Feature Article

Determination of Disulfiram by Adsorptive Stripping Voltammetry at Gold Disk Microelectrodes

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Received: June 27, 2001
Final version: October 11, 2001

Abstract
Gold disk microelectrodes (AuMEs, 50 μm ∅) have been used for the determination of the fungicide disulfiram (DSF) at low concentration levels by differential pulse adsorptive stripping voltammetry (dp-AdSV). The AuMEs were fabricated in the laboratory and characterized by scanning electron microscopy and cyclic voltammetry. The AuME was pretreated daily by polishing with 3-μm diamond powder for 60 s, and by applying successively potentials of -0.4, -0.8, -1.0, -1.2 and -1.5 V for 30 s each in 0.1 mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ (pH 6.0). In between measurements, the application of a potential of -1.5 V for 30 s was only necessary. The DSF adsorption on the AuME surface allows its determination at trace levels by dp-AdSV using low supporting electrolyte concentrations (3.0 mmol L^{-1}) with an accumulation time of 120 s, a pulse amplitude of 50 mV, and a scan rate of 50 mV s^{-1}. A detection limit of 6.3×10^{-8} mol L^{-1} and a RSD of 1.3% at a 5.0×10^{-7} mol L^{-1} DSF concentration level ($n = 10$) were obtained with a two-electrode system and no stirring during the deposition step. The effect of the presence of several potential interferences on the DSF stripping signal has been tested. The developed method has been applied to the determination of DSF in spiked pea seeds with good results.

Keywords: Disulfiram, Gold disk microelectrode, Differential pulse adsorptive stripping voltammetry

1. Introduction

In the last few years the use of microelectrodes for analytical purposes has been increasing gradually due to their advantages as compared with conventional electrodes. Among these, the high current densities obtained due to the nonlinear diffusion, the minimal *iR* and capacitance effects which increase the signal-to-noise ratio, their rapid responses, and the fact that the signals are almost unaffected by convection, can be pointed out. These advantageous properties have been exploited for working in organic solvents of low dielectric constant [1], in the study of rapid electron transfer reactions [2], and coupled reactions [3], in flow systems where microelectrodes are not affected by flow rate variations and can be used with small sample volumes [4], for in vivo measurements in tissues or biological fluids [5], and also to improve the analytical characteristics of stripping methods [6].

The great number and variety of applications of stripping voltammetry in different fields due, above all, to its great sensitivity, justifies the continuous development and interest it rises. In this context, the use of microelectrodes in stripping voltammetry implies a decrease in the deposition time [7, 8], together with work in unstirred solutions during this step, thus increasing the measurements precision [9], and the possibility to work with low sample volumes [10]. Pt, Au and Hg microelectrodes have been used in stripping analysis for the determination of trace metals [11–13] while only carbon fiber microelectrodes have been employed for the determination of organic compounds [14, 15].

In this article, the possibility of using gold disk microelectrodes (AuMEs) for the determination of the fungicide disulfiram (DSF), at low concentration levels by differential pulse adsorption stripping voltammetry (dp-AdSV) is evaluated. Home-made AuMEs were characterized and the DSF oxidation response was studied in order to explore its adsorptive nature. DSF, tetraethylthiuram disulfide, constitutes the main component of some pesticides used in agriculture, and it is also used as antioxidant in polymers' fabrication processes [16], as well as in alcoholism treatments [17]. When DSF is employed in agriculture, during fumigation processes, it can penetrate the skin or the respiratory tract with negative effects on the free sulfhydryl groups of hemoglobin, which cause alterations at a cellular level [18]. The maximum dithiocarbamate concentration allowed by the FAO/WHO Committee ranges within 0.1 mg kg^{-1} in potatoes, and 5 mg kg^{-1} in cereals, while in the European Union the limits are 2–7 mg kg^{-1}, given as carbon disulfide [19]. Although chromatographic methods are the most widely employed in the determination of DSF and other dithiocarbamates [20–23], DSF, like other thiocompounds, is capable of adsorption and oxidation on several electrode surfaces. Thus, DSF has been determined on a graphite-Teflon composite electrode by AdSV with a detection limit of 5.4×10^{-8} mol L^{-1} [24].

