

DETERMINATION OF GUAIACOL AT A CARBON PASTE ELECTRODE USING CATHODIC STRIPPING VOLTAMMETRY

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Abstract

Guaiacol is an undesired compound in some natural products, mainly because of its aroma. In this work, the voltammetric determination of guaiacol by oxidation at a carbon paste electrode following a cathodic accumulation was first tried, with no success, because there was no accumulation of the compound. On the contrary, it was found that there is accumulation of a product formed after oxidation of guaiacol, probably a dimeric product, that can be determined by reduction. Using an accumulation time of 5 minutes and a potential at which guaiacol is being oxidized, a determination limit of 2 µg/L was obtained by cathodic stripping voltammetry, a value about ten times lower than that obtained in the anodic determination. The method was applied to the determination of guaiacol in cork stoppers.

Keywords: guaiacol; accumulation; cathodic stripping voltammetry

Introduction

Guaiacol is a compound having a characteristic medicinal, smoky and phenolic aroma. The presence of this compound in cork stoppers can influence in an undesired way the organoleptic properties of wines. The level of guaiacol in cork material has been related with several factors, which include formation by lignin breakdown, the presence and formation of vanillin and the presence and activity of microorganisms capable of degrading vanillin to guaiacol. Some extraction of cork components by the wine would be expected and by that reason, guaiacol has been associated, among other compounds, with the problem of "cork taste" in wine. Its aroma threshold in dry white wine has been appointed to be 20 µg/L (1).

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The methodology normally used in the determination of guaiacol is gas chromatography with selective mass detection (2). Voltammetric methods have also been proposed for the determination of phenolic compounds, based on their oxidation at the carbon paste electrode. Cañete et al. (3) have been able to determine phenol, guaiacol and 2,4-dichlorophenol simultaneously, using a flow injection/cyclic voltammetric method. More recently, phenols were determined in sea water using liquid chromatography with electrochemical detection, after enrichment by using a C-18 solid-phase extraction column (4).

The accumulation of several organic compounds at carbon paste electrodes has been used in their determination by anodic stripping voltammetry (5, 6). A typical example of application was reported by Wang and Freiha (7), who have performed the voltammetric determination of butylated hydroxyanisole, after a pre-concentration step in open circuit conditions.

In acidic conditions, the oxidation of phenols is irreversible (8, 9), due to the fast hydrolysis of the oxidation products. In neutral or basic conditions, ionized guaiacol undergoes a reversible oxidation with eventual dimerization of the product of the electrochemical reaction (10).

In this work, it was found that, although guaiacol does not accumulate at the carbon paste electrode, there is accumulation of a product of its oxidation, probably a dimer, that can be reduced at the electrode. Consequently, an increase in sensitivity can be obtained if accumulation is performed at a sufficiently high potential to oxidize guaiacol, followed by the cathodic stripping voltammetry of the accumulated product.

Experimental

Apparatus

The working electrode material was carbon paste with Nujol as the pasting liquid, purchased from Metrohm. The paste was packed into the end of a Metrohm glass support (inner diameter, 8 mm). A fresh carbon paste was used at least each day. The working electrode, the Ag/AgCl (3M KCl) reference electrode and the platinum wire auxiliary electrode were introduced through the holes of the cell cover. A magnetic stirrer and a bar provided the stirring during accumulation step. Differential-pulse voltammograms were recorded with a Metrohm equipment (detector E611 and scanner E612) and a Houston Omnigraphic 2000 recorder. Instrumental settings were: 10mV/s, scan rate; 50 mV, amplitude; 0.8 s, time between pulses.

Reagents and solutions

All chemicals used were of analytical grade. Deionized and distilled water was used for preparation of solutions. Stock solution of guaiacol was prepared from the commercial product obtained from Aldrich. Buffer solutions of pH \approx 1 (hydrochloric acid, 0.1M), pH \approx 5 (acetic acid/sodium acetate, 0.1M), pH \approx 7 (sodium dihydrogen phosphate/di-sodium hydrogen phosphate, 0.1M), pH \approx 10 (ammonia/ammonium chloride, 0.1M) and pH \approx 13 (sodium hydroxide, 0.1M) were prepared using reagents obtained from Merck.

