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Electrochemical analysis of endosulfan using a C18-modified carbon-paste electrode

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Abstract

Successful applications of different analytical procedures to determine quantitatively endosulfan and its metabolites in aqueous media can be found in recent literature. Fundamentally, they have made use of solid-phase extraction (SPE) and gas (GC) or liquid chromatography (LC), sometimes coupled to mass spectrometry (MS). In this paper, a new and alternative methodology to determine quantitatively endosulfan in aqueous media is reported. A C18-modified carbon-paste electrode has been used to determine voltammetrically endosulfan, despite its unfavourable electrochemical properties and behaviour. The methodology proposed is based on the decrease experienced by the peak intensity corresponding to voltammetric signals of Cu(II) when successive and constant additions of endosulfan are carried out. This decrease is directly proportional to the concentration of endosulfan what allows to perform an indirect quantification of the pesticide. The detection limit obtained is 40 ng l^{-1}, this value being under the limits specified by European norms and EPA reports.

Keywords: Pesticides; Endosulfan; C18; Modified carbon-paste electrodes; Differential pulse anodic stripping voltammetry

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1. Introduction

Extensive use of pesticides has raised concerns among many researchers since the behaviour and some characteristic of these substances present in the environment are responsible for ecological risks. Pesticides applied to soil may undergo microbial decomposition, photodecomposition, chemical degradation, volatilisation, plant uptake or adsorption, and may be transported in surface runoff, sediment or leached through the soil profile. The greatest potential for adverse effects of pesticides is through contamination of the hydrologic system. Water is one of the primary media by which pesticides are transported from the site of application to other compartments in the environment. Surface waters are particularly vulnerable to contamination by pesticides because most urban and agricultural areas drain pesticides into the waterways. Subsequently

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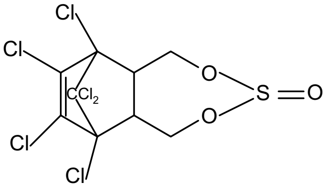

Fig. 1. Chemical structure of endosulfan.

they can be transported downstream and widely dispersed into rivers, lakes, reservoirs, and eventually the ocean. Losses from volatilisation, aerial spraying, and agricultural runoff are also considered to be important in the transport of pesticides to the aquatic environment.

Endosulfan (Fig. 1), chemical belonging to the cyclodiene subgroup, is a type of broad-spectrum organochlorine insecticide very used in many countries. This substance is poisonous by touch for a wide variety of insects and mites. Besides, it is lyposoluble and highly persistent in the environment (Worthing, 1983; Weber, 1991). Commercial products are usually sold as mixtures of two isomers: α-endosulfan and β-endosulfan. Both of them, including their other metabolites (endosulfan sulphate, endosulfan diol, endosulfan ether, endosulfan α-hydroxy ether and endosulfan lactone) are considered as very hazardous and toxic pollutants to living things and the environment, having been included in the list of priority pollutants of the US Environmental Protection Agency (EPA).

Exposure to endosulfan can occur through inhalation, ingestion, eye or skin contact and adsorption through the skin. It causes central nervous system, kidney, liver and testicular effects in animals, and central nervous system and respiratory effects in humans (Weber, 1991; US Department of Health and Human Services, 1995). The estimated lethal dose of endosulfan in humans is 50–500 mg kg^{-1} (Gosselin et al., 1984). Endosulfan is also a suspected endocrine-disruptor compound (Weber, 1991). In addition, it is highly toxic to aquatic organisms (Walker, 1984). The EPA water quality criteria for endosulfan is 56 ng l^{-1} in surface waters and 0.1–0.2 mg l^{-1} in agricultural products (Pait et al., 1984). The major degradation product of endosulfan, endosulfan sulphate, has been shown to be as toxic or more toxic than the parent compounds to some aquatic species (Shimmel et al., 1977).

The most commonly employed analytical methodology to determine quantitatively endosulfan and its metabolites in aqueous media (direct procedure) is fundamentally based on gas or liquid chromatography (GC and LC, respectively) (Thomas et al., 2001; Brito et al., 2002; Dmitrovic et al., 2002; Tan and Ali Mohd, 2003; Silva et al., 2004). Furthermore, solid-phase extraction (SPE) is almost always applied as a previous technique with the aim of pre-concentrating the specie(s). The extraction cartridges most widely utilized in SPE processes involving this type of insecticide, are based on polymeric substances such as octadecyl (C18: silicon network modified with chains of 18 atoms of carbon in its surface).