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2. Experimental

2.1. Apparatus

Electrochemical measurements were performed on a BAS 100B electrochemical analyzer coupled to a BAS C2 EF-1080 cell stand and using a BAS PA-1-MF-2200-3 preamplifier. A P-Selecta Ultrasons ultrasonic bath, a Griffin flask shaker and a P-Selecta Meditronic centrifuge were also used.

2.2. Electrodes and Electrochemical Cell

Gold disk microelectrodes (AuMEs) fabricated in our lab from single gold fibers (Goodfellow, 50 μm nominal diameter), as well as a Metrohm 6.1204.020 conventional gold disk electrode (AuE) (3-mm diameter) were used as working electrodes, the latter for comparison purposes. A BAS MF-2063 Ag/AgCl and a Metrohm 6.0728.000 Ag/AgCl/3 mol L^{-1} KCl were used as reference electrodes with the AuME and the AuE, respectively. In those cases where a three-electrode configuration was employed, a BAS MW-1032 Pt wire was used as the counter electrode. A BAS VC-2 10-mL electrochemical cell, and a Metrohm 6.1415.0210 vessel were also used.

2.3. Reagents and Solutions

Stock 1.0×10^{-3} mol L^{-1} solutions in methanol of disulfiram, ziram (zinc *N*,*N*-diethyldithiocarbamate), diram (sodium *N*,*N*-dimethyldithiocarbamate), and thiram (tetramethylthiuram disulfide) (Aldrich) were prepared by weighing. Stock solutions of 1.0×10^{-2} mol L^{-1} phenol (Scharlab) in methanol and of 1.0×10^{-3} mol L^{-1} ferrocene (Fluka) in acetonitrile were also used. More dilute standards were prepared in deionized water.

Buffer solutions of 0.2 mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ and HPO_4^{2-}/PO_4^{3-} in deionized water whose pH value was adjusted either with 2 mol L^{-1} NaOH or with 2 mol L^{-1} HCl when necessary, and a 0.1 mol L^{-1} TBAP (tetrabutylamonium perchlorate) (Fluka) solution in acetonitrile were used as supporting electrolytes. All chemicals used were of analytical-reagent grade, and water was obtained from a Millipore Milli-Q purification system.

2.4. Sample

Pea seeds (Pea Lincoln (Ganxo), Mata Baja Battle S.A.) of industrial use spiked with DSF at a 0.1 mg kg^{-1} level.

2.5. Procedures

2.5.1. AuMEs Fabrication and Pretreatment

Gold fibers previously cut to approximately 15-mm length and washed in acetone were let to dry at ambient temperature for some minutes. Then, each fiber was joined to a copper wire used as the electrical contact by means of a thin film of a silver conducting painting. After 15 min, the assembly was inserted in a Teflon holder where the Au fiber was sealed by heating with a red-hot steel wire. In order to obtain a disk geometry, the gold fiber was perpendicularly polished with SiC abrasive paper.

At the beginning of each working day, the AuME was polished with 3-μm diamond powder (BAS MF-2059) for 60 s. Next, potentials of −0.4, −0.8, −1.0, −1.2 and −1.5 V were applied to the AuME, for 30 s each, in the background electrolyte used afterwards for the voltammetric experiments. In between measurements, a potential of −1.5 V was applied to the AuME for 30 s.

2.5.2. Adsorptive Stripping Measurements

All measurements were carried out under ambient conditions. A two-electrode configuration, in which the reference and counter electrode connections were both attached to the reference electrode, was employed. The appropriate solutions were transferred into the electrochemical cell, and an accumulation potential of 0.0 V was applied to the pretreated AuME without stirring the solution throughout the accumulation period. When the accumulation time was completed, a differential-pulse scan, with a 50 mV s^{-1} scan rate and a 50 mV pulse amplitude, was initiated towards more positive potential values.

2.5.3. Determination of DSF in Spiked Pea Seeds by AdSV

Pea seeds were washed with deionized water and methanol. Then, a 5-g sample was transferred to a glass tube with screw stopper and spiked with the appropriate volume of DSF stock solution also adding 5 mL of methanol. Next, the mixture was mechanically stirred for 5 min, followed by 5 min of centrifugation at 4000 rpm. The extract was filtered through a Whatman nylon membrane filter (0.45 μm pore size). Then, 2.9 mL of the filtrate were transferred to the electrochemical cell, where the solvent was evaporated to almost dryness by passing through a N_2 stream. Finally, the obtained residue was dissolved in 5 mL of a 3.0×10^{-3} mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ buffer solution (pH 6.0) and filtered once more. DSF was determined by AdSV under the experimental conditions described above, and by applying the standard addition method which involved successive additions of a 5.0×10^{-5} mol L^{-1} DSF stock solution in water.

