulting in a $F_{52}PcZn|TiO_2$-modified SPE.[38] This droplet volume was chosen as it allows good coverage of the PS-coating on the WE and higher casted volumes did not lead to enhanced PEC responses. The PEC amperometric measurements were conducted using a µAutolab III potentiostat from Metrohm Autolab with NOVA software. As illumination source, a 655 nm diode laser from Roithner Lasertechnik was used. A laser power of 0.24 W $cm^{-2}$ was applied which was set to switch on and off at specific time intervals. The first illumination was used to position the laser to cover the WE of the SPE. This position was then fixed for the remaining measurement.

The industrial samples were measured directly by the PEC sensor. An 80 µL droplet from the sample was placed on top of the SPE surface. A potential of -0.17 V *vs.* Ag pseudo-reference of the SPE was applied. The samples were not filtered except for the sludge sample (sample 7, Figure 2). The solid particles present in this sample prevented illumination of the electrode surface and, therefore, the sample was filtered (0.45 µm size pore, Chromofil AO-45/25) to remove most of these particles. The photocurrent values were determined during the second illumination of the samples.

Standard addition was performed on the industrial samples whereby PHOH was used as standard. The determined concentration values were calculated based on the sensitivity of the PHOH standard. The samples were diluted in a pH 9 borate buffer solution containing the following components: 0.02 mol $L^{-1}$ borax and 0.1 mol $L^{-1}$ KCl for sample 2-7. For sample 1, 0.1 mol $L^{-1}$ borax was used instead of 0.02 mol $L^{-1}$. The dilution factors of the samples for the standard addition were: 328 times for sample 1, 80 times for sample 2, 68 times for sample 3, 1.7 times for sample 4 and 5, 62 times for sample 6 and 240 times for sample 7. These dilution factors were chosen so that the PEC sensor could operate in its linear dynamic range (0.94 µg $L^{-1}$ to 94 µg $L^{-1}$ PHOH). Due to these high dilution factors, no filtration step was necessary. The applied potential was -0.17 V *vs.* Ag pseudo-reference of the SPE.[38, 39]

LSV measurements were performed on hydroquinone and *o*-cresol to evaluate their sensitivity in comparison with PHOH. The concentrations were 10 µmol $L^{-1}$ and the used buffer solution consisted of 0.02 mol $L^{-1}$ $KH_2PO_4$ and 0.1 mol $L^{-1}$ KCl of pH 7. A conditioning step was first carried out at 0.10 V for 5 s. Then, the potential was scanned from 0.10 V to −0.25 V vs Ag pseudo-reference electrode with a step potential of 1.00 mV and a scan rate of 0.25 mV $s^{-1}$. The laser was consecutively switched on and off for 30 s.

## 2.4. SWV sensing

PalmSens ItalSens IS-C graphite SPEs were used for the SWV measurements. The SPEs consisted of a pseudo-RE of Ag and a CE and WE graphite (Ø = 3 mm) and the potential of the Ag pseudo-RE was +0.05 V *vs.* SCE. The SWV measurements were performed on a MultiPalmSens4 or EmStat Blue potentiostats (PalmSens, The Netherlands) with PSTrace/MultiTrace or PStouch software, respectively. The measurements were performed in an 80 µL droplet.

A buffer solution of 0.1 mol $L^{-1}$ carbonate buffer ($NaHCO_3$/$Na_2CO_3$) and 0.1 mol $L^{-1}$ KCl was used for pH 10. Adjustment of the pH-value was obtained by adding KOH solution.

For the SWV detection parameters, a potential scan range of -0.3 V to 1.1 V *vs.* Ag pseudo-reference of the SPE with a frequency of 10 Hz, amplitude of 25 mV and step potential of 5 mV were applied. All the voltammograms were background corrected using the "moving average iterative background correction" tool, with peak width = 1, in the PSTrace software. The industrial samples were diluted two times with the buffer solution without filtration.

## 2.5. HPLC-DAD

The HPLC-DAD experiments were performed with a Shimadzu HPLC system ('s-Hertogenbosch, The Netherlands) consisting of a Prominence LC-20AT with a DGU-20A5R degassing unit, a CBM-20A integrator, a cooled SIL-20AC HT autosampler, with an injection volume range of 0.1 - 100 µL and an operating pressure up to 35 MPa. This was coupled to an SPD-M20A photodiode array detector with temperature-controlled flow cell, wavelength range 190-800 nm, W-halogen- and D2-lamp, 4 channel analogue outlet, including a standard cell, 10 mm path and 10 µL volume.

The separation was done in a Kinetex C18 column (100 × 4.6 mm id, particle size 2.6 µm) with the appropriate Security Guard cartridge C18, from Phenomenex (Utrecht, The Netherlands). The injected volume was 25 µL and the flow rate was kept at 1 mL $min^{-1}$.

Mobile phases consisted of 0.07% phosphoric acid in ultrapure water (v/v) (solvent A) and acetonitrile/ultrapure water (95/5, v/v) with 0.07% phosphoric acid (solvent B) to establish following gradient elution: starting with 2% solvent B, over the following 13 minutes solvent B linearly increased to 95%, at 13.1 minutes to 15 minutes the eluent solely consisted of solvent B, at 15.1 minutes the eluents again consisted of only 2% solvent B and was kept for 7 minutes to re-equilibrate the column for the next analysis.

Data analysis was done mathematically with the software LabSolutions. The samples were detected at the selected wavelength of 220 nm. All industrial samples were filtered before HPLC-DAD analysis.

## 2.6. Comparison with Test Kits

The HI3864 Phenols Test Kit and VACUettes® phenol Kit K-8012D colorimetric test kits were purchased from Hanna Instruments and CHEMetrics, respectively. They use the reagent 4-AAP as coloring agent for the detection of phenols. The protocol was followed as described in the manual attached to the test kits.