In this paper, an alternative methodology to determine endosulfan in aqueous solution has been developed. It has to be stated that endosulfan presents unfavourable electrochemical behaviour for its determination. That is why a direct electrochemical procedure is very difficult, as the rather scarcely number of papers reported about this subject shows (Fernández et al., 1992; Reviejo et al., 1992a,b). An indirect determination method based on differential pulse anodic stripping voltammetry (DPASV) has been applied, using C18-modified carbon-paste electrodes. The methodology carried out in this communication allows the quantification of endosulfan by means of the inhibition of the Cu(II) voltammetric signal when the concentration of endosulfan is progressively increased for a fixed amount of Cu(II).

This new methodology shows several important advantages, such as the voltammetric determination of a substance with unfavourable electrochemical behaviour; a very simple and fast fabrication process of the modified electrode, as well as its cleaning procedure; a high degree of repeatability and reproducibility in the measurements; and a very good detection limit (40 ng l^{-1}), value being under the limit specified by international laws.

2. Experimental

2.1. Apparatus

The differential pulse anodic stripping voltammetry (DPASV) measurements were carried out with an Autolab®/PGSTAT20 (Ecochemie, Utrecht, The Netherlands) electrochemical system coupled to a VA 663 Stand (Metrohm, Herisau, Switzerland). An electrochemical three electrode cell, with a platinum auxiliary electrode, silver/silver chloride/3 M KCl reference electrode and an octadecyl (C18)-modified carbon-paste working electrode (surface area 7 mm^2), was employed.

2.2. Reagents and materials

Analytical reagent grade chemicals were used throughout the experiments. The modified carbon-paste was prepared by mixing 5 g of spectroscopic grade graphite (Ringsdorff-Werke GMBH, Bonn, Germany) with 1.8 ml of mineral oil (Aldrich, Milwaukee, WI) and the required amount of the modifier (octadecyl-C18, Strata, Phenomenex, Torrance, CA) to obtain the desired mass proportion. The resulting paste was packed into the electrode and the surface was smoothed. After each measurement, the paste was removed from the cavity of the electrode, or cleaned with water to re-use the electrode.

A 0.2 M Britton–Robinson buffer solution was used for the pH studies. Different pH values were obtained by addition of NaOH (Merck, Darmstad, Germany). Trihydrated copper (II) nitrate salt (Merck) was used for quantification of Cu(II) signal. Endosulfan sulphate (from Labor Dr. Ehrenstorfer-Schaïfers, Augsburg, Germany) was prepared in acetone (Merck). Working solutions were prepared daily by dilution with water. Nanopure water was obtained by passing twice-distilled water through a Milli-Q system (18 MΩ cm, Millipore, Bedford, MA). Bentonite was from Aldrich and tetrabutylammonium iodide (ammonium salt) was from Merck.

2.3. Voltammetric procedure

For the preliminary studies, a 0.2 M Britton–Robinson buffer solution at different pH values was used. From a set of parameters as initial conditions, the study of each variable was carried out, using each optimised value for the subsequent studies.

The optimal voltammetric parameters obtained were as follows: accumulation potential, −1.2 V; accumulation time, 300 s; rest period, 5 s; initial potential, −0.5 V; end potential, 0.2 V; scan rate, 10 mV s^{-1}; pulse amplitude, 0.15 V; pulse repetition time, 0.6 s; rotation rate, 1500 r.p.m.

The voltammetric procedure can be described as follows: 25 ml of buffer solution at pH 4 were placed in the electrochemical cell. After accumulation at room temperature (25 ± 1 °C), a differential pulse voltammogram was recorded in the potential range from −0.5 to 0.2 V. After adding a certain volume of Cu(II) solution, the accumulation process was repeated and a new voltammogram was obtained. Once the electrode was cleaned and dried, the packing procedure was accomplished again and, after addition of endosulfan, another voltammogram was scanned. A 10% C18-modified carbon-paste rotating electrode was used as the optimised working electrode.

The cleaning procedure of the working electrode was controlled by means of measurements on electrolyte support (0.2 M Britton–Robinson, pH 4), what confirm the possibility of re-using the electrode for subsequent analyses.