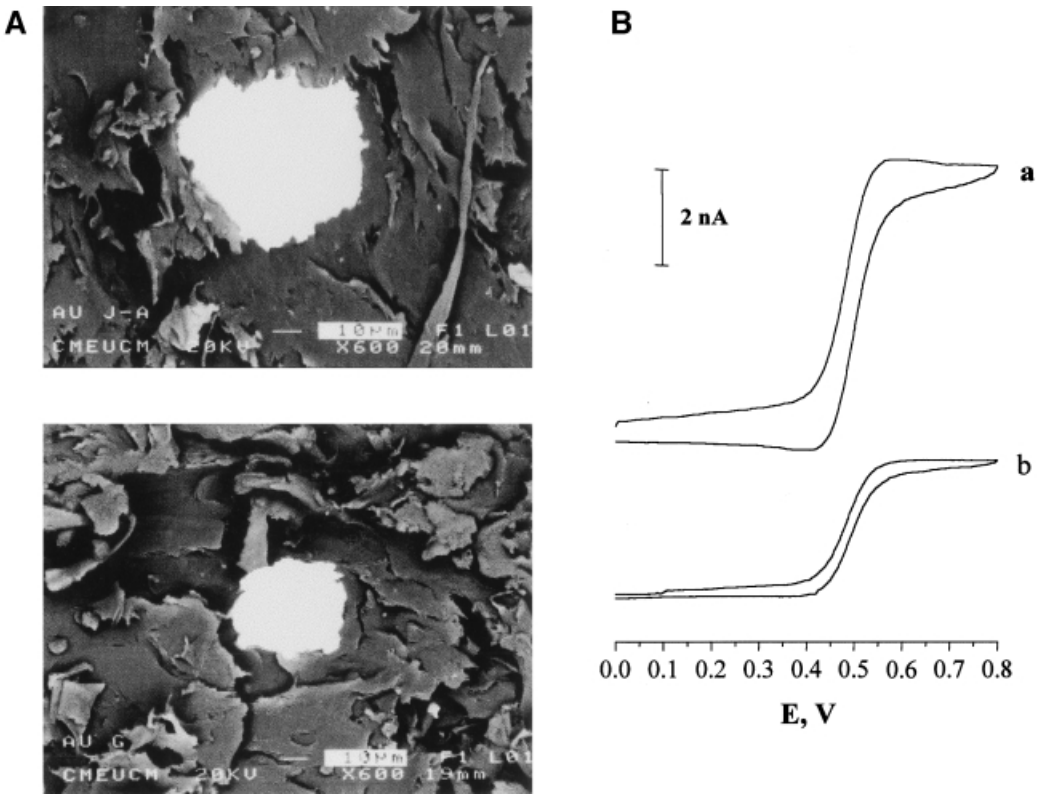

Fig. 1. A) Scanning electron micrographs for a nominal a) 50 μm-diameter and b) 25 μm-diameter AuME. B) Cyclic voltammograms for 1×10^{-4} mol L^{-1} ferrocene in acetonitrile at a nominal a) 50 μm-diameter and b) 25 μm-diameter AuME; supporting electrolyte, 0.01 mol L^{-1} TBAP; $\nu = 50$ mV s^{-1}.

3. Results and Discussion

3.1. Characterization of the AuMEs

The AuMEs fabricated in our lab from nominal 25 and 50 μm diameter gold fibers following the procedure described in Section 2. were characterized by both scanning electron microscopy and cyclic voltammetry. Figure 1A shows scanning electron micrographs of these AuMEs, where the average diameters measured were 34 ± 3 and 58 ± 2 μm ($n = 10$), respectively.

