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(Spectro-) Electrochemical Detection of Diclofenac with Different Screen-Printed Electrodes

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Abstract- A drastic increase in the consumption of pharmaceuticals has resulted in a high load of pharmaceuticals in waste water. Many pharmaceuticals are non-biodegradable and are resistant to conventional waste water treatments. For this reason there is an obvious need to first detect these substances and, second, to detoxify them. Diclofenac (DCF) is a typical representative of an analgesic non-steroidal anti-inflammatory drug. Since the ecotoxicity of DCF is rather low, an overall accumulation increases its toxicity.

In this study, a rapid, sensitive, and inexpensive detection method with different commercial screen-printed electrodes (SPEs) (i.e. MWCNT, graphene, graphite and Au SPE) were used to quantitatively detect diclofenac. (Spectro-) Electrochemical methods such as cyclic voltammetry (CV), electrogenerated chemiluminescence (ECL), and amperometry (AM) are discussed in detail and the sensitivities of the electrochemical methods are compared to the sensitivity of conventional gas chromatography-mass spectrometry detection (GC-MSD). The limit of detection (LOD) is 1 µmol/L for GCMS and 50 µmol/L for ECL depending on the electrode used.

Keywords- *Diclofenac, Screen-Printed Electrodes, Amperometry, Electrogenerated Chemiluminescence*

I. INTRODUCTION

Diclofenac (DCF), a nonsteroidal anti-inflammatory drug used for the treatment of pain and inflammation, can also help relieve the symptoms of arthritis, swelling, and joint pain [1]. However, diclofenac may also cause serious effects on the stomach and intestines, including bleeding and perforation [2]. In Germany alone 90 t are used annually, of which 63 tons enter the waste water after being excreted in urine [3].

The exceptional use of DCF and its release into the environment may cause risks to human health and aquatic environments. Although the ecotoxicity of DCF is quite low, prolonged exposure increases the environmentally relevant concentration with considerable negative effects on the environment.

In analytical and environmental chemistry, two strategies are followed: (1) The fast and sensitive detection of DCF and (2) the degradation and removal of residual DCF from aqueous systems [4]. In this paper we focus on the analytical aspects.

- A data search on DCF in the SciFinder database returned approximately 30,000 references. Amongst the medical aspects, there are three principal electrochemical issues surrounding DCF:
- The simultaneous detection of DCF and other pain-relieving drugs such as morphine [5], ibuprofen [6], and paracetamol [7]. Oliveira et al. [8] reported the simultaneous electrochemical detection by hanging mercury drop electrode of several emerging organic contaminants (such as diclofenac) in sewage treatment plants.
- The investigation of different modified electrodes for detecting DCF: Afkhami [9] used gold nanoparticles / multiwall carbon nanotubes (MWCNT). Goorarzian [10] used ionic liquid MWCNT, Ghoreishi [11] incorporated $Cu(OH)_2$ nanoparticles into carbon-paste electrodes for simultaneously determining diclofenac and methyldopa. Mokhtari [12] used MWCNT paste electrodes for simultaneously determining diclofenac and morphine. Cheng [13] used graphene-hemin hybrid materials and Arvand [14] multiwall / $Cu(OH)_2$ glassy carbon electrodes. The kinetics and mechanisms of electrochemical oxidation of DCF on a carbon-paste electrode (CPE) were studied by Cid-Ceròn et al. [15]. The authors postulated an EC mechanism during the electrochemical oxidation on the CPE. The experimental evidence (UV-VIS spectroscopy and GC-MSD) gives strong support to bond cleavage of the N-C bond by forming 2,6-dichloroaniline and 2-hydroxyphenylacetic acid. We will come to this point later. Mohamed [16] outlined the pharmaceutical applications and recent developments of screen-printed electrodes. Overall, the results show a limit of detection in the micromolar range; however, the procedure for preparing the electrodes is quite time consuming and elaborate and is therefore restrictive for routine analysis.
- The simultaneous electrochemical detection and degradation: TiO_2 nanoparticle decorated nanorods and nanotubes were used for electroenzymatic and photoelectrocatalytic degradation of diclofenac [17]. In a review article, Klavaroti [18] summarized the oxidation

methods that can remove residual pharmaceuticals such as diclofenac from aqueous systems. Besides electrooxidation processes, photolysis, Fenton oxidation, heterogeneous photocatalysis, and ultrasound irradiation are methods of choice. Important in our context are the investigations of Vogna [19] and Zwiener [20], because these authors proposed different reaction pathways depending on the oxidant; however, in each case C-N cleavage and hydroxylated intermediates resulted.

In addition, the HPLC and GC-MSD methods are described as broad and versatile analytical methods for studying oxidative degradation of environmentally relevant pharmaceuticals [21].