3. Results and discussion

The objective of this paper is the electrochemical determination of endosulfan. Nevertheless, endosulfan shows unfavourable electrochemical behaviour. We have carried out an indirect procedure based on the decrease of the Cu(II) peak intensity when adding endosulfan. This decrease is directly proportional to the concentration of the pesticide. We have selected Cu(II) because of its electrochemical wave, which appears in a potential zone no interfered by other metallic ions. Moreover, Cu(II) signal determined by differential pulse anodic stripping voltammetry (DPASV) using a C18-modified carbon-paste electrode has several important characteristics that make it adequate to this kind of study: low half-width, great peak intensity and sensibility, and good symmetry. The advantage of utilizing adsorptive species like octadecyl lies in that its use is very extended in chromatographic columns to detect endosulfan, favouring the adsorption procedure of this pesticide. As a previous step to the applicability of this indirect detection method, we have carried out a complete optimisation of the experimental variables of the Cu(II) signal.

3.1. Experimental variables for Cu(II)

3.1.1. Influence of the modifier and pH

We have studied the influence of two typical adsorbents: octadecyl (C18) and bentonite, on the Cu(II) signal. C18 is widely employed in chromatographic columns and solid-phase extraction (SPE) cartridges, as quoted previously; bentonite is used as modifier in carbon-paste electrodes due to its adsorbent properties (Naranjo-Rodríguez et al., 1997; Cordero-Rando et al., 1998). C18 has very scarce relevance in electrochemistry, excepting for its use as monomers on indium–tin oxide surfaces (Markovich and Mandler, 2000, 2001).

Table 1 shows the peak potential and peak height values. As it can be observed, on one hand, the presence of bentonite in the carbon-paste causes a decrease on peak height in comparison with the signal of the unmodified carbon-paste. On the other hand, the presence of C18 in the paste leads to an increase on peak height value. Consequently, we selected C18 as modifier for the carbon-paste.

The peak height increases with the C18 percentage; however, although the peak height value obtained with the 15% C18-modified carbon-paste is higher, it is difficult to obtain a smooth surface of the electrode after

Table 1
Influence of the modifier on peak height (I_p) and peak potential (E_p) for a Cu(II) concentration of 0.4 mg l^{-1}

Modifier	E_p (V)	I_p (μA)
None	−0.12	47.1
C18 (5%)	−0.11	49.9
C18 (10%)	−0.11	75.9
C18 (15%)	−0.10	93.3
Bentonite (5%)	−0.10	33.2

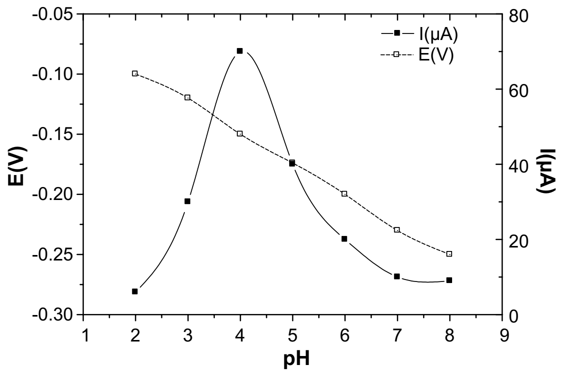

Fig. 2. Influence of pH on E_p and I_p for 0.4 mg l^{-1} of Cu(II) using a 10% C18-modified carbon-paste electrode. Initial potential, −0.5 V; end potential, 0.2 V; accumulation potential, −1.2 V; accumulation time, 90 s; pulse amplitude, 100 mV; scan rate, 10 mV s^{-1}; pulse repetition time, 0.6 s; rotation rate, 1500 r.p.m.

polishing. Moreover, higher percentages of C18 gave less compact pastes that fall off the electrode with the rotation movement. These reasons led to select a 10% C18-modified carbon-paste for latter studies.

Studies about the influence of pH were carried out in the pH range from 2 to 8. Fig. 2 shows the dependence of peak potential and peak height for Cu(II) versus pH; well-defined peaks were obtained for all voltammograms recorded. As it can be seen, the peak potential shows a clear dependence on pH, decreasing with pH. The peak height reached its maximum value in moderately acid media. The highest Cu(II) peak was obtained at pH 4 (optimal value for further studies).