Procedure

In the accumulation step, the carbon paste electrode was immersed in a stirred (500 rpm) 25 mL sample solution for a given time period (usually 5 minutes). After this, the stirring was stopped and the differential-pulse cathodic stripping voltammetric determination was made, scanning the potential between +600 mV and -100 mV. At the end, the electrode was held at +1.4 V for 1 minute in a blank solution, consisting of a buffer solution (usually phosphate buffer), to clean it from any remaining adsorbable species. See discussion for specific details.

Results and Discussion

The use of carbon paste electrode is difficult as the determination often depends, among other factors, on the efficient cleaning of the electrode between experiments, in order to obtain reproducible results. A problem that also appeared in the determination of guaiacol. This situation was not unexpected as it is known that phenol is an effective electrode poison because it forms, on oxidation, an insoluble product on the surface (11). Three different procedures were tried to solve the problem, based on adopted approaches suggested in literature. A first strategy consisted in treating the electrode with a solution of 0.1 M sodium hydroxide, at -300 mV; apparently the electrode was cleaned, since there was no signal for the blank, but the sensitivity was low. Renewing the surface of the electrode mechanically was another methodology; results were not good, because there was no reproducibility, with a considerable waste of carbon paste. Finally, the anodic activation of the electrode at a very positive potential (+1.4 V) was tried (12), with success, as no signals were obtained with the blanks, there was an increase in sensitivity and results were

reproducible (see Figure 1); 4 successive voltammetric measurements on a 30 μ g/L guaiacol solution resulted in a peak current of 195 ± 5 nA. This further cleaning can be explained assuming that the electrochemical oxidation of the electrode presumably produces a more hydrophilic surface state, which can promote organic layer displacement by water (13). Hence, this cleaning procedure was adopted in the following work.

With a carbon paste electrode prepared from ultra-pure carbon powder and silicone grease, Canete et al. (3) have noticed the existence of adsorption of the phenolic compounds on the electrode surface. They also referred that the pH had a significant influence on the adsorption on the electrode: at pH values lower than pKa of guaiacol the adsorption was instantaneous, while at pH values above pKa, adsorption was not significant.

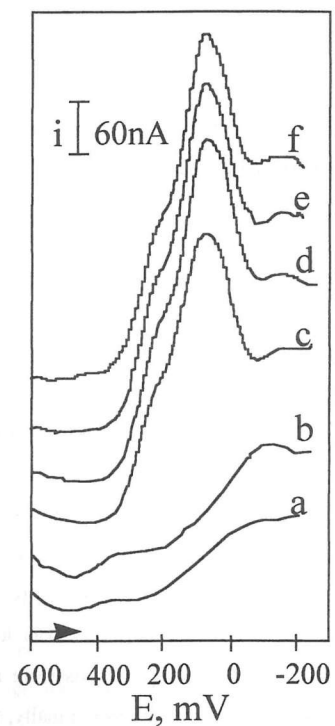


FIG. 1 - Efficiency of cleaning of the electrode using anodic activation. Cathodic stripping voltammograms, in phosphate buffer (0.1M, pH=7.4), following anodic activation of the carbon paste electrode: a) blank; c), d), e) and f) repeated analysis of a 30 μ g/L guaiacol solution; b) blank, after the repeated analysis of the guaiacol solution.

TABLE 1 - Characteristics of the voltammetric peaks obtained in the voltammetric determination of 350 µg/L of guaiacol at different pH

pH	Oxidation peak			Reduction peak ^{a)}		
	E _p (V)	-i _{p1} ^{b)} (nA)	-i _{p2} ^{c)} (nA)	E _p (V)	i _{p1} ^{b)} (nA)	i _{p2} ^{c)} (nA)
1	0.79	38	83	0.52	60	71
5	0.60	97	98	0.25	143	462
7	0.48	262	262	0.11	252	925
10	0.37	135	135	0.00	360	966
13	0.30	128	128	-0.07	20	20

^{a)} guaiacol is oxidized at the accumulation potential.
^{b)} no accumulation; ^{c)} 1 minute of accumulation.

