

STUDY OF THE INTERFERENCES OF MCPA ON THE ELECTROCHEMICAL DETERMINATION OF BENTAZON ON PHITOPHARMACEUTICAL PRODUCTS

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ABSTRACT

An electroanalytical method for the quantification of bentazon in the presence of MCPA has been developed. Both bentazon and MCPA are herbicides used in rice cultures and bentazon appears alone or mixed with MCPA in a proportion of 7:1 in commercial formulations. In this work the interference caused by MCPA was evaluated and it was shown that the use of Triton in the supporting electrolyte solution leads to the elimination of its interference with bentazon.

Keywords: Bentazon, MCPA, herbicides, square wave voltammetry, interferences.

INTRODUCTION

Bentazon (3-isopropyl-1H-2,1,3-benzothiadiazin-4-(3H)-one-2,2-dioxide) and MCPA (4-chloro-2-methylphenoxyacetic acid) are herbicides that are commercialised, in a relative proportion of 7:1, in the commercial product (Quitt) used in the treatment of rice cultures. Bentazon is a photosynthetic electron transport inhibitor and MCPA concentrates in the meristematic regions where it inhibits growth. Their structures are shown in Fig. 1.

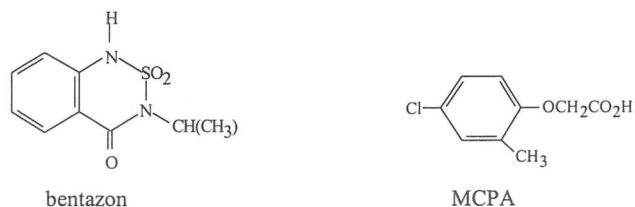


Fig. 1- Structures of a) Bentazon, b) MCPA.

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An electroanalytical procedure for the determination of the herbicide bentazon in a commercial product that only contains bentazon as the active ingredient was developed [1]. The oxidation mechanism of bentazon at a glassy carbon electrode, corresponds to an electrochemical step followed by chemical dimerization reaction of the products, which causes severe adsorption problems and consequent poisoning of the electrode surface. The effect of addition of Triton surfactant was used to enable determinations with good reproducibility, the limit of detection obtained with the electrochemical method was 10^{-5} M.

However, other phitopharmaceutical compounds, such as MCPA, are associated with bentazon in most commercial products so it is very important to investigate the possible interference of MCPA in the electrochemical response for bentazon, which was the motivation for this study.

EXPERIMENTAL

Apparatus

All experiments were performed using a 663 VA Metrohm system containing a glassy carbon working electrode (Metrohm 6.1204.000) ($d = 3.0$ mm), a glassy carbon rod counter electrode (Metrohm 6.1247.000) and a Ag/AgCl reference electrode (Metrohm 6.0728.000) attached to a Autolab PSTAT 10 potentiostat/galvanostat running with model GPES version 3 software, from Eco-Chemie, Netherlands. The potential range studied was from +0.2 to +1.2 V.

The glassy carbon working electrode was polished every day using a polishing kit (Metrohm 6.2802.010) first with α -Al₂O₃ (0.3 μ m) and water during 60 s and after with only water during 60 s. After polishing the electrode surface was thoroughly washed with purified water.

The pH measurements were obtained with a pH-meter E 520 from Metrohm with a combined glass electrode (Metrohm 6.0202.000).

HPLC experiments for the AOAC Method [2], were done using a HPLC Sykan system, model A1210 with a variable wavelength detector and a colum Nova-Pack Silica C₁₈ (3.9 mm x 150 mm).

Reagents and solutions

Bentazon and MCPA (acid form) were from Riedel de Haen. All reagents were analytical grade and aqueous solutions were prepared using purified water from a Millipore Milli-Q system (conductivity < 0.1 μ S cm⁻¹). The stock solution of bentazon and MCPA were prepared in ethanol at a concentration of 10^{-2} M. The buffer solutions used were in the pH range 1.9 to 12.8 [2]. Quantitative determinations were carried out in 0.2M acetate buffer (pH = 3.4).

