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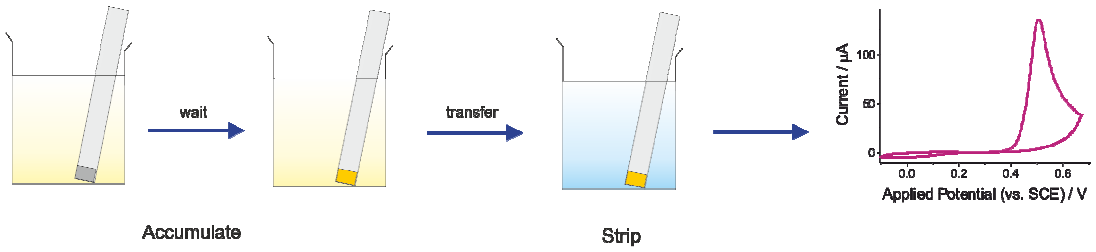

"Absorptive Stripping Voltammetry", a new electroanalytical method, is validated by phenol detection.

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Introducing Absorptive Stripping Voltammetry: Wide Concentration Range Voltammetric Phenol Detection

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Abstract

Carbon Paste Electrodes are developed for the detection of phenols via a procedure in which the phenols are allowed to accumulate in the paste via transfer from an aqueous solution prior to electro-oxidation. Importantly, the use of such paste electrodes is shown to substantially overcome the "self-passivating" behaviour of the phenol oxidation which usually constrains the electrode process to low concentrations and single-shot experiments. In this paper, 4-phenoxyphenol could be detected in the range from 2.5 to 40 µM, phenol from 2.5 µM to 60 mM and 4-methoxyphenol from 5.0 to 40 µM. The electrodes were re-usable without surface renewal for concentrations up to 1.0 mM. The use of a bulk phenol solution for pre-concentration via absorptive uptake into a bulk phase followed by electrochemical quantification represents a new form of electroanalysis, namely "absorptive stripping voltammetry" complementary to "adsorptive stripping voltammetry" where accumulation occurs via adsorption on an electrode surface.

Key Words: absorptive stripping voltammetry, phenol detection, carbon paste electrode, liquid-liquid interfaces, 4-phenoxyphenol, 4-methoxyphenol

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1. Introduction

Both substituted and unsubstituted phenols, known for their high toxicity and relatively long-term persistence in ground water – depending on temperature and pH[1] – are common bi-products of numerous industrial processes. They are thus frequent contaminants in both waste and fresh water[1,2]. At the same time, they have also been found in several food matrices[3].The development of appropriate analytical techniques is extremely important, both for the assessment of the environmental impact of phenols[2] as well as for their sensitive detection and accurate quantification.

Various sensing methods for phenolic compounds are used, including electrochemical techniques[4-6], high performance liquid chromatography[1,7-9], which is sometimes used in conjunction with electrochemical techniques[1, 7 ,8], and spectrophotometry[10, 11].

Given their high reliability and their speed of response significant recent research has focussed primarily on *electrochemical* sensors[12,13]. In phenol sensing, carbon paste, glassy carbon and very often platinum electrodes are used. In the case of carbon paste electrodes (CPEs), extensive work has been done using tyrosinase as the paste modifier[3, 14-18], with some of those investigations having also examined the effect of the pasting liquid on the stability of these biosensors[16-17]. With regards to glassy carbon electrodes, they are also usually modified, for example with surfactants in which the phenols can be accumulated[19]. Although phenolic compounds are readily oxidised on platinum, such surfaces are quickly fouled[20, 21] and are hence not ideal for electrochemical studies.

A major issue with the use of electrochemical oxidation to detect phenols is that the reaction leads to radical cations and radicals which can further rapidly polymerise. Thus, for all but very dilute samples, the phenol oxidation is intrinsically "self-passivating"[20-22] and electrodes are often constrained to "single-shot" usage before either renewal or disposal. Overcoming this problem is key to the development of practical electrochemical sensors for phenols.

The aim of this paper is to develop an electrochemical method which is both sensitive but also applicable to high concentration phenol quantification. In contrast to earlier work with CPEs, rather than using direct electroanalysis at the CPE-solution interface, we use the bulk

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phase paste to pre-concentrate the target. The ability of four carbon paste electrodes to accumulate an analyte of interest in their paste component is explored. This takes analytical advantage of recent fundamental studies of the reduction of oxygen[23] and of the oxidation of ferrocene[24]. In the present work we use a bulk carbon paste electrode to pre-concentrate phenol and substituted phenols prior to electrochemical detection. This novel approach might be termed "absorptive stripping voltammetry" by analogy with "adsorptive stripping voltammetry" where accumulation occurs via adsorption on an electrode surface.

Four carbon paste electrodes were here used to establish the optimum paste composition for the determination of phenol, 4-phenoxyphenol and 4-methoxyphenol, in aqueous solutions of pH 10.01.Pre-concentration experiments were carried out to determine the optimum exposure time of each carbon paste electrode to each phenol solution. The oxidation peaks of phenol, 4-phenoxyphenol and 4-methoxyphenol were observed at peak potentials of ca. +0.60, +0.40 and +0.30 V [vs. saturated calomel electrode (SCE)] respectively and used as the detection signals.

It will be shown below that practically useful analytical limits of detection in the low micromolar range can be obtained and, in the case of phenol, concentrations as high as 10 mM can be detected before the detection becoming limited by the uptake ability of the paste. Importantly, for concentrations up to 1.0 mM, the electrode surface did *not* need to be renewed; this indicates that surface fouling becomes an issue much later than is observed with other electrode surfaces which are conventionally used[20-22].