II. EXPERIMENTAL

As previously mentioned, a wide range of applications exist for detecting pharmaceuticals by SPE [16]. SPEs are sensors based on screen-printing technology that print on different substrates with various compositions of the ink. Several types of such devices are commercially available [22]. The main advantages of SPEs are their great utility, versatility, simplicity, and reliability, as well as their small instrumental setup and modest costs.

Despite these advantages, Bernalte et al. [23] have shown that the electrode surface of SPEs may be complex. Differences in the ink's composition and the variable temperature conditions during the curing of the printing layer can affect the electrochemical behavior of the SPE. The authors investigated the behavior of different temperature-cured Au SPEs by cyclic voltammetry (CV), and proposed that these electrodes be used only at positive potentials because an interference peak around 0 V may disturb the results. Therefore, in our own experiments, CV with an SPE was used as a first check on the quality of the SPE. When the results differed significantly between SPEs of the same type, we dumped that SPE. Another quality feature of the SPE that was tested was the absence of any electrochemical activity with the used solvent. Overall, all used SPE have a high quality, because the electrochemical behavior does not differ.

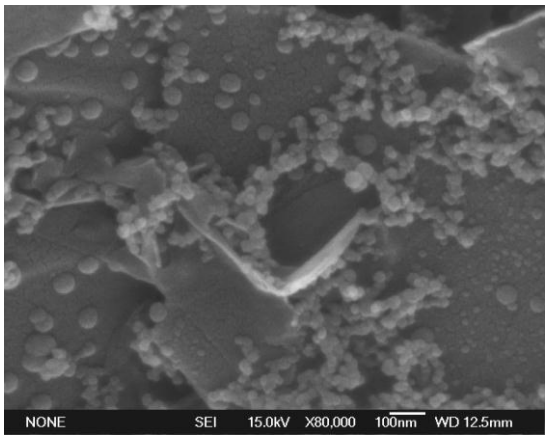
Chemicals and instruments: Diclofenac-Na (5210, Caelo, Hilden, Germany), double-distilled water, 1 mol/L aqueous solution of $(NH_4)_2HPO_4$ (pH≈8) (5596.1, Carl Roth, Karlsruhe, Germany).

Electrochemistry: Potentiostat (μ-STAT 400, DropSens) and ECL-Potentiostat (μ–STAT ECL, DropSens).

SPE:

- *DropSens*: DRP 110 (C as working electrode, C as counter electrode, Ag as reference electrode), DRP 250 AT (Au as working electrode, high temperature cured, Pt as counter electrode, Ag as (pseudo)reference electrode), DRP 110 CNT GNP (Au nanoparticles on carbon nanotubes as working electrode), DRP AUTR 10 (optically transparent gold electrode; thin layer of gold sputtered over plastic).
- *Orion High Technologies*: Customized graphene decorated with TiO_2: graphene / TiO_2 as working electrode, C as counter electrode, Ag/AgCl as reference electrode

MWCNT: OHT-067



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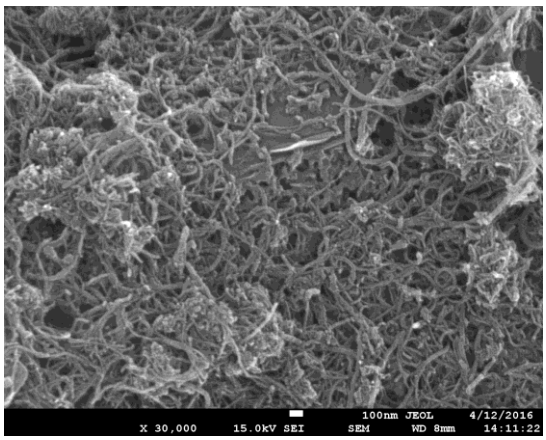

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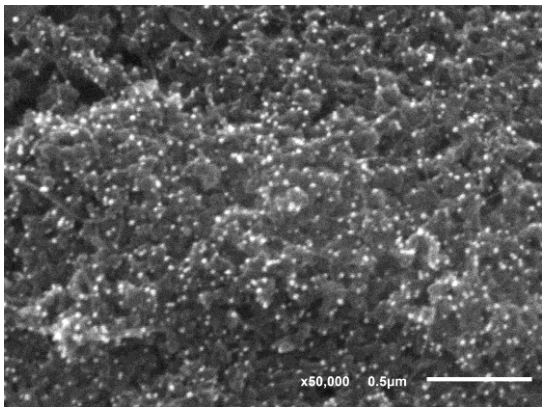