In brief, the Phenols Test Kit of Hanna Instruments used two vials each filled with 10 mL sample (A and B). In vial A, no reagents were added as it served as the blank. In vial B, the reagents (buffer, 4-AAP and $K_2S_2O_8$) were added and mixed. The reaction occurred over a period of 10 minutes which led to a yellow to orange colored solution in the presence of phenols. The vials were placed in the checker disc where the color of the blank vial (A) was compared with the color obtained in the vial after the reaction of phenols with 4-AAP (B).

For the phenol test kit of CHEMetrics, the following protocol was used. First, distilled water was added in the diluter snapper cup. Then, the crystals on top of the ampoule ($K_3Fe(CN)_6$) were dissolved in distilled water. Afterwards, a VACUette tip was placed on the ampoule tip. This ampoule contains 4-AAP and buffer solution. Via this VACUette-ampoule tip, the sample could be taken up by capillary effects. The ampoule tip was snapped by the diluter snapper cup so that $K_3Fe(CN)_6$ entered inside the ampoule and the reaction between the phenols and 4-AAP could be initiated. The solution was mixed and after 1 minute, the color of the solution could be compared with the reference solutions inside the comparator. The amount of phenols in the samples was expressed, by these test kits, as mg $L^{-1}$ according to a PHOH reference scale.

The COD test kit, LR COD Vials Kit K-7356, was acquired from CHEMetrics. For this test kit, a digestor block was first preheated to 150 °C. Then, 2 mL of the sample was pipetted into the

COD vials containing $H_2SO_4$, $Ag_2SO_4$ and $K_2Cr_2O_7$. The vials were mixed and inserted in the digestor block. A blank vial was also prepared where only Milli Q ultrapure water was added to the COD vial. The vials were heated in the digestor block for 2 hours at 150 °C. Afterwards, the digestor block was turned off in order to cool down the vials for the next 15-20 minutes. The vials were removed from the digestor block, mixed and stored in dark for 30 minutes to further cool down to room temperature. At last, UV-Vis spectra were recorded of the different vials using an Avantes AvaSpec-2048L spectrophotometer. The obtained absorbance value of the dichromate ion (at 446 nm) was compared with the absorbance values of the PHOH COD calibration plot to assess the level of phenols in the samples. The amount of phenols in the samples were expressed in mg PHOH per liter sample in reference to the COD measurement of the PHOH standards.

Industrial samples 1 and 4 were measured by the three test kits. However, due to the high concentration of phenols and oxidizable organics in sample 1, this sample was diluted 125 times for the Hanna Instruments test kit and 100 times for the COD test kit. No dilution was needed for the VACUettes test kit. Sample 4 was measured directly without dilution.

# 3. Results and discussion

## 3.1.PEC and SWV analysis of the industrial samples

**PEC measurements.** The PEC sensor uses a PS type II, namely $F_{52}PcZn|TiO_2$ to generate aerobically $^1O_2$ under red light illumination (by a 655 nm laser) (Figure S2). $^1O_2$ is a strong oxidant, and efficiently oxidizes phenolic compounds present in the sample. The oxidized phenolic compounds are subsequently reduced at the electrode surface by the application of a reductive potential. The produced phenolic compounds after this reduction can, furthermore, be oxidized by $^1O_2$, generating an electrocatalytic redox cycle which leads to low nmol $L^{-1}$-level detection limits. The PS is deposited on a $TiO_2$ matrix to minimize the direct electrochemical reduction of $^1O_2$, which is produced in the vicinity of the electrode surface, and to enhance the oxidation of the phenolic compounds.[31, 32] Also, the PEC sensor provides unique features. While $^1O_2$ is a strong oxidant, it can oxidize many compounds,[40-42] it is only the compounds that generate a redox cycle, similar as phenols, that will contribute to the photocurrent response. Moreover, electro-active species, that may reduce/oxidize at the applied potential will not interfere in the determination of

the phenols since the phenol measurement is only triggered by the illumination of the electrode surface and these electro-active species will only lead to an alteration of the baseline current.[32] The industrial samples were first analyzed by the PEC sensor without any pre-treatment such as dilution with buffer solution. These measurements are indicative for the performance of the sensor directly into the process stream. The concentration of the phenols was estimated via standard addition with PHOH as standard and is, as a result, expressed by the sensitivity of PHOH. Table 1 presents the values of the recorded PEC responses of the direct measurements of the industrial samples and standard addition. The photocurrents of the direct measurement and the standard addition plots are in Figures S3-6.

**Table 1.** Results of the direct measurement and standard addition on the different industrial samples by the PEC sensor. Photocurrent response values were determined during the second illumination of the direct measurement. Standard addition was performed in pH 9 borate buffer with PHOH as standard. Error values mark the standard deviation of three SPEs (N = 3).

| Industrial sample | Direct PEC response | Concentration via standard addition |
|---|---|---|
| 1. | -3.5 ± 0.3 µA | 29 ± 6 mg $L^{-1}$ |
| 2. | -198 ± 25 nA | 2.9 ± 0.3 mg $L^{-1}$ |
| 3. | -189 ± 11 nA | 3.2 ± 0.2 mg $L^{-1}$ |
| 4. | -16 ± 1 nA | 0.026 ± 0.004 mg $L^{-1}$ |
| 5. | -9 ± 1 nA | 0.009 ± 0.002 mg $L^{-1}$ |
| 6. | -234 ± 40 nA | 2.5 ± 0.1 mg $L^{-1}$ |
| 7 | -413 ± 23 nA | 9.4 ± 0.4 mg $L^{-1}$ |

The direct measurements with the PEC sensor elucidate photocurrent values in the low µA to nA-range (Table 1). The high photocurrents observed in sample 1 indicate a higher concentration level of phenolics compared to the other samples. Indeed, this sample was taken after the extraction with MiBK and may contain a PHOH concentration up to 25 mg $L^{-1}$. Consequently, we might operate outside the measurement range of the PEC sensor and small increases in the amount of

phenolics during standard additions or application in industrial streams might, therefore, be missed by the PEC sensor.

