Voltammetric determination of methyl parathion, ortho, meta and para nitrophenol with a carbon paste electrode modified with C_{18}

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Summary. The determination of methyl-parathion (MPT), ortho (ONP), meta (MNP) and para nitrophenol (PNP) has been studied by differential pulse voltammetry with a carbon-paste electrode modified with 50% (w/w) of C_{18}. A study of the influence of the pH in the preconcentration cell and the measurement cell was carried out for an electrode with 50% modifier and an accumulation time of 5 min. The voltammograms were recorded with a sweep rate of 40 mV s^{-1} and a pulse amplitude of 50 mV. With the optimum conditions of pH for both of the steps, various other variables were studied. The variables for each compound were optimized and the possibility of application to the determination of a mixture of the four compounds was investigated. The determination limits found for all the compounds are: 2 ng ml^{-1} for ONP, 5 ng ml^{-1} for MNP, 4.3 ng ml^{-1} for PNP and 7.9 ng ml^{-1} for MPT. The method was applied to samples of a small lake which gathers rain water and water filtered from land on which cereals are grown.

Introduction

Modified electrodes are being used more frequently in the voltammetric determination of organic compounds because of their efficieny, the selectivity that can be obtained by varying the modifier and the sensitivity which is equivalent to that reached in anodic and cathodic stripping.

The use of chromatographic column filling materials, (gas and liquid columns), produces an effective preconcentration of organic substances in a wide range of matrices, thus facilitating methods for selective and sensitive determination by oxidation and reduction of different molecules with electroactive functional groups.

C_{18} was used as a modifier of carbon paste electrodes, for the direct determination of Tifluadon [1] by measuring the anodic current obtained by cyclic voltammetry. From 0.5 to 5.0 µg ml^{-1} Bentazepan could also be detected among

other benzodiazepines by using the oxidation wave obtained by differential pulse voltammetry [2].

This present study is focused on voltammetric behavior, in a C_{18} CPME, of methyl-parathion, and o-, m- and p-nitrophenol in order to determine these compounds globally in samples of environmental interest. The need for determining the compounds together, arises from the use of MPT as an insecticide that, on hydrolysis, generates PNP as a metabolite. It is difficult to distinguish them using conventional techniques because of their structural similarity.
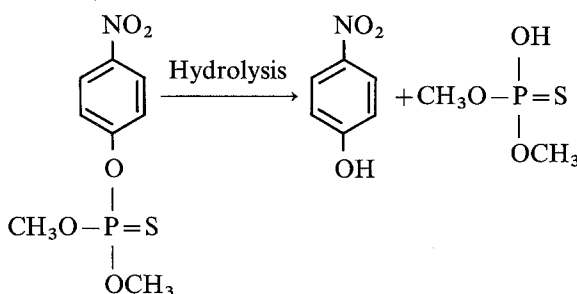
The origin of contamination can be deduced from the distinction of these compounds whenever the MPT and PNP present proceed from the use of the insecticide.

Methyl-parathion ($C_8H_{10}NO_5PS$) is a quasi-systemic organophosphorus insecticide widely used throughout the world. It is highly toxic (3—10 mg/kg) and persistent and, therefore, a pesticide that needs to be controlled when used on fruit, green vegetables and natural water. Chromatographic and spectrometric analyses [3—6] were the methods carried out, but a process of separation or clean up was necessary in the stage prior to the identification and determination in water, blood serum, urine, cereals and vegetables. Smyth and Osteryoung [7] determined ethyl-parathion and PNP together electrochemically by following the reduction of the nitro group in dpp, detecting them at levels of ng ml^{-1} in blood.

The purpose of this study is to find a method by which these compounds can be determined directly, together, in the original matrix.

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Experimental

Apparatus and reagents

Spectroscopic graphite was subjected to an electric arc for 5 min in a Spectrographic Analyzer from ARL. Subsequently the graphite was ground to particles finer than 0.4 μm^2, ready for the preparation of a carbon paste, which is carried out using nujol oil as pasting liquid.

Quantities of C_{18} column packing (Waters) were added to the graphite in equal weight proportions in order to obtain the desired percentage of modifier.

Contact with the paste, previously placed in a polyethylene tube with a surface of 1.6 mm^2, was made by mean of a copper wire.

All experiments were carried out with a Metrohm E-506 Polarecord polarograph equipped with a saturated calomel electrode used as reference electrode and a platinum electrode as a counter electrode. Separate cells were used for preconcentration and measurement.