Irrespective of the pH, in this work we did not find any signs of significant adsorption of guaiacol at the electrode. On other hand, there was accumulation of a compound formed by oxidation of guaiacol. The effect of pH on the anodic determination and on the cathodic determination of guaiacol can be seen in table 1. The cathodic signal can be explained assuming that, after oxidation of guaiacol, a dimer is formed which can be adsorbed at the carbon paste electrode and reduced at a more negative potential. As the sensitivity of the determination is quite similar in a broad region of pH (the signal only reduces in very acid or alkaline conditions), it was decided to adopt a pH=7.4, the same value that was used by Wang and Freiha (7).

In Figures 2 and 3, some voltammograms are illustrating the influence of accumulation time on the voltammetric signal obtained in the anodic and in the cathodic determination of guaiacol, respectively.

The accumulation potential was another parameter studied. The best accumulation was obtained at +600 mV, as can be seen in figure 4; the response is drastically reduced for more cathodic accumulation potentials because guaiacol is no more oxidized; the peak current also decreases for more anodic accumulation potentials, probably because guaiacol is further oxidized, in an irreversible way.

Figure 5 represents a calibration curve for guaiacol, showing the proportional relation between reduction peak current and the concentration of this compound in bulk solution. The

analysis was performed using solutions with concentrations of guaiacol ranging from 2 to 60 µg/L. A linear regression was obtained, $i(\text{nA}) = 6.06 + 5.02C(\mu\text{g/L})$, with a correlation coefficient of 0.985. Using an accumulation period of 5 minutes, a determination limit of 2 µg/L was obtained for the cathodic stripping voltammetric determination of guaiacol, a value about ten times lower than that obtained using the normal anodic determination.

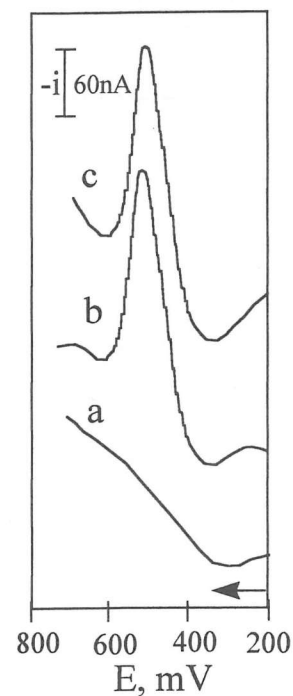


FIG. 2 - Anodic voltammograms for a blank solution (a) and for a 350 µg/L guaiacol solution (b and c) in phosphate buffer (0.1M, pH=7.4), at different accumulation periods: a and b) 0 min; c) 5 min. Accumulation potential, 0.2V; Scanning between 0.2 and 0.8V.

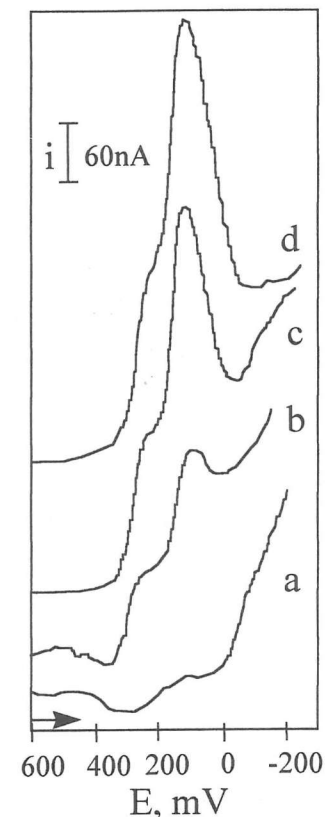


FIG. 3 - Cathodic stripping voltammograms for a 60 µg/L guaiacol solution in phosphate buffer (0.1M, pH=7.4), at different accumulation periods: a) 0 min; b) 1 min; c) 3 min; d) 5 min.