Indeed, as shown in Figure 2.A, the added PHOH concentrations did not elevate the photocurrents as such. This means that if during the production process the concentration of phenols would be altered, the PEC sensor would not be able to detect this alteration. As a result, sample 1 needs to be diluted to overcome this issue. The sample was, therefore, diluted 10 and 100 times with pH 9 borate buffer, to investigate the performance of the PEC sensor upon increasing concentration of PHOH in different dilutions of sample 1. The addition of the pH 9 buffer solution not only improved the electrochemical performance, but also enhanced the oxidation rate of PHOH with $^1O_2$ as this is pH-dependent.[43, 44] As shown in Figures 2.B and C, the dilution improved the measurement of increasing concentration levels. Small increases in the PHOH concentration were better intercepted by the PEC sensor and, moreover, linearity upon increasing concentration values was restored. The photocurrent values of Figures 2.A and B, expected to be different due to the dilution, were, however, similar because of the different pH of the solution which influenced the oxidation rate of PHOH with $^1O_2$.[43, 44] The measurement of sample 1, furthermore, demonstrates that the applicability of the PEC sensor is suboptimal for detecting high phenol concentrations.

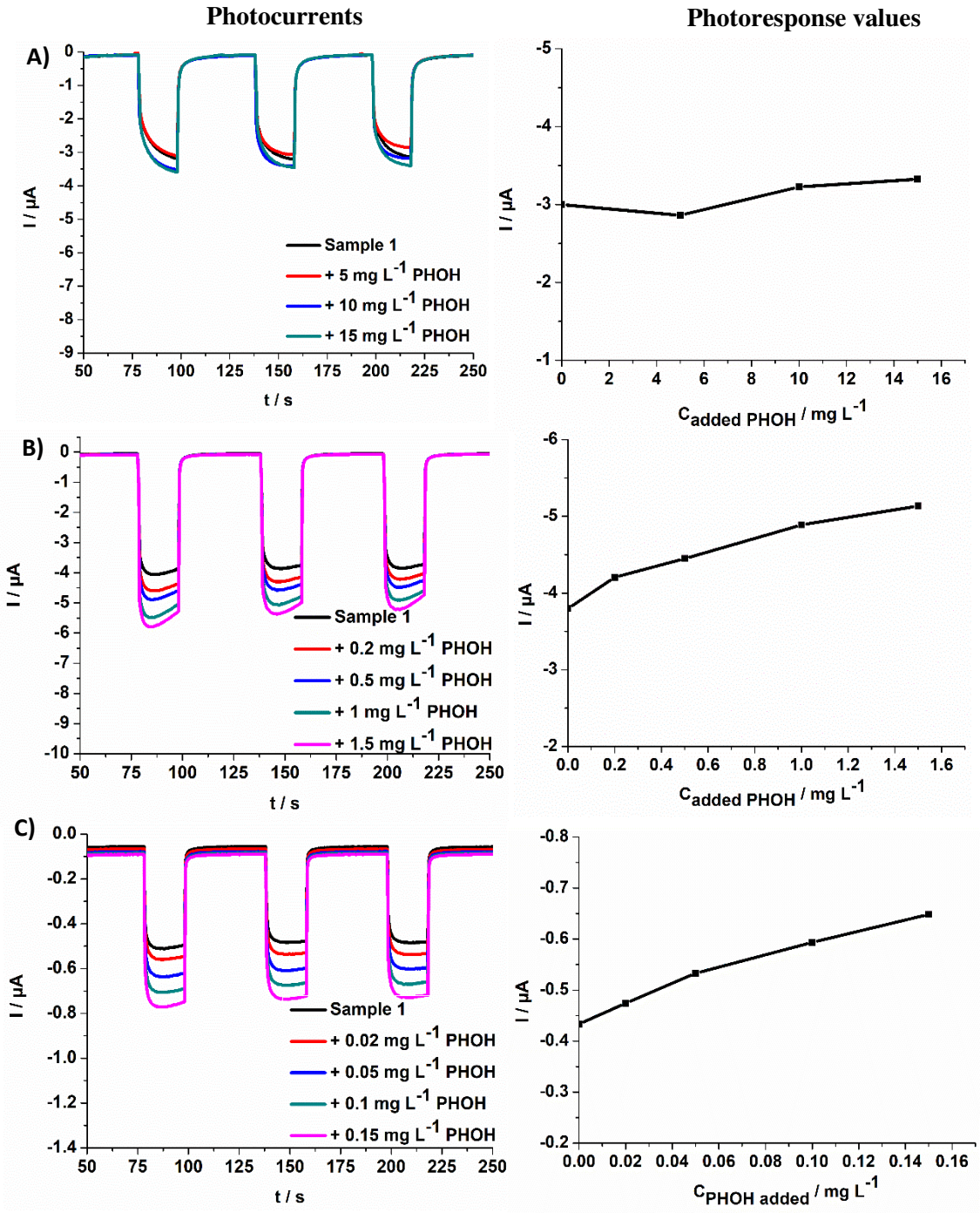


**Figure 2.** Spiking of sample 1 with PHOH standard with left the photocurrents and right the determined photoresponse values for the different spiked PHOH concentrations. The photoresponse values were determined based on the average response of three illuminations in the photocurrent measurements by the PEC sensor. In (A) sample 1 was undiluted while in (B) sample 1 was 10 times diluted and (C) 100 times diluted (N = 1) with pH 9 borate buffer.

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The determined amount of phenolic compounds in sample 1 was 29 ± 6 mg $L^{-1}$ which was close to the determined extraction parameter of 25 mg $L^{-1}$ PHOH.

The photocurrents of the remaining samples (2-7) from the WWT plant are in the nA-range, indicating a much lower concentration of phenols. The recorded photocurrents before and after the sand filter (samples 2 and 3) are in the same range since the sand filter removes the solid particles from the stream and only the solubilized phenolic compounds contribute to the photocurrent response in sample 2 and 3. The same reasoning was made with sample 6, which is the aqueous stream from the plate filter towards the sand filter, and has a photocurrent value in the same range as samples 2 and 3. This was supported by the standard addition results; the determined concentration of phenols in the samples were 2.9 ± 0.3 mg $L^{-1}$, 3.2 ± 0.2 mg $L^{-1}$ and 2.5 ± 0.1 mg $L^{-1}$, respectively for samples 2, 3 and 6.