The 99% pure MPT was supplied by Industrias Aragonesas S.A. and the ONP, MNP and PNP by Carlo Erba R.A. Stock solutions were prepared in methanol and those of lower concentration were diluted directly from the main reagents with de-ionized water, using the Milli-Ro and Milli-Q (Waters) system.

The other reagents employed were of analytical grade.

Procedure

The preconcentration cell contains the compound under study, dissolved in the correct base electrolyte, and the measurement cell contains the electrolyte at a fixed pH. The electrode was submerged with an open circuit for a prefixed time, the solution is stirred constantly with a magnetic bar. At the end of that time, the electrode was extracted, washed with water and dried and then it was placed in the measurement cell which contains the electrolyte appropriate for each experiment. Subsequently the corresponding voltagramms, from −0.40 to −1.40 V were recorded, by dpv maintaining the latter potential for 60 s in order to regenerate the electrode.

Results and discussion

To determine mixtures of different compounds satisfactorily, it is necessary to observe their behavior at the accumulation stage and their electrochemical response; a study was made to see how the accumulation and measurement conditions depended on the electrode employed.

Electrochemical response measurements were set and all the factors that could intervene in the accumulation phase were varied.

When the accumulation step was thus optimized, a study was made of the measurement conditions that provided the best results in sensitivity and selectivity for the electrochemical response.

A study of pH influence was carried out in both preconcentration und measurement cells, with an electrode with 50% modifier. Solutions of 0.5 mg ml^{-1} of the analyte and 5 min preconcentration times were used for this study.

For the preconcentration step, Britton-Robinson (B.R.) 0.04 mol/l buffer solutions, adjusted to the required pH values, were used. The measurements were taken in indepen-
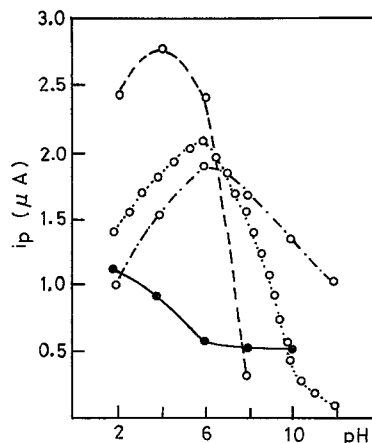

Fig. 1. Influence of pH on i_p, in the preconcentration step. Measurements at pH 6 in 0.04 mol/l BR buffer. (– – – – –) ONP; (–.–.–.–.–) MNP; (O———O) PNP; (———) MPT)
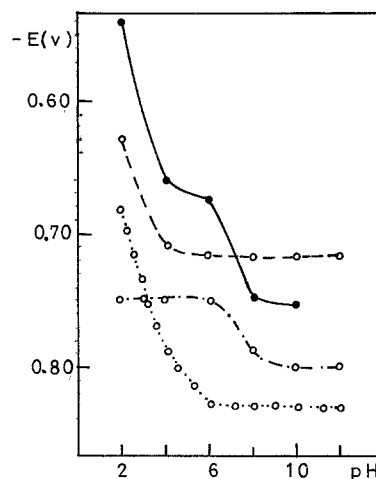

Fig. 2. Variation of peak potential with pH in the measurement cell. Conditions of accumulation: ONP at pH 4, MNP and PNP at pH 6 and MTP at pH 2

dent cells with a supporting electrolyte of B.R. buffer at pH 6, with a scan rate of 40 mV s^{-1} and a pulse amplitude of $\Delta E = -50$ mV.

The results are shown in Fig. 1. The best accumulation conditions were at pH 4 for the ONP derivative, pH 6 for MNP and PNP, and a range of pH 2−4 for MPT.

Using these accumulation conditions, the pH in the measurement cell was modified, maintaining theB.R. buffer as the supporting electrolyte.

The results can be seen in Fig. 2. An analysis of the measurement cell curves showed the following variation for each stage and compound

Compounds	pH	Slope
Ortho nitro phenol	< 6	0.039
Para nitro phenol	< 6	0.038
Meta nitro phenol	6−8	0.050
Methyl-parathion	2−5	0.052
Methyl-parathion	5−9	0.025