In order to check the electrochemical behavior of these AuMEs, ferrocene in pure acetonitrile was used as a model of a reversible electrochemical system. Figure 1B shows the cyclic voltammograms from 0.0 to 0.80 V registered using a two-electrode configuration for a 1.0×10^{-4} mol L^{-1} ferrocene solution with 0.01 mol L^{-1} TBAP as background electrolyte. From the oxidation currents obtained for each microelectrode (1.72×10^{-9} and 3.00×10^{-9} A for the 25 μm-diameter and the 50 μm-diameter microelectrodes, respectively), and using the equation for the steady state limiting current at disk microelectrodes [25].

$$i_l = 4nFDCr$$

the diameters of the AuMEs tested were also calculated. Thus, considering $n = 1$ e^-, $F = 96487$ C mol^{-1}, $C = 1.0 \times 10^{-7}$ mol cm^{-3}, and $D = 2.7 \times 10^{-5}$ cm^2 s^{-1} as calculated from the average limiting current ($n = 5$) of the ferrocene voltammograms obtained with a Pt microdisk ($r = 5$ μm) electrode, diameters of 33.0 and 57.6 μm were obtained respectively. These results agree fairly well with those measured by scanning electron microscopy. Although similar values of the signal to background ratio were

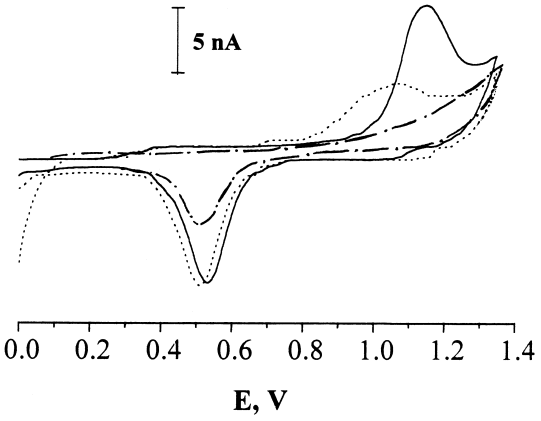

Fig. 2. Cyclic voltammograms for 1.0×10^{-6} mol L^{-1} DSF in 3.0×10^{-3} mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ (pH 6.0): (·····) with no accumulation period and (–) with $E_{acc} = 0.0$ V and $t_{acc} = 120$ s; $\nu = 50$ mV s^{-1}; (–·–·–) blank voltammogram.

observed for both microelectrodes, nominal 50-μm AuMEs were used for further work in order to obtain higher absolute current values.

Figure 2 shows cyclic voltammograms obtained for 1.0×10^{-6} mol L^{-1} DSF in 3.0×10^{-3} mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ (pH 6.0) with a nominal 50-μm diameter AuME, as well as the corresponding blank voltammogram. As can be seen, when no accumulation was carried out, the voltammogram showed an oxidation peak at approximately +1.1 V. When an accumulation potential of 0.0 V was applied for 120 s, the oxidation peak current increased while the peak potential was shifted to more positive potential values. Thus, the adsorption of DSF on the AuME can possibly be used as an effective preconcentration step before quantitative measurements are undertaken. The reduction peak observed in the reverse scan at a potential value of +0.50 V, which also appeared when no DSF was present in solution, was attributed to the reduction of the oxides formed during the anodic scan in the working medium employed.

3.2. Pretreatment of the AuME

Preliminary studies performed with no pretreatment of the AuME showed that no suitable electroanalytical responses could be obtained for DSF. Consequently, different pretreatment (conditioning and cleaning) procedures were assayed. Figure 3 displays the dp-AdSV voltammograms obtained for 1.0×10^{-6} mol L^{-1} DSF in a 0.1 mol L^{-1} phosphate buffer solution, pH 6.0, after applying different pretreatments to the AuME. In all cases, an accumulation period of 120 s at a potential of 0.0 V was applied after the pretreatment. The different procedures tested included: a) polishing with 0.3-μm diameter alumina (Figure 3a); b) polishing with diamond powder with various particle sizes (1, 3, and 5 μm diameter) (Fig. 3b); c) immersion of the AuME in 0.1 mol L^{-1} H_2SO_4 and application of five successive cyclic scans between −1.5 and −0.3 V at 100 mV s^{-1} (Fig. 3c); and d) polishing with 3-μm diameter diamond powder for 60 s, followed by an electrochemical treatment consisting on applying potentials of −0.4, −0.8, −1.0, −1.2 and −1.5 V, to the AuME for 30 s each (Fig. 3d). Taking into account the reproducibility of the measurements, the background current and the sensitivity of the electroanalytical response, this latter pretreatment procedure was selected.