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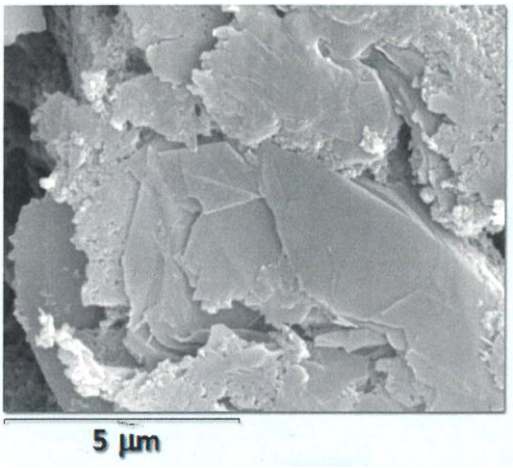

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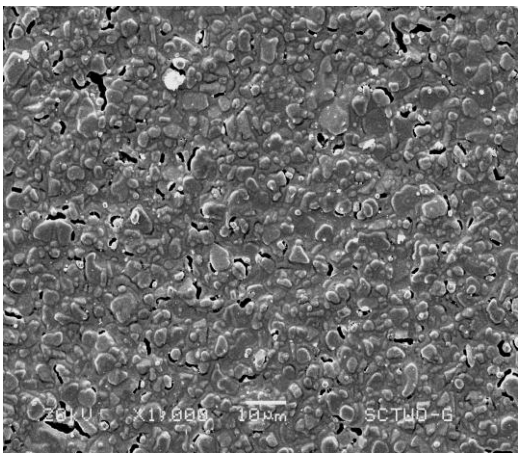


(e)

Figure 1. (a) MWCNT graphene decorated with TiO_2. (b) MWCNT. Both from Orion High Technologies. (c) DRP 110 CNT-GNP decorated with nanogold, (d) DRP 110, (e) DRP 250AT. All from DropSens

Mass Spectrometry: GC-MSD with autosampler (GC: Hewlett Packard 5890, MSD: Hewlett Packard 5972, autosampler: Hewlett Packard 6890), column: RTX-35; carrier gas: He 5.0.

UV-VIS Spectroscopy: UV-VIS spectrometer (Perkin Elmer Lambda XLS+), transmission cell with focusing lens and fiber optics (DRP-TRANSCELL, DRP-CLENS, DRP-TFIBER, DRP-RPROBE, DropSens), light source (HPLC detector 432, Kontron), photomultiplier (Hamamatsu, R4220P with power supply: MH5781).

HPLC cell (DRP-HPCELL, DropSens)

III. RESULTS AND DISCUSSION

A. Cyclic Voltammetry

Figure 2 shows the cyclic voltammogram and the changing color of the (transparent gold) working electrode (DRP AUTR 10) before and after one CV scan. The color of the working electrode changes from grey to brown. This reflects the CV. The oxidation peak of DCF appears at 0.4 V only in the first CV. The reduction peak (0.1 V) has a comparable low intensity. This implies an EC mechanism as proposed already by Cid-Ceròn et al. [15]; DCF reacts after the electron transfer. The oxidation product shows a reversible electron transfer with ΔE (oxidation-reduction) ≈ 59 mV (one electron transfer; indicated with the stars in Figure 2).

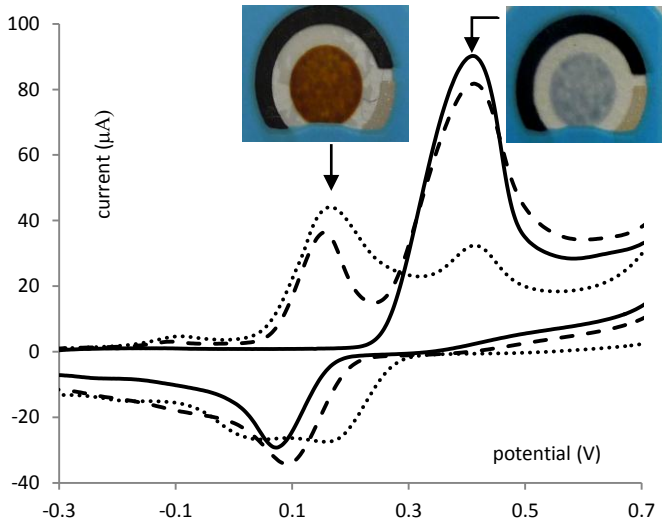


Figure 2. Cyclic voltammogram of 100 µmol/L diclofenac in $(NH_4)_2HPO_4$ three times in a row. Working electrode: DRP AUTR 10. Solid line: first scan, dashed line: second scan, dotted line: third scan.

Rinsing the SPE with ethanol does not completely clean the electrode (see the oxidation peak near 0.25 V in the square wave voltammogram; Figure 3). After electrolysis at 0.5 V for 20 s, the oxidation peak of DCF decreases and that of the oxidation product increases. This suggests that the electrooxidation may be a possible degradation route for DCF. More details later in this paper.