2. Experimental

2.1 Chemical Reagents

All reagents were purchased from Aldrich (Gillingham, U.K.), at the highest grade available, and were used as received, without any further purification. These were phenol (P), 4-phenoxyphenol (4PP), 4-methoxyphenol (4MP), dioctyl phthalate, mineral oil, graphite powder (particle diameter < 20 μm), nanocarbon powder (particles of 27 nm diameter), sodium hydroxide (NaOH), sodium tetraborate ($Na_2B_4O_7$) and potassium chloride (KCl). All aqueous solutions were prepared daily, at 298 K, using deionised water of resistivity of no less than 18.2 MΩ cm (25^{o} C, Millipore UHQ, Vivendi, U.K.) as the solvent and KCl (0.1 M) as

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the supporting electrolyte. They were made at pH = 10.01, achievable through the use of appropriate NaOH/ $Na_2B_4O_7$ borate buffers (BBS solutions) and confirmed using a Hannah pH 213 pH meter. Where experiments required the absence of oxygen, solutions were deoxygenated using oxygen-free nitrogen (N_2, BOC, Guildford, U.K.), in an air-tight environment, for at least 30 minutes. The measurements themselves were carried out under a light N_2 flow. Unless otherwise stated, the solutions used were stationary.

2.2 Equipment and Experimental Set-Up

Cyclic voltammetric as well as square wave voltammetric measurements were recorded using a computer controlled Autolab potentiostat (PGSTAT 101, EcoChemie, Utrecht, Netherlands), in a home-built Faraday cage. A standard three-electrode configuration was used, with a CPE (1.97 mm radius, 1.00 mm depth, made in-house) acting as the working electrode. A platinum wire (99.99% GoodFellow, Cambridge, U.K.) was utilised as the counter electrode and a Saturated Calomel reference electrode (SCE, BAS Inc, Japan) completed the assembly. All experiments were carried out in a thermostated water bath, at a temperature of 25 ± 0.1 ^{o} C.

2.3 Fabrication and Characterisation of the Carbon Paste Working Electrodes

The carbon paste electrode holder was made from a copper rod of radius of 1.97 mm running through a Teflon rod (for electrical contact), leaving a 1.00 mm deep cavity at the edge. Four pastes were used, fabricated by mixing each powder with each liquid binder. The graphite/dioctyl phthalate paste has previously been characterised in aqueous potassium ferricyanide[23]; the same ratio of carbon powder to pasting liquid was thus used to make the graphite/mineral oil paste. The nanocarbon particles have also been previously characterised[24]. Their size was determined by field-emission scanning electron microscopy (SEM, Leo Gemini 1530, Zeiss).

2.4 Working Electrode Surface Preparation

It was found that the carbon paste electrodes did not need to be polished. Their surface was instead renewed between each scan by cleaning the holder and packing fresh paste; this renewal was *not* done when the effect of "fouling" was investigated.

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2.5 Deconvolution of Square Wave Voltammetric Responses

The Peak Analyser Function of OriginPro 9 was used to deconvolute square wave voltammetric responses. The function allowed for the voltammogram to be modelled as a sum of three Gaussian functions.

3. Results and Discussion

Carbon paste electrodes have been shown to have the ability to "store" reactants in their paste component. This accumulation can be made under open circuit conditions by immersing the electrode in a solution that contains the analyte of interest to allow the transfer of the analyte from the solution into the paste. By then transferring the electrode to a buffered supporting electrolyte solution and running the appropriate measurement, the electrochemistry of the analyte can be studied. The electrochemical process likely takes place at the triple phase boundary that exists at the carbon-oil (binder)-water triple interface[23]. The accumulation of the analyte in the paste can thus be confirmed and utilised. This property has successfully been studied for oxygen[23], ferrocene[24] and nitroblue tetrazolium chloride[12].

The accumulation of any chosen analyte must first be quantified. This can be done by varying the immersion time of the carbon paste electrode in the analyte solution, i.e. the pre-concentration time of the electrode with the analyte. Only after determining the minimum pre-concentration time needed for the paste to be equilibrated with the analyte, can further experiments be carried out. At the same time, as can be expected, the composition of the paste used can greatly affect the observed uptake, leading to the additional need of optimising the paste "recipe" to achieve as high an accumulation of an analyte as possible.

In this section, a new electroanalytical approach, "absorptive stripping voltammetry", is introduced. An optimum paste, made from graphite powder and dioctyl phthalate, is chosen based on the observed phenol and 4-phenoxyphenol uptake (further discussion of the optimisation of the paste composition can be found in the Supporting Information section of this article). It is then used with different phenol, 4-phenoxyphenol and 4-methoxyphenol concentrations, with the aim of determining analytical limits of detection for each

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compound. The oxidation signal of each phenol is used as the detection signal. A study into the possible variation of the background current is done and the use of square wave voltammetry to address the issue of simultaneous detection of the three phenols is also presented and discussed.

3.1 The Electrochemistry of 4-Phenoxyphenol and Phenol on the Graphite/Dioctyl Phthalate Carbon Paste Electrode

3.1.1 Determining the Oxidation Products of 4-Phenoxyphenol

To determine the products of the 4-phenoxyphenol oxidation, each paste electrode was immersed in a deoxygenated aqueous borate buffer solution of pH 10.01 that contained 35 µM benzoquinone and 0.1 M KCl. This was done under open circuit conditions, for 30 s. The electrode was then transferred to a deoxygenated aqueous borate buffer solution of pH 10.01 that only contained 0.1 M KCl. 100 mV s^{-1} *reductive* scans were then run between +0.80 V and -0.40 V (vs. SCE). Peaks attributed to the reduction of benzoquinone (see below) were observed at peak potentials of -0.16 V, -0.15 V and -0.30 V (vs. SCE) on the graphite/dioctyl phthalate, graphite/mineral oil and nanocarbon/mineral oil pastes respectively; no peaks were observed with the nanocarbon/dioctyl phthalate paste. The graphite/dioctyl phthalate, graphite/mineral oil and nanocarbon/mineral oil paste electrodes were each then immersed in a deoxygenated aqueous borate buffer solution of pH 10.01 that contained 7.0 µM 4-phenoxyphenol and 0.1 M KCl. This was done under open circuit conditions, for 60 s. They were each then transferred to a deoxygenated aqueous borate buffer solution of pH 10.01 that only contained 0.1 M KCl, in which *oxidative* 100 mV s^{-1} scans were run between -0.40 V and +0.80 V (vs. SCE). Peaks corresponding to the reduction of the 4-phenoxyphenol oxidation product were again seen at peak potentials of -0.16 V, -0.15 V and -0.30 V (vs. SCE) on the graphite/dioctyl phthalate, graphite/mineral oil and nanocarbon/mineral oil pastes respectively. Typical responses obtained for the reduction of benzoquinone and the oxidation of 4-phenoxyphenol, on the graphite/dioctyl phthalate paste, are overlaid in Fig. 1. Given that the peaks due to the reduction of benzoquinone were observed at the same peak potentials as those due to the reduction of the 4-phenoxyphenol oxidation product, on each of the three pastes used, it was concluded