Furthermore, it was also observed that a cleaning procedure of the AuME was still necessary in between measurements to avoid fouling of the electrode surface as a consequence of the oxidation electrochemical reaction. An electrochemical cleaning procedure was then considered by applying different potentials during different periods of time. As the potential applied for 30 s was shifted to more negative values in the range 0.0 to −2.0 V, an increase in the stripping peak current together with a somewhat lowering of the peak potential was observed. By considering also the reproducibility of the response, a potential value of −1.5 V was chosen for further studies. The influence of the cleaning

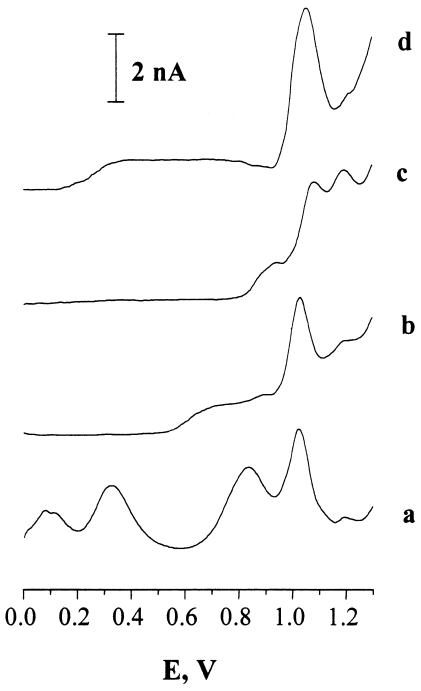

Fig. 3. Differential-pulse adsorptive stripping voltammograms obtained on a AuME for 1.0×10^{-6} mol L^{-1} DSF in 0.1 mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ (pH 6.0). $E_{acc} = 0.0$ V, $t_{acc} = 120$ s; $\nu = 20$ mV s^{-1}, $\Delta E = 50$ mV. Pretreatment procedure: a) polishing with 0.3-μm alumina for 60 s; b) polishing with diamond powder for 60 s; c) cyclic voltammetry (five scans) in 0.1 mol L^{-1} H_2SO_4 between −1.5 and −0.3 V at $\nu = 100$ mV s^{-1}; d) polishing with diamond powder for 60 s followed by application of several potentials (see text) for 30 s in 0.1 mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ (pH 6.0).

time was evaluated in the range 10–60 s. A significant increase in the DSF stripping peak current was observed up to 30 s from where the signal was stabilized up to 50 s. For longer times than 50 s a decrease in the DSF stripping signal was observed, probably as a result of the hydrogen evolution at −1.5 V. No influence of the cleaning time on the stripping peak potential was observed so, taking into account all these results, a cleaning time of 30 s was chosen for further studies. Under these pretreatement and cleaning conditions, a RSD of 3.0% was obtained for ten successive i_p measurements.

Finally, the possibility of using a two-electrode arrangement was verified by comparing the stripping voltammograms for 1.0×10^{-6} mol L^{-1} DSF with those obtained with a three-electrode system. The responses obtained with both arrangements were practically identical, and a two-electrode system was then used for further work, in order to simplify the measurement cell.

3.3. Cyclic and Differential Pulse Adsorptive Stripping Voltammetric Behavior

Cyclic voltammetry was used to evaluate the suitability of the DSF adsorption process on the AuME. If, once the accumulation step had been applied, several successive

potential scans were carried out, a high decrease in the DSF peak current was observed from the first to the second scan. Moreover, both this i_p value and the peak potential approached those values obtained when no accumulation of the fungicide was carried out. These results showed that DSF was quickly desorbed from the electrode surface. The plot of log i_p vs. log ν, in the 5 – 100 mV s^{-1} range yielded a slope value of 0.66 ± 0.03 when no accumulation was carried out, which is close to the theoretically expected for diffusion-controlled processes. However, when accumulation at 0.0 V was performed for 120 s, the slope of the log i_p vs. log ν plot in the same scan rate range was 0.87 ± 0.03, indicating as expected a higher adsorption contribution to the electrode process. Moreover, a shift of the peak potential to more positive values was observed when the scan rate increased. A rapid increase of the current function ($i_p/C\,\nu^{1/2}$) when increasing scan rate was also observed mainly for scan rates higher than 40 mV s^{-1}, which agrees with the DSF adsorption on the AuME surface [26].