A considerably large decrease in the photocurrent was noted in between and after the AC filters (samples 4 and 5, Table 1) compared to sample 3. This means that the phenolic concentration dropped over the different samples due to their removal by the AC filters. Indeed, the amount of phenols decreased from 3.2 ± 0.2 mg $L^{-1}$ to 0.026 ± 0.004 mg $L^{-1}$ (sample 4) after the first AC and to 0.009 ± 0.002 mg $L^{-1}$ (sample 5) after the second AC.

The sludge sample 7 was filtered before the measurement to allow illumination of the electrode surface. It measured the highest photocurrent response of the WWT plant, indicating that the majority of the phenolic compounds were accumulated in the sludge (Table 1). An estimated 9.4 ± 0.4 mg $L^{-1}$ phenols were present in this sample. These phenols are likely highly substituted low polar phenol derivatives as they have a low mobility in water and tend to accumulate more in sediments.[12, 45]

The fact that the PEC sensor was able to follow the decrease of the phenolic photocurrent, throughout the WWT plant without any pre-treatment steps, confirms the practical feasibility of the measurements with the PEC sensor directly into these streams. The direct and standard addition measurements, moreover, confirm the sensitive performance of the PEC sensor in industrial samples. The PEC sensors could measure phenolic compounds in all samples with photocurrent responses ranging from µA to nA-level. The corresponding concentration of these phenols were in the mg $L^{-1}$ to µg $L^{-1}$ range. Moreover, due to the high sensitivity of the sensor even the lowest concentrated phenolic samples could be successfully measured.

**SWV analysis.** To elaborate the observed PEC responses, the industrial samples were also subjected to the SWV analysis. Via this sensor, not only the phenolics present in the sample can be identified but also all electrochemical oxidizable organic compounds based on their voltammetric fingerprints.[34]

The corresponding voltammogram of sample 1 (Figure 3.A), which is the aqueous phase after MiBK extraction, shows one broad oxidation peak, peak I at 0.30 V *vs.* Ag pseudo-reference, indicating that different organic components contribute to this redox process. The intensity of peak I in sample 1 was high, i.e. 4.48 µA, indicating a high level of oxidizable chemicals which is expected as it originates from the extraction of a PHOH-rich stream. Moreover, diluting sample 1, shows another oxidation process at a high much higher oxidation potential, 0.78 V *vs.* Ag pseudo-reference of the SPE, peak II.

Similar as the PEC sensor where samples 2, 3 and 6 had comparable PEC responses, their corresponding voltammograms contain the same characteristics. They all exhibited two redox processes, III and IV at 0.32 V and 0.74 V *vs.* Ag pseudo-reference of the SPE, respectively (Figures 3.C, D and G). In sample 2, the peak height of process III was 0.51 µA while for IV this was 0.03 µA. The peak height of III decreased slightly after the sand filter for sample 3, this was 0.48 µA while the intensity of peak IV increased to 0.09 µA. Sample 6 again gave rise to two oxidation processes III and IV with intensities of 0.47 µA and 0.02 µA, respectively. Indeed, as in this part of the WWT plant (from sample 2 to 6) only the solid particles are filtered out, it can be expected that the voltammograms of the corresponding samples are comparable.

Although peaks I (sample 1) and III (sample 2, 3, 6) are redox processes from a similar potential region, peak I has an oxidation potential shifted towards slightly less positive values (0.30 V compared to 0.32 V *vs.* Ag pseudo-reference of the SPE). It is contemplated that the components of peak I (sample 1) also contribute to peak III, observed in sample 2, 3 and 6, as the stream of sample 1 enters the WWT plant. However, the concentration of these species in sample 2 is much lower compared to sample 1 due to the dilution in the storage tank with other process streams. Furthermore, as sample 2 is taken after the storage tank, it also contains components of the PHOH-poor stream and, therefore, peak III constitutes out of more electro-active components than peak I. The same reasoning can be made for peak IV, which most likely also contains the same oxidizable species as peak II.

Interestingly, after the first AC filter (sample 4), peak III disappeared and only IV remained, also with elevated intensity (0.20 µA) (Figure 3.E). The increase in intensity of peak IV in sample 4 compared to the voltammogram of sample 3 is not the result of an increase in concentration of oxidizable species, but it is the result of the removal of peak III (Figures 3.D and E). Phenols have the tendency to form a passivating layer due to the polymerization of phenoxy radicals, generated by the oxidation of phenols.[46-49] This passivating layer, formed during oxidation process III in Figure 3.D, inhibits the oxidation of the species from peak IV leading to a lower observed intensity of peak IV in the voltammogram compared to Figure 3.E.[33]

Nonetheless, after the second AC filter (sample 5), oxidation process IV was barely detected (Figure 3.F). The concentration level of phenolic compounds in this sample reaches the LOD for SWV and as a result, the oxidation peaks were barely observed. The absence of redox processes III and IV in sample 5 confirms the successful removal of the redox-active contaminants by the AC filters.

The fact that peak III was efficiently removed by the first AC filter and disappeared in the voltammogram of sample 4, gives insights in the nature of the electro-active species behind oxidation peak III. Clearly, the species responsible for redox process III show higher affinity towards the AC filter than the species responsible for redox process IV. Therefore, it is expected that the species of peak III are more apolar, with a lower solubility in water, compared to IV. This latter finding was, furthermore, supported by the voltammogram of the sludge sample (sample 7, Figure 3.H). Only peak III with high intensity of 1.12 µA was observed indicating a high level of accumulated chemicals. As discussed with the PEC sensor, persistent and less water-soluble (phenolic) chemicals have a large tendency to accumulate in solids and are, in this case, expected to cause redox process III.[12, 45] Clearly, those species are also efficiently removed by the first AC filter. As peak IV was not present in the sludge sample, it indicates that these are species with a higher solubility in water, and have, as a result, a lower affinity towards the AC filters. For this reason, these species are completely removed after the second AC filter.