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that the mechanism followed in the 4-phenoxyphenol oxidation reaction was likely the one summarised in Scheme 1, where benzoquinone is the identified oxidation product.

3.1.2 Determining the Oxidation Products of 4-Phenol

The products of the phenol oxidation were next investigated. Given that known soluble products of the oxidation of phenol are oxidised 1,2-dihydroxybenzene (oxidised catechol) and oxidised 1,4-dihydroxybenzene[21], their electrochemistry was fingerprinted on the four paste electrodes. Each paste electrode was thus first immersed in a deoxygenated aqueous borate buffer solution of pH 10.01 that contained 1.0 mM catechol and 0.1 M KCl. This was done under open circuit conditions, for 60 s. The electrode was then transferred to a deoxygenated aqueous borate buffer solution of pH 10.01 that only contained 0.1 M KCl. 100 mV s^{-1} *reductive* scans were then run, between +0.80 V and -0.10 V (vs. SCE). Peaks due to the reduction of oxidised catechol (orthoquinone[25]) were seen at peak potentials of -0.010 V on all four pastes. An analogous experiment was then carried out with 1,4-dihydroxybenzene. Each paste electrode was immersed in a deoxygenated aqueous borate buffer solution of pH 10.01 that contained 1.0 mM 1,4-dihydroxybenzene and 0.1 M KCl. This was again done under open circuit conditions, for 60 s. Each electrode was then transferred to a deoxygenated aqueous borate buffer solution of pH 10.01 that only contained 0.1 M KCl, in which *reductive* 100 mV s^{-1} scans were run between +0.80 V and -0.35 V (vs. SCE). Peaks due to the reduction of oxidised 1,4-dihydroxybenzene (benzoquinone[26]) were seen at peak potentials of -0.15 V, -0.14 V, -0.20 V and -0.21 V (vs. SCE) on the graphite/dioctyl phthalate, graphite/mineral oil, nanocarbon/mineral oil and nanocarbon/dioctyl phthalate pastes respectively. Each paste electrode was finally immersed in a deoxygenated aqueous borate buffer solution of pH 10.01 that contained 40 µM phenol and 0.1 M KCl. This was once again done under open circuit conditions, for 90 s. The electrode was then transferred to a deoxygenated aqueous borate buffer solution of pH 10.01 that only contained 0.1 M KCl. 100 mV s^{-1} *oxidative* scans were run, between -0.10 V and +0.80 V (vs. SCE). Two peaks that can be attributed to the reduction of the phenol oxidation products were observed at peak potentials of +0.20 V and +0.11 V (vs. SCE), with the graphite/dioctyl phthalate and graphite/mineral oil pastes. Only one back peak is seen with the nanocarbon/dioctyl phthalate paste, at a peak potential of +0.11 V (vs. SCE), while no peaks are seen with the nanocarbon/mineral oil paste. Typical responses, obtained on

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the graphite/dioctyl phthalate paste, are overlaid in Fig. 2. Given that the peaks due to the reduction of both orthoquinone and benzoquinone were observed at more negative peak potentials than the phenol oxidation products, it was concluded that the mechanism followed in the phenol oxidation reaction was the one summarised in Scheme 2, where polymeric products are assumed to be formed upon the oxidation of phenol, under the conditions identified.

3.2 Obtaining Analytical Limits of Detection for Phenol, 4-Phenoxyphenol and 4-Methoxyphenol

3.2.1 Testing the Chosen Paste in Wide Phenol Concentration Ranges

Focussing on the optimum graphite/dioctyl phthalate paste electrode, the sensor was then tested with a wide concentration range of phenol. The aim was not only to obtain an analytical limit of detection but to also investigate how high a phenol concentration could be detected through cyclic voltammetry, a task often limited in other electroanalyses due to rapid electrode surface fouling, especially with solid electrodes[20-22].

An analogous experiment as in Section 3.1.2 was thus carried out. The graphite/dioctyl phthalate paste electrode was immersed in a deoxygenated aqueous borate buffer solution of pH 10.01 that contained a known amount of phenol and 0.1 M KCl as the supporting electrolyte. This was again done under open circuit conditions, but this time the immersion time was fixed at 90 s, the previously identified equilibration time of this electrode with phenol, while the concentration of the source phenol solution was varied between 2.5 μM and 60 mM. Oxidative 100 mV s^{-1} scans were run in a deoxygenated aqueous borate buffer solution of pH 10.01, which contained 0.1 M KCl, in the potential range between -0.10 V and +0.70 V (vs. SCE); peaks due to the oxidation of phenol were seen at a peak potential of +0.52 V (vs. SCE).

The results are presented in Fig. 3, where the expected increase of the peak current with increasing phenol concentration is clearly seen up to phenol concentrations as high as 10 mM (Fig. 3 inlay); a plateau is reached when the phenol concentration is further increased. It was also observed that for the detection of concentrations lower than 7.0 μM the phenol solution had to be stirred and that, for up to 1.0 mM concentrations of phenol it was not

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necessary to refresh the paste before every scan to obtain reproducible results; renewing the surface only became important when larger phenol concentrations were used.