Concerning differential pulse adsorptive stripping voltammetry, systematic studies of the various experimental parameters affecting the AdSV response were carried out. The study of the solution pH was accomplished in the 3.95 – 10.1 pH range and using a 3.0×10^{-3} mol L^{-1} phosphate buffer solution as supporting electrolyte. Figure 4a shows the influence of pH on the 1.0×10^{-6} mol L^{-1} DSF stripping peak current and peak potential. As can be observed, peak potentials were shifted towards less positive values as pH increased. Two linear ranges were obtained in this plot with an intersection point at pH 8.03, which could correspond to the pKa value of the adsorbed DSF. On the other hand, only a very slight variation of the peak current with pH was observed. A pH value of 6.0 was chosen for further studies, taking into account that at lower pH values the stripping signal was close to the medium oxidation barrier, and that the stability of the fungicide solutions could not be assured for higher pH values. This choice also resulted in a very suitable medium for the AuME cleaning procedure.

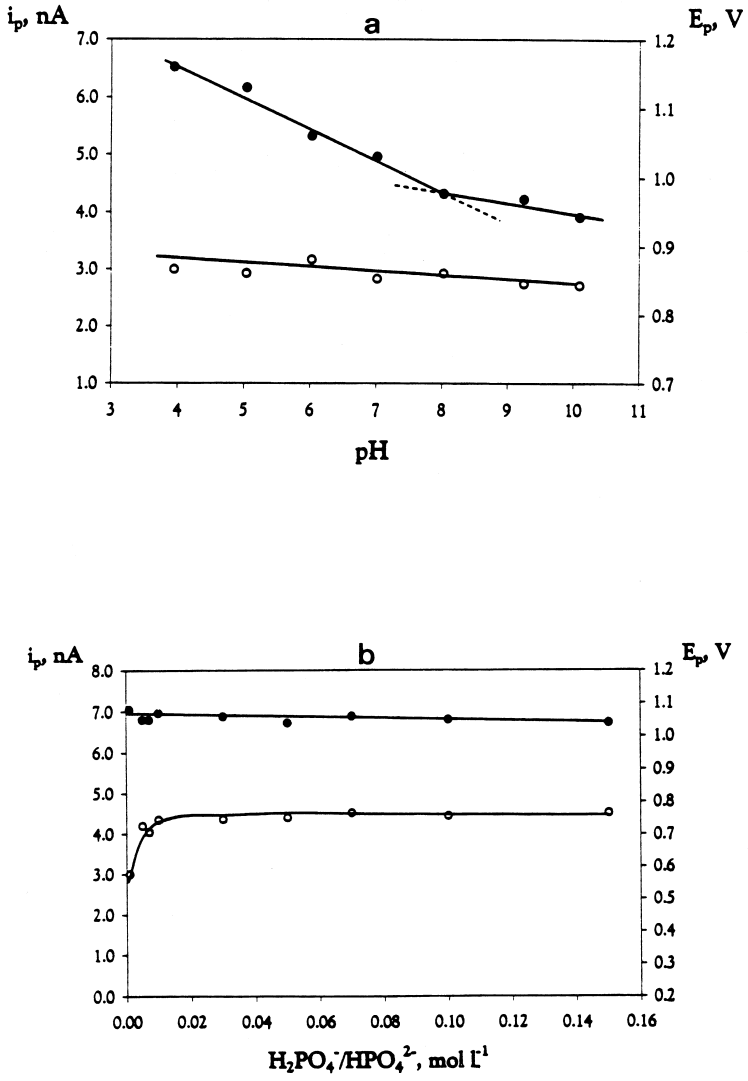

Fig. 4. Effect of a) pH (3.0×10^{-3} mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$, and b) $H_2PO_4^-/HPO_4^{2-}$ (pH 6.0) concentration on the 1.0×10^{-6} mol L^{-1} DSF dp-AdSV response. (●) E_p, (○) i_p. $E_{acc} = 0.0$ V, $t_{acc} = 120$ s; $\nu = 20$ mV s^{-1}, $\Delta E = 50$ mV.