In conclusion, the SWV sensor elucidated the different oxidizable species present in the samples and provided insights on the nature of the species based on the affinity with the AC filter and the sludge sample voltammogram. Together with the PEC sensor, which could measure phenols in the mg $L^{-1}$ to µg $L^{-1}$-level, it is shown that the combination of the PEC and SWV sensors

is a powerful tool. However, in order to verify to which oxidation process the phenolic compounds contribute, an identification study must be performed.

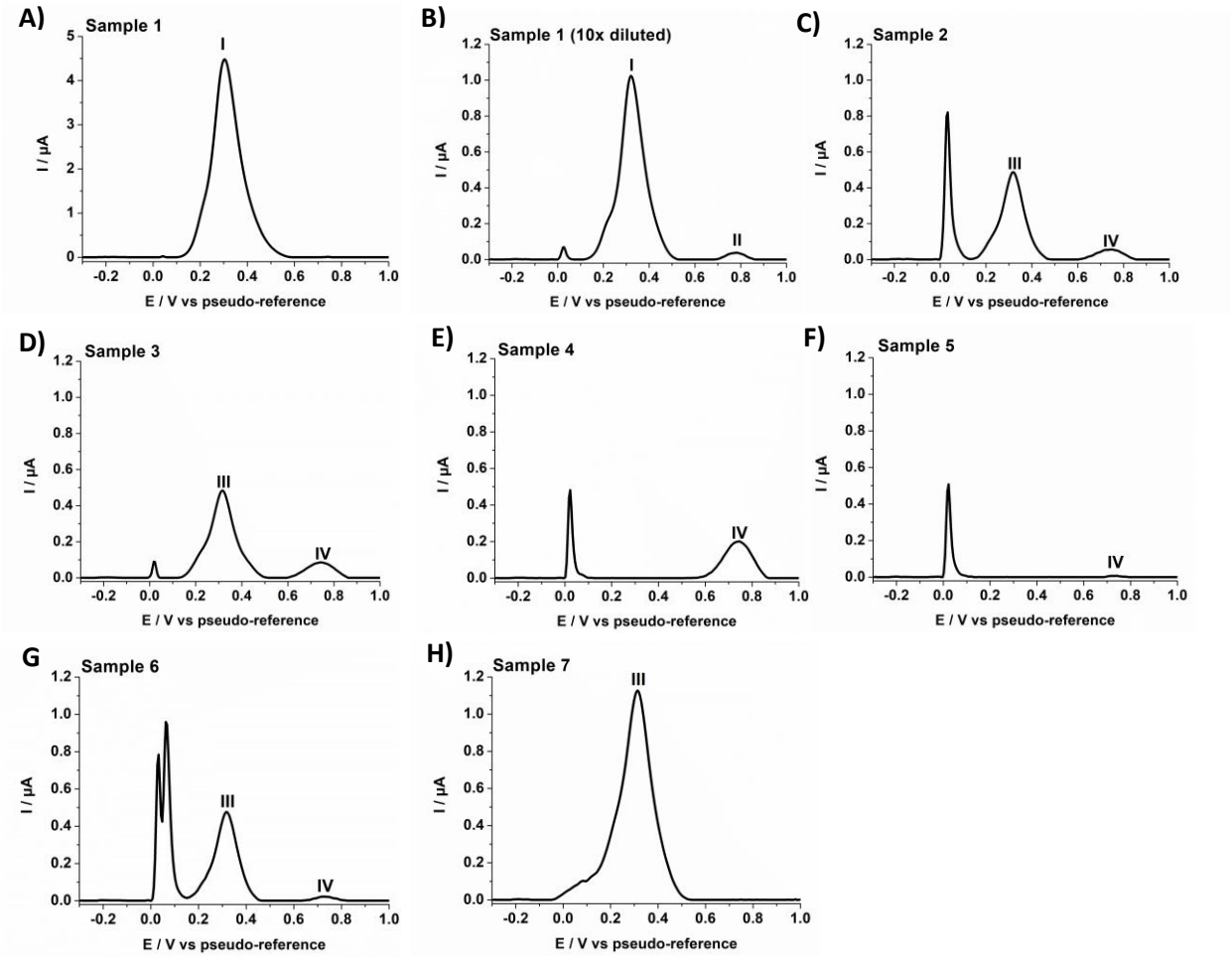


**Figure 3**. SWV measurements of the industrial samples (A) 1, (B) 1 (10 times diluted), (C) 2, (D) 3, (E) 4, (F) 5, (G) 6 and (H) 7. All samples were two times diluted in pH 10 carbonate buffer, except for (B) which was 10 times diluted. The peak around 0 V is due to oxidation of silver, originating from the Ag pseudo-reference electrode.

## 3.2. Unravelling the nature of phenolic components contributing to the PEC and SWV responses

To elucidate the PEC photocurrent responses and SWV oxidation peaks, the different contributing phenolics should be identified. This was achieved by the comparison of standards with the HPLC-DAD chromatograms of the industrial samples. However, industrial samples are often very complex samples consisting out of a wide variety of chemicals (Figure S7), e.g. reaction

products, phenolic dimers or polymer derivatives, and, as a result, their HPLC-DAD measurements lead to many peaks in the chromatogram. Moreover, both redox active and inactive compounds contribute to a chromatogram. Therefore, the focus was placed on phenolic standards, as they potentially exhibit a PEC response and are electro-active.

Two samples were analyzed in detail, sample 1 and 2, since they consist out of a different matrix, exhibit all the observed redox peaks, and, moreover, provide sufficient sensitivity to allow an unambiguous identification of the samples. Some classical phenols were selected as standards for the identification. The selection criteria was based on the environmental permit of the company which indicated their streams contain alkylphenols. Moreover, some hydroxyphenols were also included as they can be the oxidized products of PHOH.[35, 50] The HPLC-DAD analysis of the different standards can be found in Figure S8. There, it is observed that the hydroxylated phenols have a lower retention time compared to the alkylated phenols due to the lower interaction with the C18 column of the former compounds.