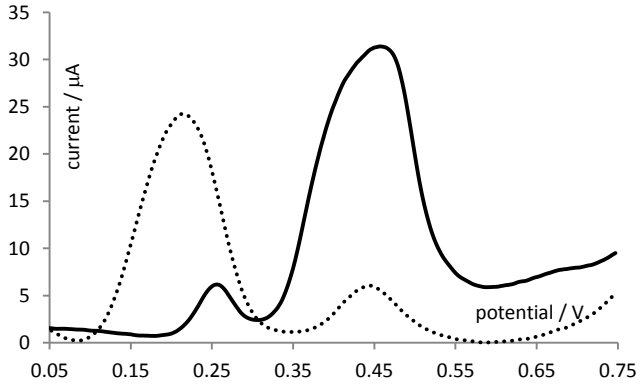


Figure 3. SWV of DCF (1 mol/L). SPE: DRP 110. SWV conditions: Estep: 0.003 V, Eamp: 0.005 V, frequency: 30 Hz. Solid line: first scan, dotted line: second scan

To identify the reaction product, we analyzed the sample (electro)spectroscopically and with GC-MSD (see 2.2).

B. Spectroelectrochemical measurements

Spectroelectrochemistry is a two-dimensional spectroscopy, combining both electrochemical and spectroscopic monitoring. This technique opens a new way to investigate electroactive species or products of redox reactions. Under potential control, spectroscopic information such as electronic absorption can be obtained about in situ electrogenerated species. Spectroelectrochemistry is a technique that can also be used to study complex reaction mechanisms [24–26].

1) Procedure

We first recorded the UV-VIS spectrum of DCF after electrolysis (0.5 V, 300 s). The SPE (MWCNT, Orion High Technologies) was inserted into a quartz cell so that the beam of the photometer glanced the SPE laterally (the SPE does not transmit UV). We could therefore simultaneously detect the absorption of both DCF (about 290 nm) and the reaction product (Figure 4).

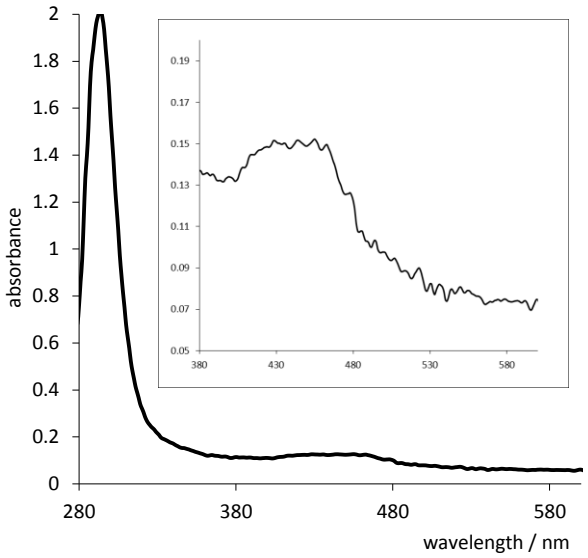


Figure 4. Absorption of DCF (290 nm) and the reaction product (after electrolysis) at 450 nm (insert)

Cid-Ceròn et al. [15] proposed that 2,6-dichloroaniline was one of the electrochemical oxidation products. However, 2,6-dichloroaniline does not absorb at 450 nm (λ_{max} (dichloroaniline) = 290 nm). In addition, our GC-MSD measurements did not detect dichloroaniline, but instead showed dichloro-methylcarbazole (molecular ion: 251, main fragments: 216: - Cl, 201: - Cl, – CH_3, 181: - Cl_2, 166: -Cl_2, – CH_3). Dichloro-methylcarbazole must be formed via ring closure reaction. However, if DCF is treated with H_2O_2 (for about 10 minutes) 2,6-dichloroanilin is one of the main products (see GC-MSD in Figure 5). But we do not think that oxidation is a successful route to detoxify DCF because dicloroaniline is much more toxic than DCF itself. A realistic detoxification may be a complete reductive dehalogenation as Habekost showed for polychlorinated biphenyl [27] and polybrominated flame retardants [28].