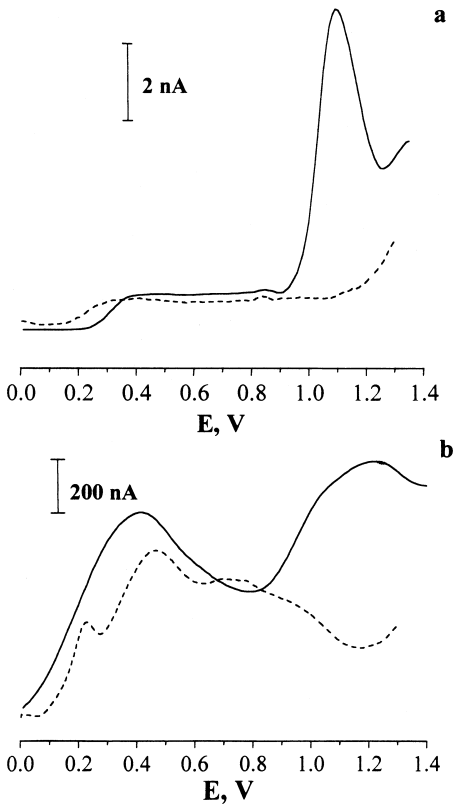

Fig. 5. Differential-pulse adsorptive stripping voltammograms for 1.0×10^{-6} mol L^{-1} DSF in 3.0×10^{-3} mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ (pH 6.0) buffer solution at: a) AuME and b) AuE. Dotted lines correspond to background voltammograms. Other conditions as in Figure 4.

One of the great advantages offered by microelectrodes is the possibility to apply voltammetric techniques in high resistance media. Thus, the effect of the $H_2PO_4^-/HPO_4^{2-}$ buffer solution (pH 6.0) concentration on the DSF dp stripping signal was studied within the range $1.0 \times 10^{-3} - 0.15$ mol L^{-1} (Fig. 4b). While only a small variation of the peak potential was observed, a significant increase in the peak current was found from 1.0×10^{-3} to 3.0×10^{-3} mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ then levelling off for higher buffer concentrations. This behavior can be attributed to the achievement of an adequate conductivity for electrolyte concentrations higher than 3.0×10^{-3} mol L^{-1}. In order to check the performance of the AuME in these low background electrolyte concentration media, which may be of interest for the analysis of natural samples, repeatability studies were carried out at two buffer concentration levels, 3.0×10^{-3} and 5.0×10^{-3} mol L^{-1}. RSD values for i_p of 1.9 and 3.3% ($n = 10$) were obtained, respectively, and a 3.0×10^{-3} mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ concentration was chosen for further studies.

Other parameters affecting the DSF stripping signal, such as the accumulation potential and time, as well as the scan rate and pulse amplitude used in the stripping process, were also optimized. The chosen working conditions, together with the ranges considered for each parameter are shown in Table 1. Although DSF was also adsorbed on the AuME at open circuit, higher peak currents, with no significant variations among them, were obtained with the application of an accumulation potential, which may also introduce a factor improving selectivity. Regarding accumulation time, using 120 s, a stabilization of the peak current was observed when working with a relatively high DSF concentration level (1.0×10^{-6} mol L^{-1}), whereas adequate analytical stripping signals were obtained for lower DSF concentration levels. Moreover, during the accumulation step no stirring of the solution was necessary, as was demonstrated by obtaining identical DSF stripping responses with and without stirring of the solution. This constitutes another of the advantages associated with the use of microelectrodes.

Table 1. Chosen dp-AdSV experimental conditions for the DSF determination at a AuME.

Parameter	*Range studied*	*Chosen value*
Cleaning potential (V)	0.0 to −2.0	−1.5
Cleaning time (s)	10 to 60	30
pH	4.0 to 10.0	6.0
$H_2PO_4^-/HPO_4^{2-}$ concentration (mol L^{-1})	0.001 to 0.15	0.003
Accumulation potential (V)	0.0 to 0.8	0.0
Accumulation time (s)	0 to 300	120
Scan rate (mV s^{-1})	5 to 100	50
Pulse amplitude (mV)	10 to 100	50

DSF stripping voltammograms obtained with the AuME were compared with those obtained with a conventional Au disk electrode (3 mm diameter) which was subjected to the same pretreatment as that used for the AuME (Fig. 5). As it can be observed, a more suitable analytical response with a lower background current, was obtained when working with the AuME. From these voltammograms, peak current densities of 2.1×10^{-4} and 3.1×10^{-6} A cm^{-2} were calculated for the AuME and the AuE, respectively. Although the use of a AuME resulted in lower peak currents, a 100-fold higher peak current-to-electrode surface ratio was obtained, thus giving rise to a signal-to-noise ratio which was twice the one observed at the AuE. Furthermore this signal-to-background ratio for the AuE was practically the same as that obtained for a DSF stripping voltammogram recorded with a higher supporting electrolyte concentration (0.1 mol L^{-1}).