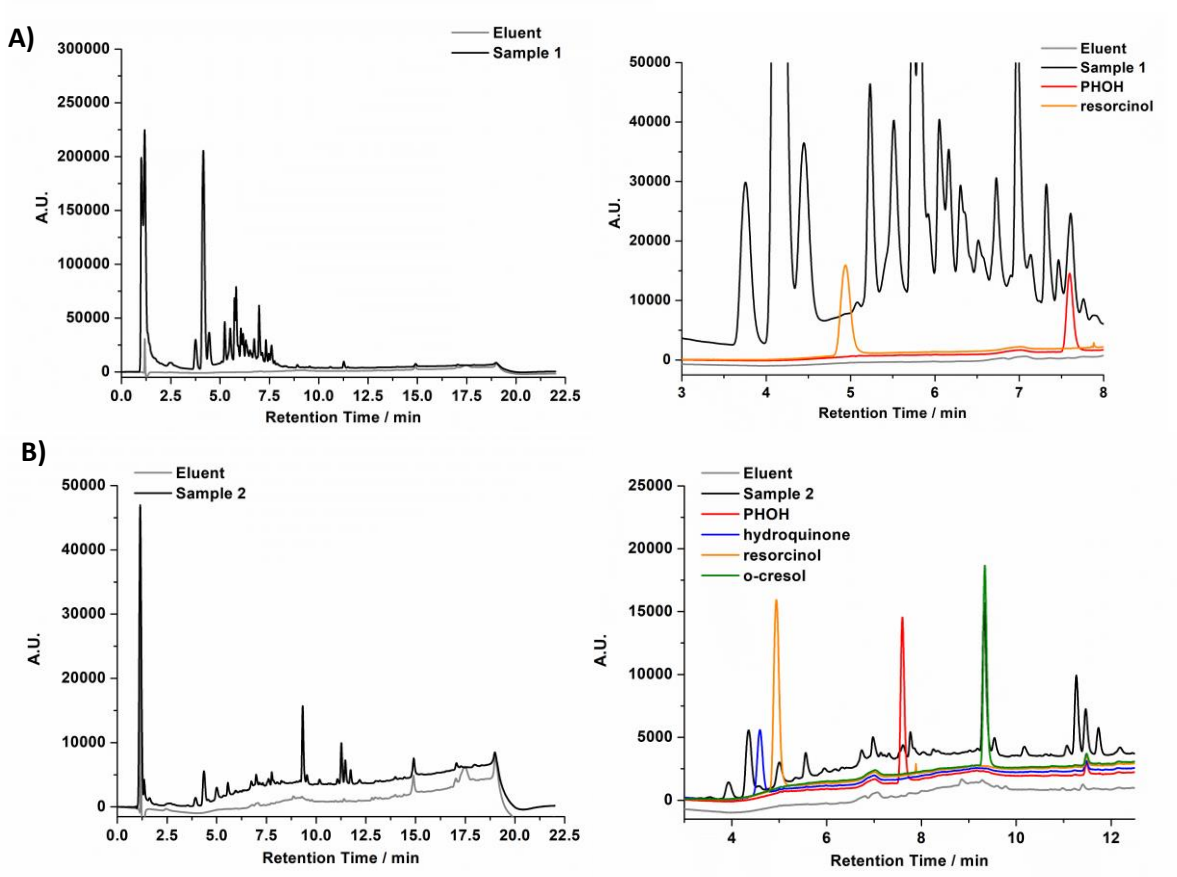


**Figure 4.** HPLC-DAD chromatograms of industrial samples (A) 1 and (B) 2 with left the full chromatogram of the sample and right zoomed in on the overlap of the peaks with standards PHOH, resorcinol, hydroquinone and *o*-cresol (10 µmol $L^{-1}$) at 220 nm wavelength. All samples were filtered and undiluted.

The HPLC-DAD analyses of sample 1 and 2 show a complex chromatogram consisting out of a wide variety of peaks (Figure 4). While for sample 2, the bands were spread out over the whole chromatogram, for sample 1, almost all compounds had a retention time shorter than 8 minutes, suggesting a higher polarity of these compounds. In both samples, PHOH could be identified. Next to PHOH, the presence of hydroquinone, resorcinol and *o*-cresol could be verified in sample 2. For sample 1, a small peak was identified as resorcinol, although in very low intensity. However, a detailed identification of this latter analysis is challenging due to the large increase in the baseline current which could easily mask lower concentrated phenols. Nonetheless, as hydroquinone and *o*-cresol are absent in sample 1 (Figure 4.A), it can be speculated that these compounds originate from the complex PHOH-poor stream which contains many additives, precursors and other chemicals.

The identified phenols were next subjected for the SWV analysis (Figure 5). All identified phenols have oxidation potentials overlapping with redox process I (sample 1) or III (sample 2) proving their presence in the samples. Only hydroquinone has a much lower oxidation potential, however, from the HPLC-DAD data it can be speculated that it is only present in small amounts, presumably lower than the detection limit of the SWV sensor.