3.1.2. *Effect of the accumulation time and accumulation potential*

The influence of the accumulation time was also investigated. This parameter could influence the adsorption degree of Cu(II) onto the electrode surface; a range from 30 to 660 s was studied. The higher the accumulation time, the higher the peak height, as well as the more asymmetric and broad peaks. However, the greatest increase occurs up to 300 s, after which a very slight increase is observed.

For future analyses, 300 s was considered the optimum value of accumulation time, in order to achieve a compromise between peak height and the duration of the full analysis.

The influence of the accumulation potential on peak height was also studied in the range from −0.4 to −1.4 V. Peak height reaches a maximum value when the accumulation potential is −1.2 V. The rest of the parameters used were those optimised previously. So, for subsequent studies, the accumulation potential was fixed at −1.2 V.

3.1.3. *Effect of rotation rate, pulse amplitude and temperature*

The application of a rotation movement to the working electrode improves its sensitivity since it aims the vertical flux of analytes towards the surface of the electrode. It can be concluded that peak height increases in the range from 0 to 1500 r.p.m., but it decreases in the range from 2000 to 3000 r.p.m. That is why the value of 1500 r.p.m was chosen as the working electrode rotation rate.

The effect of varying pulse amplitude and its influence on the peak height and the peak potential was also studied. The more positive the pulse amplitude, the higher the peak height value. In particular from 175 to 250 mV, it was also observed that the higher the pulse amplitude, the more negative the peak potential; this behaviour can lead to interferences with other metallic ions. Moreover, the Cu(II) signal widens while decrease the pulse amplitude. The optimal value was chosen in 150 mV, since it gives the highest sensitivity, the most symmetric peak, and no displacement of peak potential.

The effect of temperature was assessed in the range from 10 to 35 °C. The peak height shows a light increase with the temperature. Although high temperatures gave better results, they are not recommended because of the possibility of a partial vaporisation of the cell solution and the thermo stability of the working solution.

3.1.4. *Reproducibility studies and calibration graph*

In order to evaluate the reproducibility of the responses, after adding a certain volume of 0.1 mg l^{-1} Cu(II) in 25 ml of 0.2 M Britton–Robinson buffer solution at pH 4, five voltammograms were recorded with different 10% C18-modified carbon-paste electrodes. All electrodes showed similar peak height values, and the same peak potential values, with a relative standard deviation of 1.30% for $n = 5$.

The greatest advantage of measuring Cu(II) by DPASV is its inherent sensitivity. The signal enhancement, associated with the anodic accumulation time, results in significantly lower detection limits compared with those obtained by other procedures (Abbaspour and Moosavi, 2002; Guo et al., 2004; Lu et al., 2004). Using this method to determine Cu(II), ranging from 4×10^{-4} to 9×10^{-4} mg l^{-1}, the slope was 14.6 mA l mg^{-1}, and the correlation coefficient value equal to 0.997. The detection limit, calculated as the blank signal plus three times the blank standard deviation, was 4.5×10^{-5} mg l^{-1}. Therefore, the quantification limit value, calculated as the blank signal plus ten times the blank standard deviation, was 1.5×10^{-4} mg l^{-1}.

3.2. *Analytical application: determination of endosulfan*

Only a few papers report direct voltammetric determination of endosulfan in literature; in our experimental conditions we obtained no voltammetric response of this pesticide. That is why we have applied an indirect procedure based on the linear decrease of Cu(II) peak height caused by the adsorption of this pesticide to determine endosulfan, as can be observed in Fig. 3.

In the experimental procedure described the selection of Cu(II) is due to this metal shows very good electrochemical response (high sensitivity), and it has a peak potential far from the signal of other electroactive metals; so, no interference must be expected for the presence of other metallic ions.

To understand the behaviour of the modified electrode, we carried out some tests using different percentages of a quaternary ammonium salt in the buffer solution. Several voltammograms were recorded using 10% C18-modified carbon-paste electrodes in 25 ml of 0.2 M Britton–Robinson buffer solution of pH 4 by the optimal voltammetric parameters. The percentages of the salt were in the range from 0% to 1.3%, with increments of 0.1% (fourteen experiences).