The above results are consistent with the paste being loaded with more and more phenol as the phenol concentration is increased and with phenol concentrations of or higher than 16 mM being large enough for their detection to be limited by the ability of the paste to "store" more of the analyte. A *practical* lower limit of detection of 2.5 µM was determined, with the slope of the calibration curve giving a value for the sensitivity of 1.46 µA mM^{-1}. With regards to surface renewal, the observations indicate that the regularly observed problem of electrode surface fouling[20-22], known to increase with increasing phenol concentrations[22], is not present for phenol concentrations of 1.0 mM or lower; this gives the developed sensor a great practical advantage.

Table 1 summarises the limits of detection for phenol found in literature. As expected, when electrochemical methods are used to detect phenol, the electrodes are often modified; the most commonly chosen modifier is tyrosinase, due to the low limits of detection it can ensure. However, the reported values are *theoretical* limits of detection calculated from high concentration data that typically correspond to limits of detection where signals cannot be seen. It is in this context that the *practical* limit of detection of 2.5 µM here obtained is impressive, as it represents an observed signal.

3.2.2 Obtaining an Analytical Limit of Detection for 4-Phenoxyphenol and 4-Methoxyphenol

Analytical limits of detection were also obtained for the previously investigated 4-phenoxyphenol as well as for 4-methoxyphenol. The best suited paste electrode – the graphite/dioctyl phthalate one – acted as the working electrode. In the case of 4-phenoxyphenol, the previously determined 60 s equilibration time was used. The electrode was immersed in a deoxygenated aqueous borate buffer solution of pH 10.01 that contained a known amount of the target and 0.1 M KCl as the supporting electrolyte. Oxidative 100 mV s^{-1} scans were then carried out a in a deoxygenated aqueous borate buffer solution of pH 10.01, which contained 0.1 M KCl, in the potential range between 0.0 V and + 0.60 V (vs. SCE). A signal corresponding to the oxidation of 4-phenoxyphenol to benzoquinone was seen at a peak potential of +0.43 V (vs. SCE). This experiment was carried out with 4-phenoxyphenol solutions of concentrations of 2.5 to 40 µM.

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In the case of 4-methoxyphenol, it was assumed that its behaviour would be similar to phenol and 4-phenoxyphenol and that the longer 90 s equilibration time determined for phenol could hence be used. The electrode was immersed in a deoxygenated aqueous borate buffer solution of pH 10.01 that contained a known amount of 4-methoxyphenol and 0.1 M KCl as the supporting electrolyte. It was then transferred into a deoxygenated aqueous borate buffer solution of pH 10.01, which only contained 0.1 M KCl, in which 100 mV s^{-1} oxidative scans were run, between –0.30 V and +0.50 V (vs. SCE). The peak due to the oxidation of 4-methoxyphenol to benzoquinone was observed at a peak potential of +0.30 V (vs. SCE). Here the target concentration was varied between 5.0 and 40 µM.

Starting from 4-phenoxyphenol, Fig. 4 shows the obtained results; as expected, the signal increased with increasing target concentration (Fig. 4 inlay). Similarly for 4-methoxyphenol, the results are presented in Fig. 5, where the expected dependency of the peak height on concentration is shown in the inlay. The analytical lower limits of detection were thus determined as being 2.5 µM and 5.0 µM for 4-phenoxyphenol and 4-methoxyphenol respectively. Values for the sensitivity were also extracted from the obtained calibration curves; these were 72.1 nA μM^{-1} and 42.0 nA μM^{-1} for 4-phenoxyphenol and 4-methoxyphenol respectively.

3.3 Using Square Wave Voltammetry for the Simultaneous Detection of Phenol, 4-Phenoxyphenol and 4-Methoxyphenol

To address the issue of simultaneous detection of the three phenols, one further experiment was carried out in which a borate buffer solution of pH 10.01 was made that contained the three compounds (110 µM phenol, 110 µM 4-phenoxyphenol and 150 µM 4-methoxyphenol) as well as 0.1 M KCl. This was, as previously, deoxygenated and used to equilibrate the graphite/dioctyl phthalate paste with the three targets; an equilibration time of 90 s was used. The electrode was then transferred into a deoxygenated borate buffer solution of the same pH that only contained supporting electrolyte (0.1 M KCl) and in which square wave voltammetric responses were obtained. Firstly, the square wave parameters were optimised. The frequency, as well as the step potential, were altered to achieve the highest peak current, while the amplitude was varied to achieve as best a peak separation

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as possible. The optimum values for each parameter were determined as being 100 Hz for the frequency, 25 mV for the amplitude and 10 mV for the step potential.

The square wave voltammogram that was recorded using the optimised parameters is shown in Fig. 6, where three peaks corresponding to the oxidation of 4-methoxyphenol, 4-phenoxyphenol and phenol can be seen at peak potentials of +0.28 V, +0.38 V and +0.53 V (vs. SCE) respectively. Even though the peak due to the oxidation of phenol is more clearly separated from the other two, there is some overlap with 4-phenoxyphenol response. At the same time, the responses of 4-phenoxyphenol and 4-methoxyphenol overlap greatly. Deconvolution of the square wave voltammograms was thus required, in order to be able to quantify the amount of each phenol. This was done using the Peak Analyser Function of OriginPro 9, where the voltammogram was modelled as a sum of three Gaussian functions. The sum of the Gaussian functions and the three deconvoluted curves are overlaid with the experimental data in Fig. 6.

4. Conclusions

A sensitive method able to measure high target concentrations for the separate *and* simultaneous detection of phenol, 4-phenoxyphenol and 4-methoxyphenol has been developed. The procedure relies on the use of an optimum carbon paste electrode, made of graphite powder and dioctyl phthalate. Immersion of the paste electrode to each aqueous phenol solution, for the determined equilibration times, allows the target compound to transfer from the source solution into the paste and the equilibration of the paste with the analyte. The oxidation signal of each phenol is used as the detection signal; the peak potentials were +0.60, +0.40 and +0.30 V (vs. SCE) for phenol, 4-phenoxyphenol and 4-methoxyphenol, respectively. We label the approach “absorptive stripping voltammetry”.