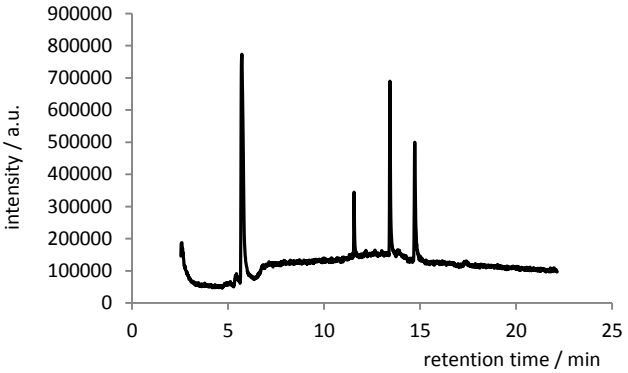


Figure 5. GC-MSD of DCF after reaction with H_2O_2 (10%) A: dichloroaniline, B: dichloro-methylcarbazol, C. unknown, D: DCF

Figure 6 shows a spectroelectrochemical setup that was used for a lower volume (50 µL): A fiber passes the light from a spectrometer through the transparent SPE (DRP AUTR 10) fixed in the transmission cell. A second fiber opposite guides the beam into a photomultiplier. The first fiber consists of six single fiber bundles around one reflection fiber that collects the reflected light beam to control the incident light intensity via another photomultiplier.

Figure 6. Spectroelectrochemical cell with a fiber from the spectrometer (top) and a fiber that guides the transmitted light to a photomultiplier (bottom). The SPE inside the cell is connected with the potentiostat.

Figure 7 shows the spectrum of the reaction product of DCF after electrolysis at 0.55 V. The value $\lambda_{max} \approx 450$ nm corresponds with those reported by Cid-Ceròn et al. [15].

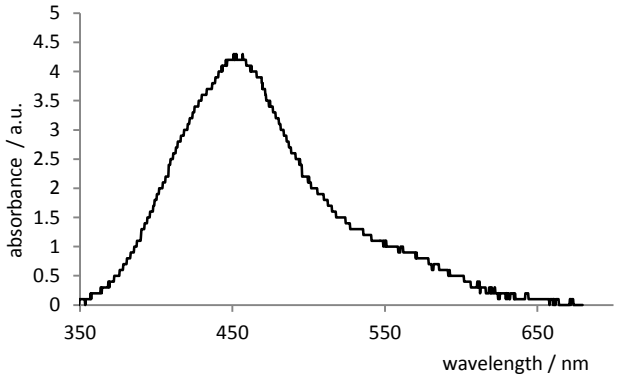


Figure 7. Spectrum of the reaction product of DCF at 0.55 V.

Figure 8 shows the absorbance at 450 nm of four potential scans in a row. Beginning at 0.25 V, the absorbance increases up to about 2.5 a.u. In the reversed scan, the absorbance remains constant and decreases at about 0.3 V to an absorbance slightly above the initial value. In the subsequent scans the absorbance shifts to higher values, indicating that the electrode is covered with the reaction product.

With each scan the oxidation and reduction peak currents of the reaction product drift apart (see insert of Figure8). This indicates that the electron transfer rate decreased. This is also evident for surface covering.

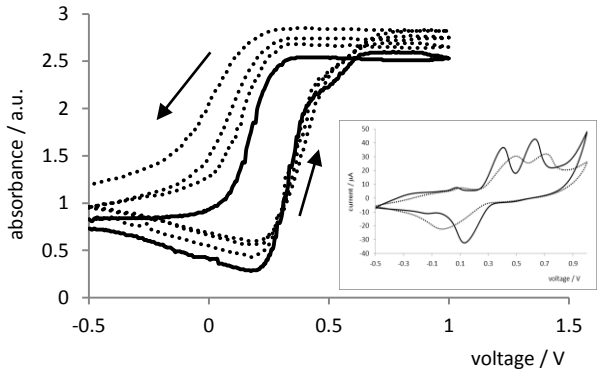


Figure 8. Spectrum of the reaction product of DCF at 450 nm. First scan (solid line) and following scans (dotted line). Insert: CV. First scan (solid line) and fourth scan (dotted line). The anodic and cathodic current peaks drift apart.

C. Amperometric detection

Amperometric detection is a standard electrochemical analysis technique in HPLC. The current that is measured results from oxidation or reduction reactions. The injection of DCF into the electrochemical HPLC cell (see Figure 9) was done via a Rheodyne valve (7125) over a µL loop. Figure10 shows the resulting current with different SPEs.

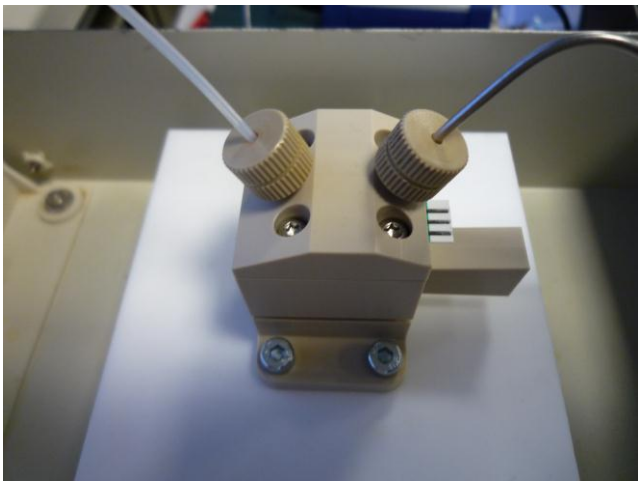


Figure 9. HPLC electrochemical cell with fixed SPE and inflow and outflow of the eluent