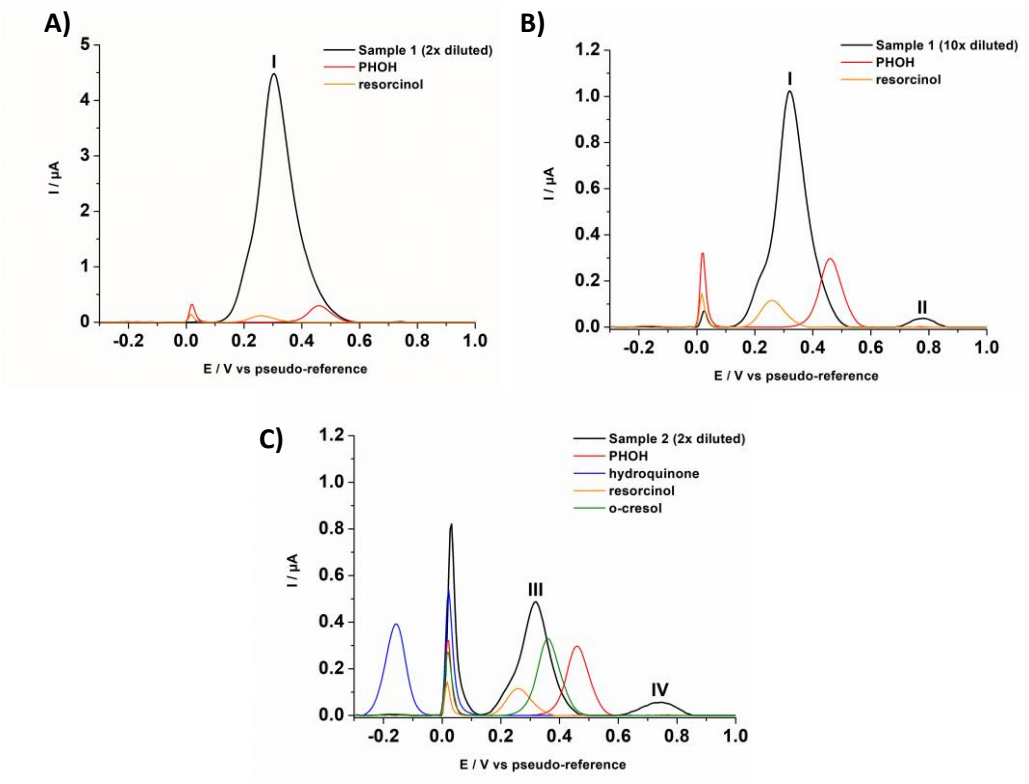


**Figure 5.** Overlay of the SWV voltammograms of the identified phenolic standards (10 µmol $L^{-1}$) with sample 1 (A) two times diluted with buffer and (B) 10 times diluted. (C) Overlay of standards with sample 2. As buffer solution pH 10 carbonate buffer was used. The peak around 0 V is due to oxidation of silver, originating from the Ag pseudo-reference electrode.

At this point, we were not able to elucidate redox processes II and IV. It is not unlikely that this redox process constitutes out of non-phenolic contaminants since in samples 4 and 5 the determined amount of phenols by the PEC sensor was close (sample 4) and even lower (sample 5) than the detection limit of the SWV sensor, and, therefore, it is speculated that the oxidation signals of these phenols have very low intensities in the voltammogram, much lower than the intensity observed in Figure 3.E.

An important side note is that, although, only *o*-cresol from the alkylated phenols was identified, that the other alkylated phenolic standards such as *m*-cresol, *p*-cresol, 2,4-dimethylphenol, 2,6-dimethylphenol, 3,4-dimethylphenol, bisphenol A, 4-cumylphenol, 4-*tert*-octylphenol and 4-nonylphenol possess redox processes similar as peak I or III (Figure 6). Therefore, it is speculated that these alkylphenols containing different side chains in their structures than the chosen standards for this research, can be present in the samples. This can be, for instance, dimers originating from the synthesis of the resins. Moreover, this motivation is supported as in the HPLC chromatogram they can easily be separated based on their substituents explaining the high number of peaks in the chromatograms.

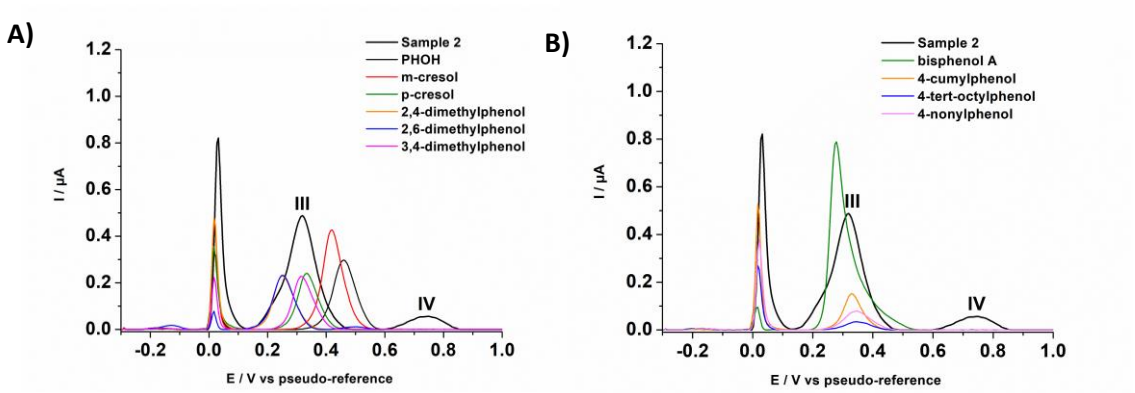


**Figure 6.** Overlay of the voltammogram of sample 2 with different alkylated phenols (A and B). The concentration of the phenols was 10 µmol $L^{-1}$ and sample 2 was two times diluted with pH 10 carbonate buffer.

From the identified phenols, only resorcinol is PEC inactive due to the instability of the *m*-quinone form which rapidly decomposes.[51] Hydroquinone and *o*-cresol are both PEC active, with PEC sensitivities higher than PHOH for hydroquinone and similar as PHOH for *o*-cresol, as depicted in Figure S9. Nonetheless, other phenolic structures, which are currently not identified, may also contribute to the PEC response. As shown in literature, the PEC sensor can also detect large phenolic structures, e.g. antibiotics,[31, 52] therefore, it would not be unlikely that the phenolic dimers or short polymers contribute to the PEC responses observed in the measurement of the industrial samples.

## 3.3.Comparison of the PEC sensor with commercially available test kits

At last, the performance of the PEC sensor was compared with commercial test kits (Table 2). More specifically, the sensor was compared with two colorimetric methods, from Hanna Instruments and CHEMetrics and one COD kit from CHEMetrics. Similar as the PEC sensor, the colorimetric kits are specific for phenols while the COD kit measures all oxidizable organic compounds, and is for this reason not an optimal measure for the phenolic content. Industrial samples 1 and 4 were subjected for analysis with the test kits (Figure S10). These samples were chosen as they contain phenols in either mg $L^{-1}$ or µg $L^{-1}$-range.