By carrying out pre-concentration experiments and fingerprinting the reduction of benzoquinone and orthoquinone, it was concluded that 4-phenoxyphenol undergoes a 2-electron 2-proton reduction to form benzoquinone. The oxidation of phenol was found to result in the likely formation of polymeric products and not the monomers of oxidised catechol or 1,4-dihydroxybenzene.

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Through calibration of the sensor in 2.5 µM to 80 mM phenol solutions, 2.5 – 40 µM 4-phenoxyphenol solutions and 5.0 – 40 µM 4-methoxyphenol solutions, analytical lower limits of detection (LODs) of 2.5 µM, 2.5 µM and 5.0 µM were obtained for phenol, 4-phenoxyphenol and 4-methoxyphenol respectively. As Table 1 clearly demonstrates, the *practical* limit of detection of 2.5 µM, here measured from an *observed* signal, is close to values found in the literature, with tyrosinase-based biosensors seemingly being able to detect even lower phenol concentrations. However, the values in Table 1 correspond to *theoretical* limits of detection that are *calculated*, usually by extrapolating the calibration curve and using the equation $\mathrm{LOD} = 3\sigma/s$, where σ is the measured standard deviation of the signal in the absence of the target and s is the sensitivity of the sensor. The *practical* (measured) limit of detection of phenol of our new sensor is thus usefully low given that the carbon paste electrode was unmodified. Importantly, it was possible to determine phenol concentrations of up to 1.0 mM, without the measurements being compromised through electrode surface fouling, and concentrations of up to 10 mM, without being limited by the uptake of the analyte.

Square wave voltammetry enabled the study of systems containing all three phenol compounds. Through modelling of the experimental data as a sum of three Gaussian functions that can then be deconvoluted, simultaneous quantification of the three targets can be achieved.

This is the first time that such low phenol, 4-phenoxyphenol and 4-methoxyphenol concentrations have been detected using an unmodified surface. It is the sensitivity of this method, provided by absorptive pre-concentration, which leads to the term “absorptive stripping voltammetry”, by analogy to “adsorptive stripping voltammetry”. This work opens up further studies into possible ways of exploiting carbon paste electrodes[32].

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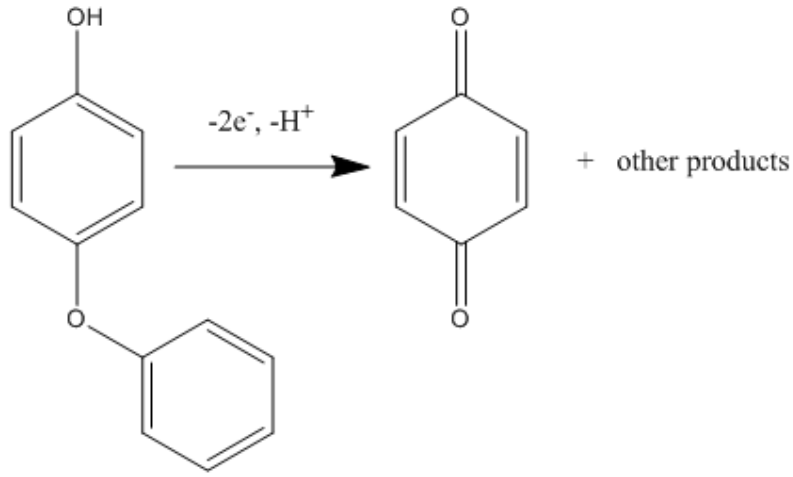
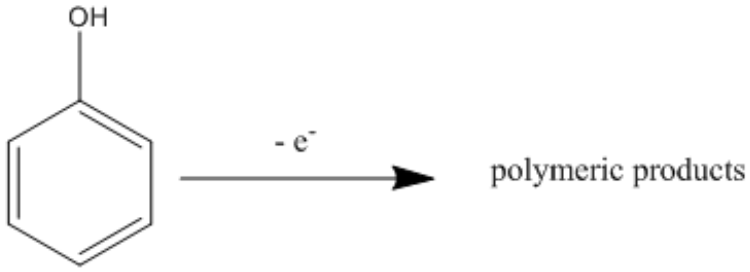
Schemes



Scheme 1: The oxidation of 4-phenoxyphenol.



Scheme 2: The oxidation of phenol.