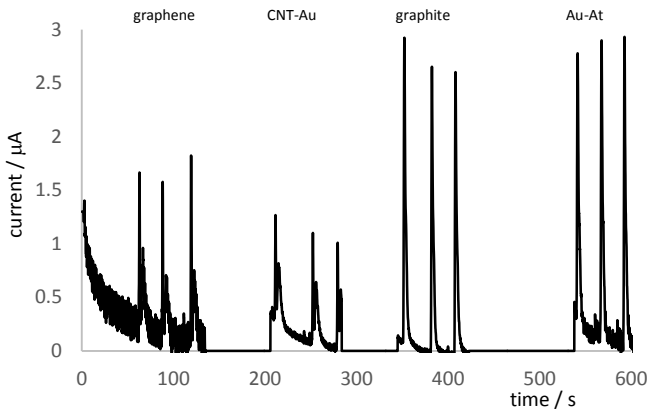


Figure 10. Amperometric detection with different SPEs. Three times injected DCF (concentration 100 µmol/L, loop volume: 10 µL).

The best signal-to-noise ratio is seen with the graphite (DRP 110) and the MWCNT (OHT-067) SPE, which noth have a detection limit of 3 µmol/L (= 30 pmol or 9 ng DCF, 3:1 signal-to-noise).

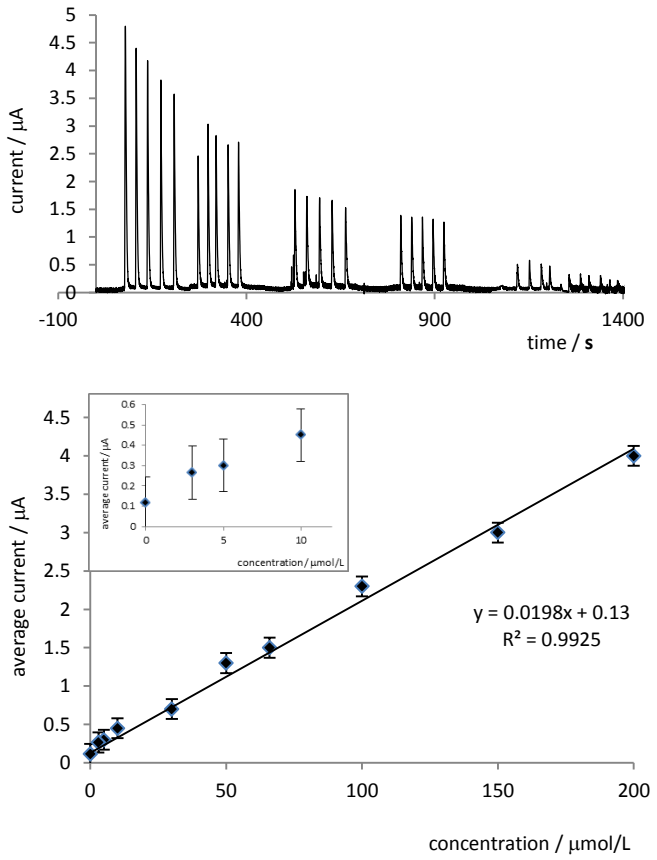


Figure 11. Amperometric detection of DCF at different concentrations (10 µmol/L to 200 µmol/L) with DRP 110 and OHT-067. Injection volume: 10 µL

D. Electrochemiluminescence (ECL)

Since the 1960s electrogenerated chemiluminescence (ECL) techniques have become increasingly attractive in analytical chemistry [29–31]. ECL involves generating an excited state in the commonly used and extensively investigated tris(2,2'-bipyridyl)ruthenium(II) $[Ru(bpy)_3]^{2+}$ on an electrode surface. $[Ru(bpy)_3]^{2+}$ is first oxidized before it undergoes an electron transfer reaction with a coreactant. During this latter process, an excited state is reached that subsequently decays and emits light. $[Ru(bpy)_3]^{2+}$ luminesces strongly. Finally, $[Ru(bpy)_3]^{2+}$ can be regenerated after the emission. Several substances exist that can quench the ECL $[Ru(bpy)_3]^{2+}$ / coreactant; for example, melatonin [32], acetaminophen, 3-acetaminophenol, and benzoquinone [33]. In summary, a variety of phenolic compounds have been shown to quench ECL [33]. The authors proposed that the intermediate formation of benzoquinone causes quenching of the excited state of the Ru-coreactant system. Complete ECL quenching is observed between 10 and 100-fold excess of the quencher.