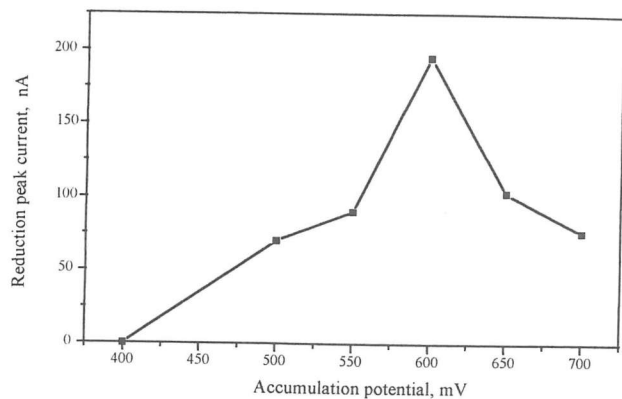


FIG. 4 - Effect of accumulation potential on the reduction peak current for a 30 µg/L guaiacol solution in phosphate buffer (0.1M, pH=7.4). Accumulation time=5 min.

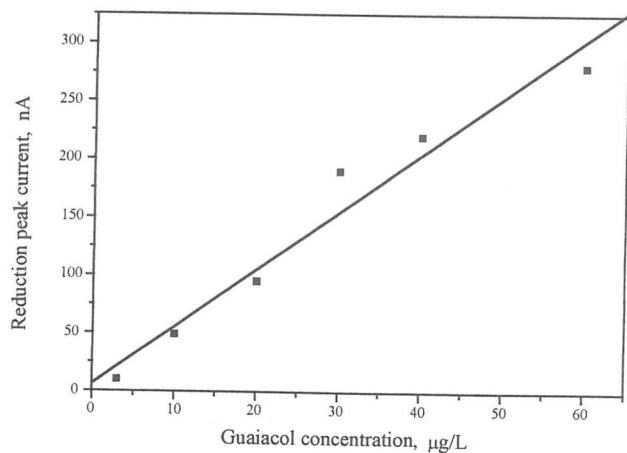


FIG. 5 - Calibration plot for guaiacol, using cathodic stripping voltammetry. Accumulation potential=600 mV; Accumulation time=5 min.

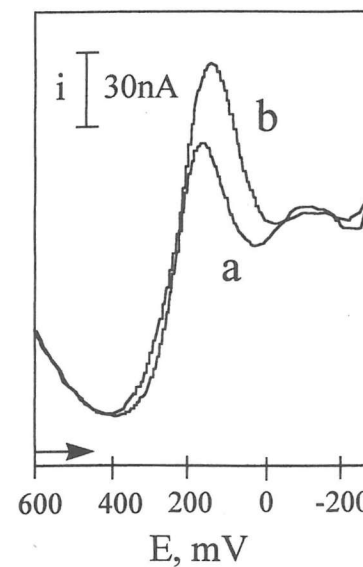


FIG. 6 - Voltammetric determination of guaiacol in cork stoppers. Voltammograms obtained for: a) analysis of cork stoppers extract; b) Standard addition of 30 µg/L of guaiacol. Accumulation potential=0.6V; Accumulation time=1 minute.

Determination of Guaiacol in cork stoppers

The methodology developed was applied to the determination of guaiacol in cork stoppers, using an extraction procedure with absolute ethanol and a dilution with redistilled water (2), but no response was found in the determination. Assuming that absence of signal was related with the presence of alcohol - which affected the accumulation process at the carbon paste electrode -, another procedure for the extraction of guaiacol from the cork stoppers was tried, using a non-ethanolic phosphate buffer. 0.3g of cork stoppers were cut in small pieces and immersed in 25mL of 0.1M phosphate buffer solution (pH=7.4). The solution was stirred during 30 minutes. After that, the extract was filtered and then analysed. In these conditions, a voltammetric peak was obtained at a potential similar to that of guaiacol, as can be seen in Fig. 6. As other phenolic compounds can be present in cork (1), it is possible that they are interfering in the determination of guaiacol, a situation to clarify in the future using HPLC, for instance. If we assume that the peak is due to guaiacol only, the concentration of compound in the solution obtained using the method of standard additions (table 2) is about 72 µg/L, corresponding to 6 µg/g in cork stoppers.

TABLE 2 - Voltammetric determination of guaiacol in cork stoppers using the method of standard additions

addition of guaiacol ($\mu\text{g/L}$)	0	30	50
$i(\text{nA})$	150	195	250

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