Table 1. Optimal measurement conditions

Variable/compound	ONP	MNP	PNP	MPT
Electrolyte pH	HAc/Ac⁻ 4.0	BR 6.0	Phosphate 6.0	Phosphate 2.0
Concentration of highest i_p [mol/l]	0.4 $i_p = 4.0\ \mu A$	0.04 $i_p = 1.8\ \mu A$	0.4 $i_p = 1.5\ \mu A$	0.008 $i_p = 2.0\ \mu A$
Measurement conditions[a]	B.R. pH = 6.0	B.R. pH = 6.0	B.R. pH = 6.0	B.R. pH = 6.0
Electrolyte pH	Phosphate 6.0	B.R. 10.0	Phosphate 6.0	Phosphate 8.0
Concentration of highest i_p [mol/l]	0.4 $i_p = 5.0\ \mu A$	0.04 $i_p = 2.2\ \mu A$	Phosphate 0.02 $i_p = 2.5\ \mu A$	Phosphate 0.04 $i_p = 1.4\ \mu A$
Preconcentration conditions[a]	HAc/Ac⁻ 0.4 mol/l pH = 4.0	B.R. pH = 6.0	Phosphate 0.4 mol/l pH = 6.0	Phosphate 0.008 mol/l pH = 2.0

[a] Other conditions: accumulation time 5 min percentage of modifier: 50% C_{18}: sweep rate 40 mV/s and AE -50 mV

Table 2. Influence of accumulation time

	ONP	MNP	PNP	MPT
Accumulation time [min]	10	15	15	10
i_p [μA]	6.0	6.7	6.0	4.8

with linear equations in their respective steps with regression coefficients of r = 0.997 to 0.999.

For acidic pH values, curves derived from ONP and PNP show a variation of Ep with a pH that corresponds to different slopes from methyl-parathion and the meta derivative in the pH 6−8 range. This difference in the value of the slopes indicates that different reduction results can be obtained from electrochemical reactions, the values being in relation to those expected for the reduction of the nitro group into amine or hydroxyl amine. The variation in the behavior of the PNP derivative and MPT could be due to the substance resulting from the prior hydrolysis of MPT that acts as a nucleophile and retards reduction to hydroxyl amine [8].

The variation in the potential observed in the reduction of the different isomers and methyl-parathion facilitates the differentiation of mixtures of these compounds, choosing the appropriate pH of the measurement cell, thus enabling their simultaneous determination.

After choosing the optimal pH conditions for both cells, a study was made on other electrolytes, different concentrations and pH. The optimum results for the four compounds are summarized in Table 1.

The following variables are studied in the preconcentration cell.

While stirring the solution constantly, the enrichment time for each compound was modified. It was observed that i_p increased in relation to the time the electrode is remained for all compounds, up to a set time, after which there was no noticeable modification, because the electrode is saturated (Fig. 3, Table 2).

Changing the percentage of modifying C_{18}-material from 20 to 75%, gave rise to a parabolic behavior of i_p for all compounds on i_p. The highest i_p is obtained with electrodes
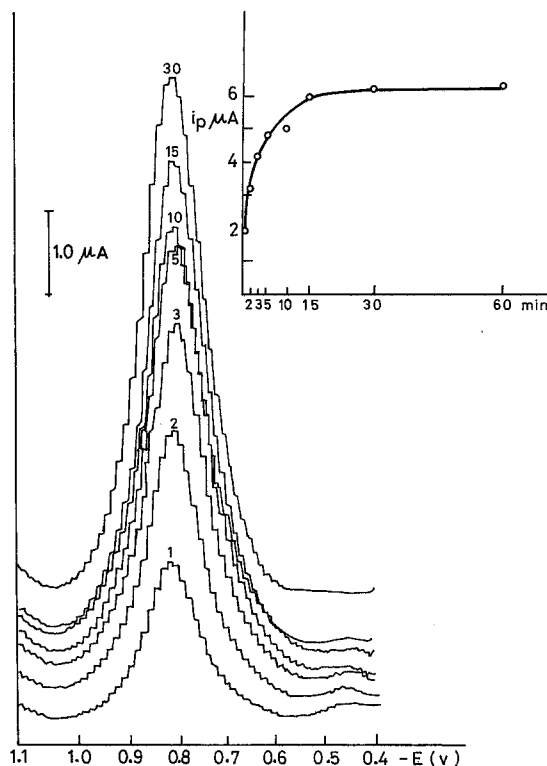

Fig. 3. Influence of accumulation time for PNP. Conditions for preconcentration, pH 6 in phosphate 0.04 mol/l and for measurement pH 6 in BR 0.04 mol/l

containing 50% C_{18}. Electrodes with over 60% produce very high residual currents and, consequently, an often large reduction in i_p.