The ECL system used here is a combination of $[Ru(bpy)_3]^{2+}$ and proline (as coreactant), which produces one of the most intense ECL results [34]. In addition, this system has excellent water solubility and is less toxic than tripropylamine, one of the most common coreactants in ECL studies. Figure 12 shows ECL quenching at two different DCF concentrations (100 µmol/L and 300 µmol/L).

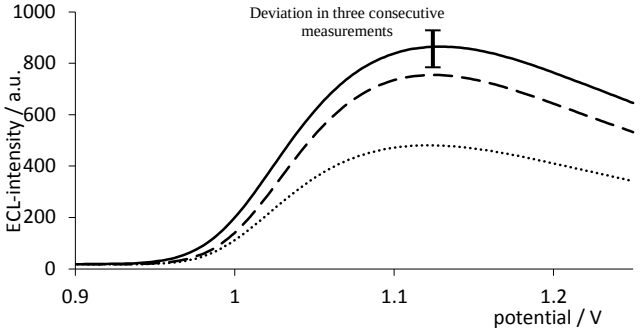
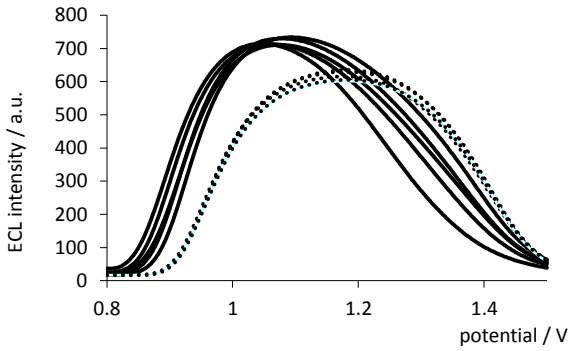


Figure 12. ECL curve of 100 µmol $[Ru(pby)_3]^{2+}$ / 100 µmol proline (solid line) with DCF concentrations of 100 µmol/L (dashed line) and 300 µmol/L (dotted line). SPE: DRP 250 AT

Figure 12 shows different quenching of the ECL by DCF, depending on the electrode material. Irrespective of the differing shapes of the ECL intensity curves, quenching of ECL on a carbon surface is more pronounced than on a gold surface, and the concentration of the quenching DCF is in the order of the Ru-proline concentration.



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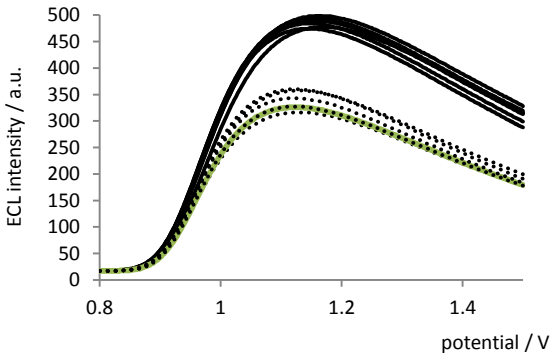

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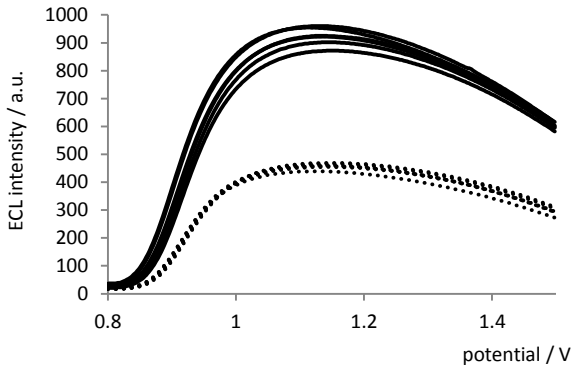

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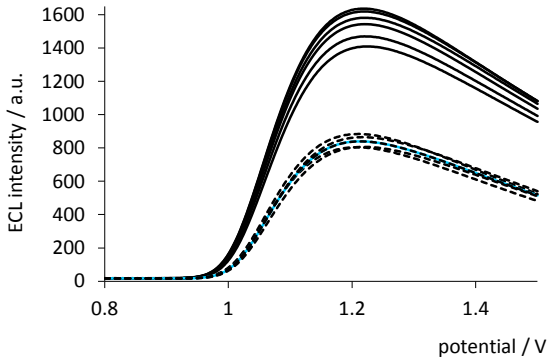