All voltammograms show a peak, whose height depends linearly on the percentage of salt used (correlation coefficient, 0.998), and whose peak potential values suffer practically no deviation. The addition of endosulfan affects the signal corresponding to the salt. A decrease on peak height values of the quaternary ammonium salt is observed when the endosulfan concentration increase. Since no inhibition of mobility is described for quaternary ammonium salt, it can be assumed that the pesticide endosulfan avoids the adsorption of the salt on the electrode surface, and therefore the peak height of salt decreases with the concentration of endosulfan; this behaviour can be extrapoled to the addition of endosulfan to a Cu(II) solution.

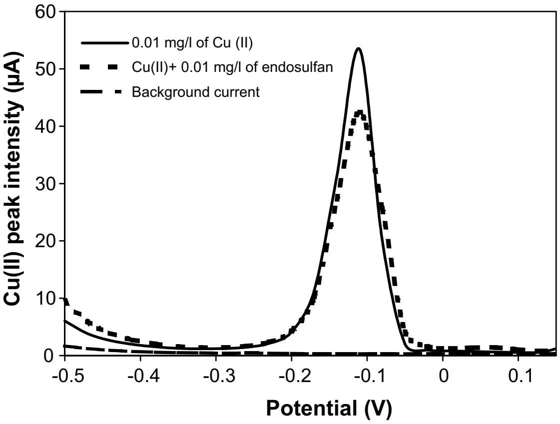

Fig. 3. Effect of the addition of 0.01 mg l^{-1} of endosulfan in a solution with 0.01 mg l^{-1} of Cu(II), using a 10% C18-modified carbon-paste electrode and a Britton–Robinson buffer at pH 4. Accumulation potential, −1.2 V; accumulation time, 300 s; rest period, 5 s; initial potential, −0.5 V; end potential, 0.2 V; scan rate, 10 mV s^{-1}; pulse amplitude, 0.15 V; pulse repetition time, 0.6 s; rotation rate, 1500 r.p.m.

The decrease on Cu(II) peak height was directly proportional to the concentration of endosulfan and can be explained in terms of ions mobility, but a contribution of the blockage of the sites of the carbon paste must be assumed, due to the previous experiences with quaternary ammonium salt. No interaction Cu(II)–C18 can be considered; the accumulation of Cu(II) does not occur on C18 sites but on carbon particles, due to the reduction of Cu(II) takes place on carbon material. C18 allows the deposition of endosulfan on the electrode surface, and it must be considered that steric effects take place due to the presence of endosulfan on electrode surface, i.e., Cu(II) (or quaternary ammonium salt) cannot reach the electrochemically active carbon sites. In the case of Cu(II) this effect is joined to the reduction of the mobility (Khan and Singh, 1999; Khan et al., 2002). These phenomena could serve us to justify the results obtained in this study.

The addition of 25 μl of endosulfan (concentration in cell, 0.01 mg l^{-1}), causes a decrease on Cu(II) peak height values. Subsequent measurements suffer a decrease versus time in the value of this parameter, resulting in a difference of intensity equal to 12.2 μA after 30 min of adding the pesticide. Subsequently, Cu(II) peak intensity values remain almost constant. This time of inhibition (30 min) will be taken into account for further studies.

The effect of the variation of Cu(II) concentration at a fixed concentration of endosulfan was also studied. The goal is to choose an appropriate concentration range to detect clearly the pesticide object of our research. In Table 2, the differences of Cu(II) peak intensities at different concentrations of this ion and at a fixed concentration of endosulfan are shown.

From these results can be noticed that the differences of intensity between Cu(II) peaks are significantly important when similar concentration ranges of Cu(II) and endosulfan are used.

Table 2
Influence of the addition of endosulfan on Cu(II) peak height using 10% C18-modified carbon-paste electrodes

Cu(II) concentration (mg l^{-1})	Peak height (μA) without endosulfan	Peak height (μA) with 0.01 mg l^{-1} of endosulfan	Peak height decrease (μA)
10^{-4}	1.10	0.20	0.90
5×10^{-4}	2.86	0.66	2.20
10^{-3}	10.2	7.19	3.02
5×10^{-3}	31.3	24.2	7.16
10^{-2}	52.4	44.1	8.32
5×10^{-2}	112	103	9.33
10^{-1}	146	136	9.65