For all samples, no concentration level of PHOH could be determined with the SWV sensor since the oxidation process of PHOH is only a shoulder of peak I, as depicted in **Error! Reference source not found.** S11; the addition of increasing PHOH concentrations did not result in an increase of the peak due to the significant amount of electro-active species present in the sample.

**Table 2.** Comparison of the performance of the PEC and SWV sensors with three commercial test kits in the measurement of samples 1 and 4. The different characteristics were obtained from the measurement procedure attached to the test kits and information provided by the manufacturer's website.

| | PEC sensor | SWV sensor | HI3864 Phenols Test Kit | VACUettes® Phenols Kit K-8012D | LR COD Vials Kit K-7356 |
|---|---|---|---|---|---|
| **Brand** | A-Sense Lab | A-Sense Lab | Hanna Instruments | CHEMetrics | CHEMetrics |
| **Sample volume** | 80 µL | 80 µL | 20 mL | 0.5 mL | 2 mL |
| **Analytes** | Phenols[a] | Redox active species | Phenols[b] | Phenols[b] | Oxidizable organics |
| **Sample 1** | 29 ± 6 mg $L^{-1}$ | / | 62.5 mg $L^{-1}$ | 30 – 75 mg $L^{-1}$ | 3.5 g $L^{-1}$ |
| **Sample 4** | 26 ± 4 µg $L^{-1}$ | / | < MDL | < MDL | 60 mg $L^{-1}$ |

a) Exclusive e.g. catechol.[53] b) Exclusive *p*-substituted phenols (alkyl, aryl, nitro, benzoyl, nitroso, or aldehyde group).[18, 19]

The COD value of sample 1 was quite high (3.5 g $L^{-1}$) due to the high level of oxidizable organic compounds. This was confirmed by HPLC-DAD analysis which indicated a high amount of

chemicals based on the amount of peaks exhibited in the chromatogram. The colorimetric phenols test kits measured a similar amount of phenols in sample 1. For the kit of Hanna instruments, a concentration of 62.5 mg $L^{-1}$ was determined while for the CHEMetrics test, it was between 30 - 75 mg $L^{-1}$. The PEC sensor predicted a lower level of phenols in this sample, i.e. 29 ± 6 mg $L^{-1}$. This is likely the result of several factors. First, the presence of resorcinol in sample 1 will not lead to a contribution to the PEC response as this compound is PEC inactive.[51] Moreover, different phenols possess different sensitivity in the PEC sensor as this is dependent on their oxidation rates with $^1O_2$ which is controlled by substituents present on the ring. For instance, substitution of the phenolic ring with bulky alkyl groups, e.g. *t*-butyl, leads to a diminished $^1O_2$ oxidation rate.[43, 53, 54] As a result, an under- or overestimation of the total phenolic concentration can occur when using PHOH as standard. Mapping the PEC sensitivity of a variety of phenols and dividing them into specific classes might overcome this issue. Each class can, then, be represented by a phenolic standard that has a sensitivity similar as the compounds in that class. Using this standard should, therefore, lead to a more accurate quantification of the samples.

The fact that the PEC sensor was able to determine the concentration of phenols in sample 4 (26 ± 4 µg $L^{-1}$), demonstrated the high sensitivity of this sensor. In contrast, the colorimetric test kits could not detect these phenols as their concentration level was lower than the method detection limit of these kits. The COD spectrophotometric method provided a value of 60 mg $L^{-1}$ which is significantly higher than the value provided by the PEC sensor (26 ± 4 µg $L^{-1}$) as it was caused by the oxidizable organic compounds present in the sample.

In general, a detailed quantification is not always required for the analysis of industrial samples as the photocurrents of the PEC sensor itself are indicative for the amount of phenols. In this, the direct measurements of the PEC sensor plays an important role. These measurements have evidenced the removal of phenolic compounds by the decrease of the photocurrents. As a result, these photocurrents can also be used to evaluate the efficiency of the WWT plant. Moreover, the high speed (results in minutes), low sample volume (80 µL), high sensitivity (µg $L^{-1}$ or nmol $L^{-1}$) and absence of laborious sample pre-treatment steps makes the PEC sensor a powerful tool for the analysis of µg $L^{-1}$-concentrated streams which are, for example, discharge streams. These latter streams are important for industries in terms of cleaning and taxation. Furthermore, in combination with the SWV sensor, insights in the nature of the phenolic compounds can be obtained.

# 4. Conclusion

We demonstrated that PEC and SWV sensors can be successfully applied for the analysis of industrial samples. The sensors can follow the removal of the phenols and oxidizable organics throughout the cleaning process. The direct measurement and standard addition of the PEC sensor showed the decrease of the phenolic concentration along the WWT plant while the SWV analysis provided valuable insights in the nature of the different oxidizable species based on the oxidation processes of the different samples. HPLC-DAD analysis played a crucial role as it elucidated some phenols present in the samples. At last, the performance of the PEC sensor was compared with three different commercial test kits. The high sensitivity of the PEC sensor was demonstrated in the analysis of the µg $L^{-1}$-level of phenols and proved the PEC sensor to be an advantageous methods compared to the other kits. Nonetheless, to improve the accuracy on the determination of the concentration value, a detailed sensitivity study is necessary in order to select a more accurate standard.

# 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.

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# Authors contributions

The manuscript was written through contributions of all authors. Liselotte Neven and Hanan Barich contributed equally.

**Liselotte Neven**: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Validation; Visualization; Roles/Writing - original draft. **Hanan Barich**: Conceptualization; Data

curation; Formal analysis; Investigation; Methodology; Validation; Visualization; Roles/Writing - original draft. **Rob Rutten**: Conceptualization; Resources; Validation; Writing - review & editing. **Karolien De Wael**: Conceptualization; Funding acquisition; Project administration; Resources; Supervision; Validation; Visualization; Writing - review & editing.

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