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Figures

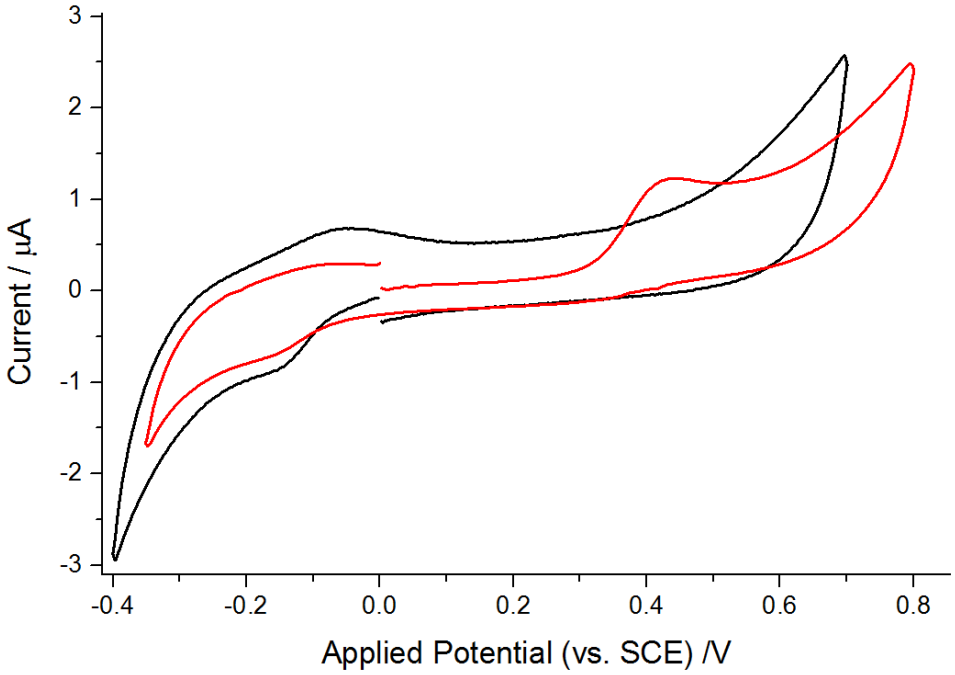

Fig. 1: The fingerprinting of the reduction of benzoquinone on the graphite/dioctyl phthalate CPE. Both 100 mV s^{-1} scans were obtained in deoxygenated BBS solutions (0.1 M KCl, pH=10.01, 298 K) after immersing the CPE in BBS solutions that also contained 35 µM benzoquinone (black line) and 7 µM 4-phenoxyphenol (red line), for 30 s, respectively. The peak corresponding to the reduction of benzoquinone, observed at -0.16 V (vs. SCE), is seen at the same potential as the peak that is due to the reduction of the 4-phenoxyphenol oxidation product.

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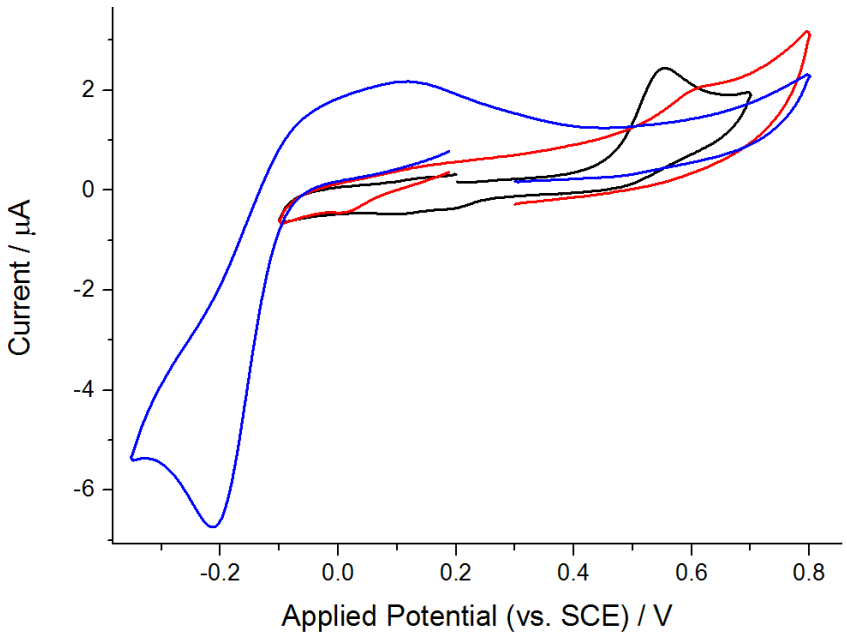

Fig. 2: The fingerprinting of the reduction of 1,2-dihydroxybenzene (catechol) and 1,4-dihydroxybenzene on the graphite/dioctyl phthalate CPE. The three 100 mV s^{-1} scans were obtained in deoxygenated BBS solutions (0.1 M KCl, pH=10.01, 298 K) after immersing the CPE in identical BBS solutions that contained 40 µM phenol (black), 1.0 mM catechol (red) and 1.0 mM 1,4-dihydroxybenzene (blue) respectively for 60 s. The peak corresponding to the reduction of catechol was observed at -0.01 V (vs. SCE), while that corresponding to the reduction of 1,4-dihydroxybenzene as seen at -0.15 V (vs. SCE). Both these peaks were at the more negative potentials compared to the peaks that can be attributed to the reduction of the phenol oxidation product, seen at +0.20 V and +0.11 V. Polymeric products were thus assumed to be formed upon the oxidation of phenol.

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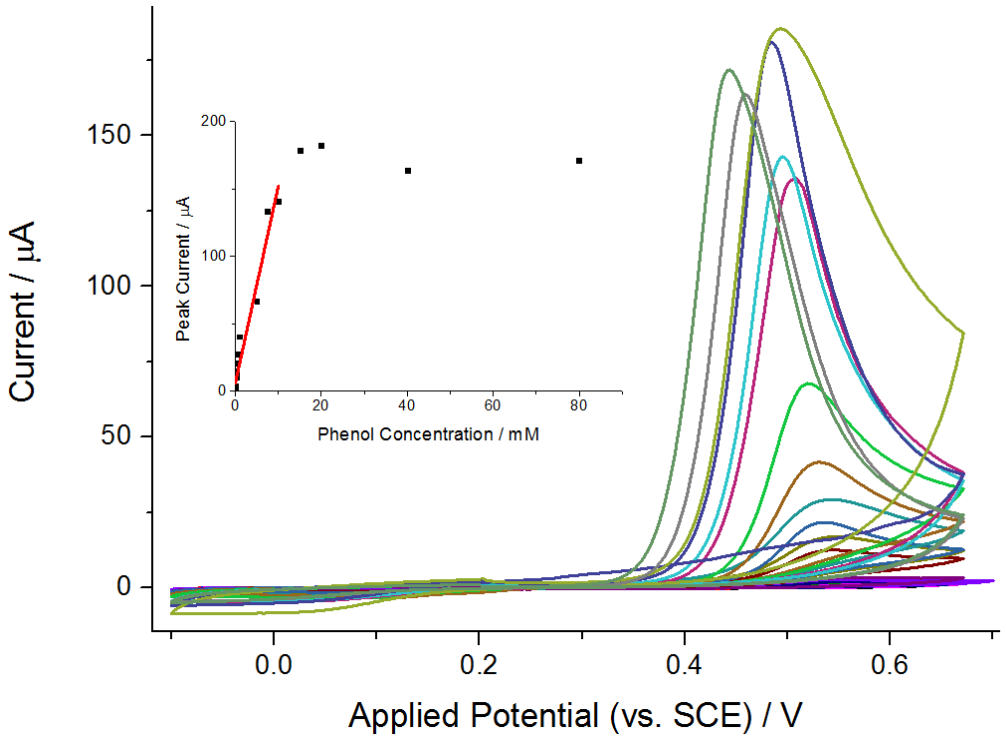