Commercial sample preparation

In the commercial product (Quitt), sample stock solution was prepared by accurately weighing 0.59 g of the commercial sample and adding a few drops of glacial acetic acid until complete precipitation of the acid form of bentazon and MCPA occurred. Ethanol was added to the mixture until complete dissolution occurred, and the total volume was adjusted to 100.0 cm³. The sample stock solution was diluted with buffer electrolyte in order to obtain a concentration within the calibration curve range.

RESULTS AND DISCUSSION

Square wave voltammetry of MCPA showed that the oxidation of MCPA occurs at the potential of + 1.2 V vs. Ag/AgCl at a glassy carbon electrode. Fig. 2 presents the square wave voltammograms of a mixture with bentazon, which oxidises at a potential of + 0.95 V.

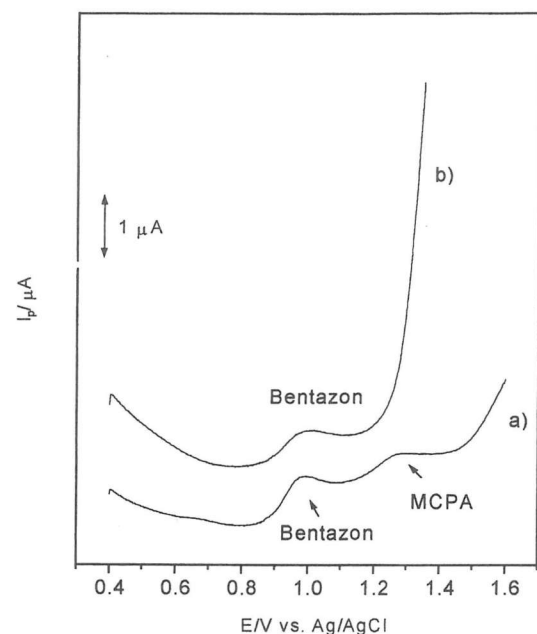


Fig. 2 Square wave voltammogram of a 3.9×10^{-4} M bentazon and MCPA in 0.2M acetate buffer (pH = 3.4): a) without addition of Triton; b) with addition of Triton.

Differential pulse voltammetry showed that the oxidation of MCPA is independent of pH for supporting electrolytes of pH less than 9, but the peak practically disappears for higher pH values.

However, for the electrochemical oxidation of bentazon [1], studies over a wide pH range using differential pulse voltammetry showed a linear relationship between E_p and pH with a slope of 40 mV per unit of pH, for pH values smaller than 3.4, meaning that the reaction mechanism corresponds to an electron transfer followed by a chemical reaction, probably a dimerization leading to irreversible products which were adsorbed on the electrode surface. For higher pH values, E_p is constant and independent of pH.

The oxidation current was highest for both herbicides in pH 3.4 acetate buffer with oxidation potentials + 0.95 V vs. Ag/AgCl for bentazon and + 1.2 V vs. Ag/AgCl for MCPA, Fig. 2. This difference was not sufficient to completely separate the current peaks, but the MCPA peak disappeared after adding 1% Triton to the electrolyte solution. The presence of Triton in the solution decreased the adsorption on the electrode surface and leads to the elimination of the interference with bentazon.

This electroanalytical procedure was used for the determination of bentazon in a commercial compound that contained both bentazon and MCPA as the active ingredients. The results were compared with those obtained by the AOAC method [3] and the relative error was 1.0%. The recovery obtained using the electrochemical method was 99.3%.

CONCLUSIONS

The electroanalytical method developed can be successfully used to quantify the herbicide bentazon in a commercial product without interference from MCPA. It is simple and permits the study of the oxidation of MCPA, which involves the formation of adsorbed products on the electrode surface.

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