Using 0.01 mg l^{-1} as the Cu(II) concentration, and concentration values ranging from 0.001 to 0.011 mg l^{-1} (with increments of 0.001 mg l^{-1}) for endosulfan. Although the representation of the differences of Cu(II) peak intensities versus the concentration of endosulfan is linear (correlation coefficient, 0.998; a slope of 0.90 mA l mg^{-1}, and an intercept of −1.07 μA), the detection limit obtained in these conditions was 3×10^{-4} mg l^{-1} (300 ng l^{-1}) (Miller and Miller, 1993). However, this value remains superior to the one fixed by the European norm of water potability (100 ng l^{-1}), defined by the guideline CEE 80/778 of July 15, 1980. To increase the sensitivity and diminish, at the same time, the value obtained for the detection limit, we used a Cu(II) concentration of 0.001 mg l^{-1} and concentrations of endosulfan ten times more diluted than those used previously.

The variation of Cu(II) peak intensity versus different pesticide concentrations ranged from 10^{-4} to 10^{-3} mg l^{-1} (with increments of 10^{-4} mg l^{-1}), shows a slope of 1.40 mA l mg^{-1}, and an intercept of −0.07 μA; the correlation coefficient value was equal to 0.998. The detection limit, calculated as the blank signal plus three times the standard deviation, was 4.0×10^{-5} mg l^{-1} (40 ng l^{-1}, under the legal limits) (Miller and Miller, 1993). Therefore, the quantification limit, calculated as the blank signal plus ten times the standard deviation, was 1.3×10^{-4} mg l^{-1}. A relative standard deviation of 2.5% was obtained for eleven measurements (endosulfan concentration, 0.001 mg l^{-1}).

By the US EPA standard GC/ECD method for endosulfan (Method 608), a detection limit of 4×10^{-6} mg l^{-1} is obtained; although this limit is lower than that reported for our electrochemical procedure, the sensitivity reached with our method is enough for any legal norm, and allow us the use of a electroanalytical technique very useful in many other applications.

Some tests were carried out for spiked drinking and superficial water samples; endosulfan concentrations in cell of 10^{-3} and 5×10^{-4} mg l^{-1} were used. The results show recoveries of 99.2% and 98.8%, respectively, for three measurements of each concentration. In all cases the paste was removed from the electrode, giving relative standard deviations for the repeated measurements of 2.4% and 2.8% for 0.01 and 0.005 mg l^{-1} endosulfan concentrations. As a previous step, the absence of Cu(II) in the real samples was tested by ICP (Inductively Coupled Plasma). If the presence of Cu(II) had been confirmed, then an extraction step (usually solid-phase extraction) would have been necessary as a previous technique with the aim of pre-concentrating endosulfan and to assure the absence of Cu(II) for the electrochemical procedure.

The selectivity of electrochemical responses depends on several factors such as composition of the sample (i.e., presence of other similar compounds) or peak potential value for analyte with respect to the value for background or other components of the sample. However, many analyses require only information about global content, and this is an important application in the field of the analysis of real samples. If several similar compounds are present in a sample, a global content can be obtained by the proposed electrochemical procedure. However, and according to the origin of the sample, sometimes only the presence of one compound must be expected, and thus the quantification of the analyte can be carried out without additional techniques.

4. Conclusions

In this paper, a new and alternative methodology to determine indirectly and quantitatively endosulfan in aqueous solution has been presented. This methodology makes use of an electrochemical procedure (DPASV) using modified carbon-paste electrodes. C18, a polymeric substance that constitutes the most part of extraction cartridges and chromatographic columns used in determination processes involving this type of insecticide, has been the modifier employed in the electrodes. Despite the unfavourable electrochemical behaviour of endosulfan, the determination method described here allows the quantification of endosulfan by means of the inhibition of the Cu(II) voltammetric signal when successive and constant additions of endosulfan are carried out. The decrease in the Cu(II) peak intensity is directly proportional to the concentration of endosulfan and has been explained in terms of ion mobility and the blockage of the active sites of the C18-modified carbon paste.

Besides the high degree of repeatability and reproducibility achieved in the measurements, as well as the voltammetric determination of ensodulfan itself, other important advantage of this methodology lies in the fabrication and cleaning process of the C18-modified carbon-paste electrode, which is very simple and fast. The detection limit obtained for this insecticide has been very low (40 ng l^{-1}). The quoted value is smaller than those reported in other related papers, but fundamentally it is under the limits specified by European norms and EPA reports.

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