Fig. 3: Testing the graphite/ dioctyl phthalate paste in a wide concentration range of phenol (2.5 µM to 80 mM). Main graph: The 100 mV s^{-1} voltammetric responses for the oxidation of phenol on that paste. The scans were obtained in a deoxygenated BBS solution (0.1 M KCl, pH=10.01, 298 K), after immersing the electrode in an identical solution that also contained 2.5 µM to 80 mM phenol for 90 s. Inlay: The expected linear increase of the peak current with increasing phenol concentration. The lower and higher practical limits of detection were determined as being 2.5 µM and 16 mM respectively; at concentrations higher than 16 mM, the detection is limited by the ability of the paste to "store" more of the target. The slope of the calibration curve gave a sensitivity value of 1.46 µA mM^{-1}.

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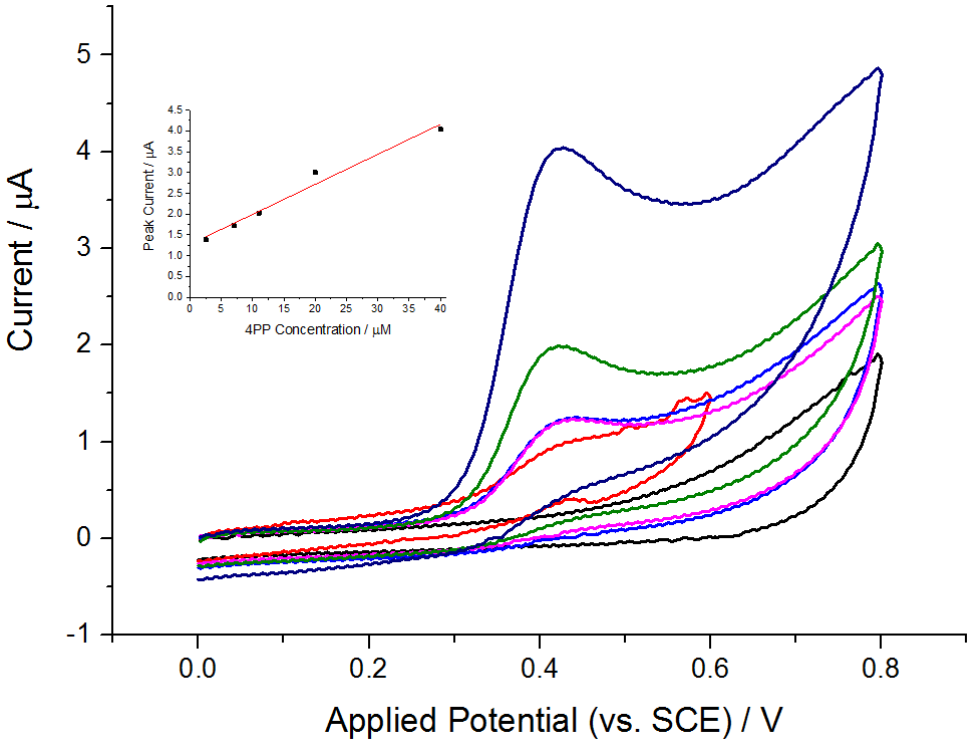

Fig.4: Testing the graphite/ dioctyl phthalate paste in a variety of 4-phenoxyphenol concentrations (2.5 to 40 µM). Main graph: The 100 mV s^{-1} voltammetric responses for the oxidation of 4-phenoxyphenol on that paste. The scans were obtained in a deoxygenated BBS solution (0.1 M KCl, pH=10.01, 298 K), after immersing the electrode in an identical solution that also contained 2.5 to 40 µM 4-phenoxyphenol for 60 s (black: 0.0 µM, red: 2.5 µM, blue: 5.0 µM, magenta: 7.0 µM, olive: 10 µM, dark blue: 40 µM). Inlay: The expected linear increase of the peak current with increasing 4-phenoxyphenol concentration. The lower practical limit of detection was determined as being 2.5 µM.

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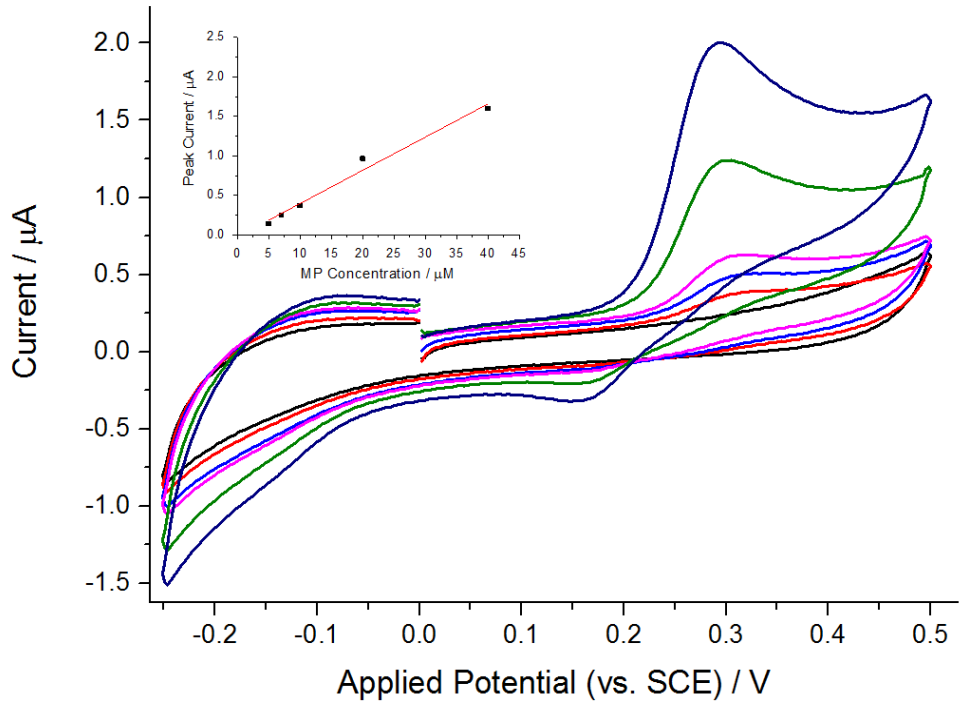