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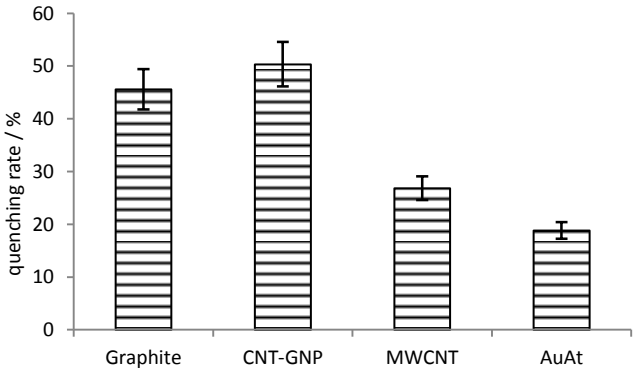


(e)

Figure 13. ECL of Ru^{2+}-proline (100 µmol/L) without (solid lines) and with DCF in $(NH_4)_2HPO_4$ (100 µmol/L) with different SPEs. The CV was taken five times in a row. Before each scan the solution was stirred manually. Top left: DRP 250 AT; Right: MWCNT OHT-067; Middle left: DRP CNT GNP; Right: DRP 110; Bottom: quenching rate of DCF on the SPE used.

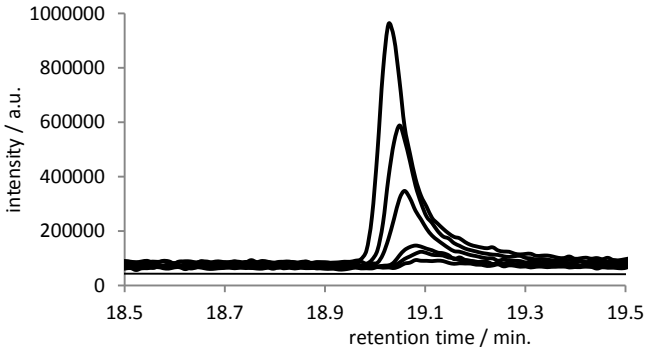
E. GC-MSD of DCF

1) Procedure:

Different concentrations of DCF in acetone were injected and analyzed by GC-MSD.

The temperature profile of the GC was 100°C in the first minute with 280°C as a final temperature. The temperature increased at a rate of 15°C/minute. The MS detector started after the solvent peak at 2.5 minutes.

In the GC of DCF, only one remarkable peak at 19 minutes was detected (detection quality of the EI mass spectrum: 99% compared to the Wiley library). Therefore, no degradation occurred on the column. Figure 14 shows a part of the GC, and the dependence between the peak intensity of DCF and the DCF concentration; 50 µmol/L can be easily detected (5:1 signal to noise).



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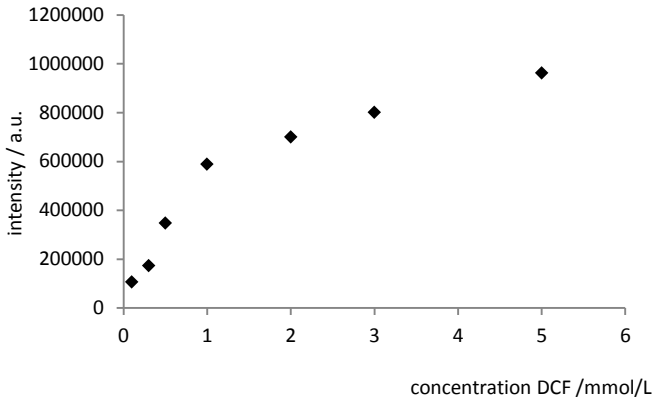

(b)

Figure 14. (a) GC-MSD for DCF at different concentrations (100 µmol/L–5 mmol/L). Experimental conditions were as follows: Column: RTX-35 (Restek); carrier gas: helium; temperature profile: 100°C (1 min isotherm); temperature rate: 15°C/min; final temperature: 280°C; 5 min isotherm. Injection volume: 1 µL. (b) Dependence between the peak intensity of DCF and the DCF concentration.

TABLE I. SUMMARIZES THE LOD OF THE METHODS USED.

Method	Amperometry	ECL	GCMS
LOD / µmol/L	1	50	50

IV. CONCLUSION

This paper has described (spectro)electrochemical methods (ECL and fast amperometry) for identifying diclofenac. The

results were compared with the results obtained by GC-MSD. Amperometry has a limit of detection (LOD) in the range of 1 μmol/L which is better than GCMS (50 μmol/L). DCF has been shown to effectively quench the ECL of $[Ru(bpy)_3]^{2+}$-proline with the minimum quenching concentration of DCF being about 50 μmol/L. The LOD differs with respect to the SPE used.

The main advantages of SPE include very easy handling and rapid feasibility, therefore, SPE can give a preliminary estimation of diclofenac concentrations. For the detection of low quantities of DCF amperometry is favorable.

Further work will be done to exactly identify the reaction products and to show whether the methods used are also applicable to determining diclofenac in waste water.

ACKNOWLEDGEMENT

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