3.4. Calibration Plot and Analytical Characteristics

Under the chosen experimental conditions, a linear calibration graph ($r = 0.994$) was obtained for DSF over the $1.0 \times 10^{-7} - 1.0 \times 10^{-6}$ mol L^{-1} concentration range with a slope of $(5.85 \pm 0.08) \times 10^6$ nA mol^{-1} L and an intercept of (0.45 ± 0.05) nA. The $3\,s_b/m$ and 10 s criteria, where m was the slope of the calibration curve, s_b the standard deviation ($n = 10$) of the signal from 1.0×10^{-7} mol L^{-1} DSF and $s = s_b/m$, were used to calculate the detection and the determination limits. Thus, a detection limit of 6.3×10^{-8} mol L^{-1} and a limit of determination of 2.0×10^{-7} mol L^{-1} were obtained. Furthermore, a relative standard deviation of 1.3% ($n = 10$) was obtained at the 5.0×10^{-7} mol L^{-1} DSF concentration level. Finally, the reproducibility of the stripping responses obtained

with five different AuMEs was also checked. A RSD of 2.2% was obtained for i_p at a 1.0×10^{-6} mol L^{-1} DSF concentration level, indicating a good reproducibility in the microelectrodes fabrication procedure. All these results confirm the suitability of the constructed AuMEs for the adsorptive stripping voltammetric determination of disulfiram.

The effect of the presence of various compounds on the 1.0×10^{-6} mol L^{-1} DSF dp-AdSV signal was also evaluated. The compounds tested were several pesticides such as diram, thiram, ziram, and zineb, and phenol. As expected taking into account the similarity of the structures of the different dithiocarbamic acid derivatives assayed, all these compounds were adsorbed on the AuME. They showed stripping signals at potential values of 1.09, 1.12, 1.14, 1.04 and 0.96 V, respectively, all of them close to the DSF peak potential. The higher interference-to-analyte ratios which gave relative errors in the DSF stripping signal up to 10% were of 2:1 for phenol, 0.5:1 for thiram and ziram, and of 0.2:1 for diram and zineb. Therefore, although it is unusual that mixtures of these compounds are present in real samples, in such a case, a separation method by chromatography would be necessary prior the application of AdSV.

3.5. Determination of Disulfiram in Pea Seeds

The proposed method was applied to the determination of DSF in pea seeds samples spiked with the analyte at the 0.1 mg kg^{-1} level, which is the maximum limit allowed for dithiocarbamates in oleaginous seeds. The procedure described in Section 2. was followed, and thus the final concentration of the fungicide in the analytical solution was 2.0×10^{-7} mol L^{-1}.

A calibration plot in the range $2.0 \times 10^{-7} - 8.0 \times 10^{-7}$ mol L^{-1} was constructed by adding aliquots of a DSF stock solution to a blank of pea seeds which had been subjected to the treatment previously described. The slope of this plot, $(3.7 \pm 0.2) \times 10^6$ nA mol^{-1} L, was considerably lower than that obtained with DSF stock solutions, indicating the existence of a matrix effect. Consequently, the standard addition method was used to determine the fungicide. A mean DSF recovery for ten determinations of (0.096 ± 0.003) mg kg^{-1} $(96 \pm 3\%)$ was obtained, the confidence interval being calculated for a significance level of 0.05.

4. Conclusions

All the above results demonstrate fairly well that gold disk microelectrodes can be advantageously used for the development of adsorption stripping voltammetric analytical methodologies for the determination of compounds, such as disulfiram, capable to be adsorbed onto gold surfaces. The use of microelectrodes implies a series of advantages with respect to conventional size electrodes, which can be profitted for the improvement of the electroanalytical responses of the corresponding analytes, especially concerning the signal-to-noise ratio and the precision of the measurements.

5. Acknowledgements

The financial support of the Spanish DGICYT, Project PB97/0331 and CAM, Project 07G/0023/2000 is gratefully acknowledged. Lourdes Agüí acknowledges the post PhD grant of the Community of Madrid (789/99 BOCM 4/05/99).

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