Fig.5: Testing the graphite/ dioctyl phthalate paste in a variety of 4-methoxyphenol concentrations (5.0 to 40 µM). Main graph: The 100 mV s^{-1} voltammetric responses for the oxidation of 4-methoxyphenol on that paste. The scans were obtained in a deoxygenated BBS solution (0.1 M KCl, pH=10.01, 298 K), after immersing the electrode in an identical solution that also contained 5.0 to 40 µM 4-methoxyphenol for 60 s (black: 0.0 µM, red: 5.0 µM, blue: 7.0 µM, magenta: 10 µM, olive: 20 µM, dark blue: 40 µM). Inlay: The expected linear increase of the peak current with increasing 4-phenoxyphenol concentration. The lower practical limit of detection was determined as being 2.5 µM.

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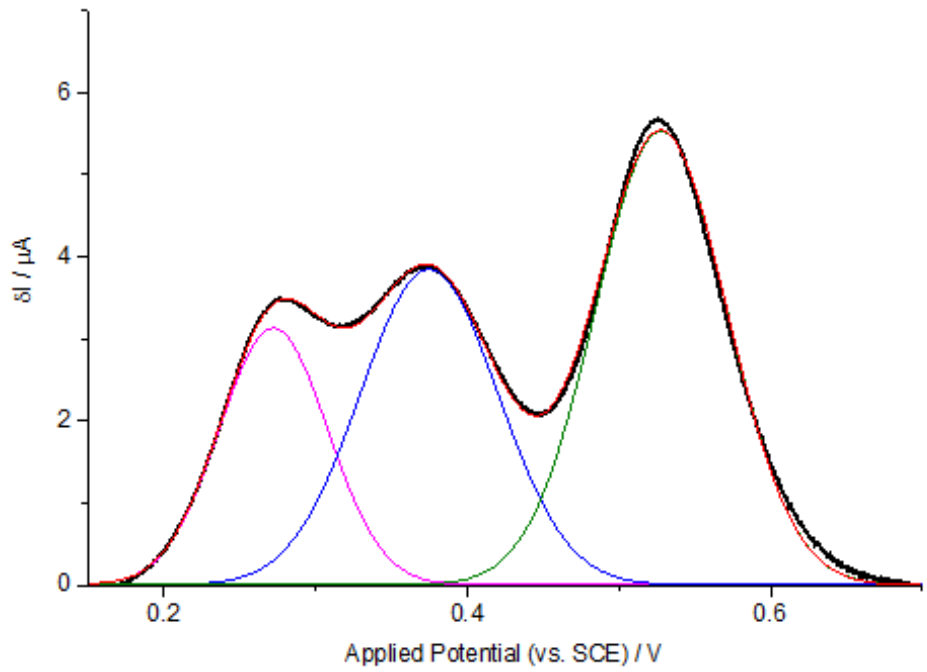

Fig. 6: Square wave voltammograms (frequency: 100 Hz, amplitude: 25 mV, step potential: 10 mV) for the oxidation of 4-phenoxyphenol and phenol, seen at +0.28 V, +0.38 V and +0.53 V (vs. SCE) respectively, on the graphite/dioctyl phthalate paste electrode (black line: experimental data, red line: sum of the three Gaussian functions, olive, blue and magenta lines: the deconvoluted curves). The measurement was obtained in a deoxygenated BBS (0.1 M KCl, pH=10.01, 298 K), after immersing the electrode in an identical solution that also contained 110 μM phenol, 110 μM 4-phenoxyphenol and 150 μM 4-methoxyphenol, for 90 s.

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Tables:

Theoretical Limit of Detection / µM	Method Used	Reference
0.006	ECD: Tyrosinase-Colloidal Gold modified CPE	14
0.070	ECD: Tyrosinase-Au NP-modified BDD electrode	27
1.06	HPLC + ECD (porous graphite electrodes)	1
1.10	ECD: MWCNT-DTDAB-tyrosinase modified CPE	3
1.35	CLSM + ECD (tyrosinase-MWCNTs modified carbon SPEs)	28
2.00	IL-film modified Pt wires	29
7.10	ECD: CPE modified with pAp and MWCNTs	2
10.6	Capillary LC + ECD (glassy carbon electrodes)	30
85.0	ECD: H_2 plasma-pre-treated BDND electrodes	31

Table 1: Literature values for phenol limits of detection. ECD: Electrochemical Detection, CPE: Carbon Paste Electrode, NP: Nanoparticle, BDD electrode: Boron Doped Diamond electrode, HPLC: High Performance Liquid Chromatography, MWCNT: Multi-Walled Carbon Nanotube, DTDAB: dimethylditetradecylammonium bromide, CLSM: Confocal Laser Scanning Microscopy, SPE: Screen Printed Electrode, IL: Ionic Liquid, pAP: p-Aminophenol, GO-Au-NP-tyrosinase: Graphene-Oxide-Gold-Nanoparticle film with immobilised tyrosinase, LC: Liquid Chromatography, BDND electrodes: Boron Doped Nanocrystalline Diamond electrodes.

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