Modification of instrumental variables in the measurement cell, (sweep rate and pulse amplitude), produced a linear increase in i_p within the margins studied (between 5 and 40 mV s^{-1} and 10 and 100 mV for pulse amplitude). For that reason the optimum conditions chosen for the four compounds were: 40 mV s^{-1} as sweep rate and 100 mV as pulse amplitude.
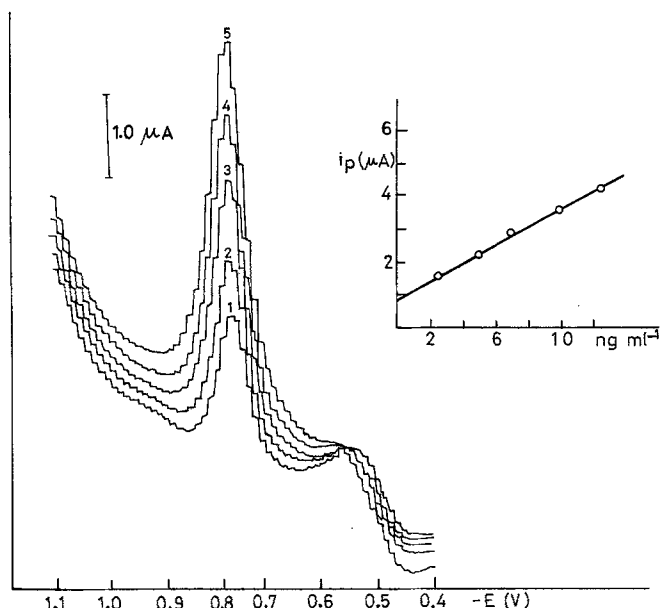
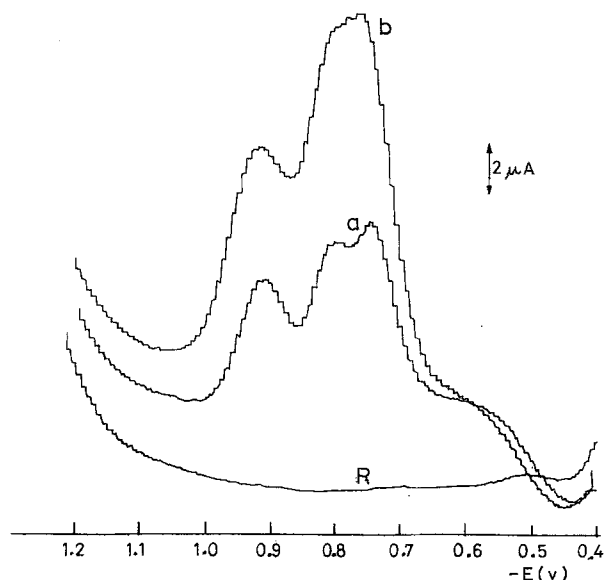**Fig. 4.** Influence of concentration for the MNP. Conditions see text

Fig. 5. Voltammogram of the four compounds studied under optimum conditions for methyl-parathion. (R) residual current (a) equimolar mixture of MNP, PNP and MPT and (b) mixture

Figure 4 shows the voltagramms and the corresponding calibration plot for meta-nitrophenol. There is a linear relationship between i_p and concentration for values ranging from 1 to 26 ng ml^{-1} for the 4 compounds studied.

Table 3. Characteristics of the method

	ONP	MNP	PNP	MPT
y = ax + b	y = 0.31 +0.21x	y = 0.87 +0.27	y = 0.77 +0.15x	y = 0.31 +0.14x
r	0.996	0.998	0.990	0.999
Limit of determination[a]	2.0	5.0	4.3	7.9
Relative error %	2.1	3.0	2.7	3.2
Standard deviation %	7.8	7.3	5.5	6.0

y in μA; x in ng ml^{-1}
[a] In ng ml^{-1} calculated as 10 σ
r correlation coefficient

The equations in Table 3 show the data obtained in solutions ranging from 1 and 26 ng ml^{-1} and statistical data of 10 solutions of 10 ng ml^{-1} and three different electrodes.

Mixtures of the four compounds were studied, always under optimum conditions, can be seen in Fig. 5, where the voltammogram (R) represents the residual current; (a) represents an equimolecular mixture of meta-, para-nitrophenol and methyl-parathion and (b) a mixture of all four.

The three reduction waves can clearly be distinguished in mixtures of MNP, PNP and MPT, but when the four compounds are present the ONP shades out the MPT and MNP waves so that the four compounds cannot be determined together. It is possible to determine derivatives of meta- and para-nitrophenol and methyl-parathion together.

The method for determining these compounds was applied to samples from a small lake which gathers rain water and water filtered from land on which cereals were grown. As the quantities were smaller than the limit required for determination, quantitative values could be confirmed. By adding 3 ng ml^{-1} methyl-parathion, an identification was possible.

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