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Indirect Determination of Dichlorodiphenyltrichloroethane (DDT) After Dechlorination with Magnesium/Palladium Bimetallic Particles and Potentiometric Measurements

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Abstract Determination of chlorine ions of pesticides was performed after dechlorination reaction using a palladium/magnesium system. Chlorine ions were quantified by potentiometry with ion-specific electrode. Rates of dechlorination of 100 μg of DDT as a function of reaction time and percent (wt/wt) of palladium deposited on the magnesium particles were determined. The best reaction conditions to DDT dechlorination were achieved with an acetone/water (1:1) solution and DDT reaction with a 0.27% (wt/wt) palladium/magnesium bimetallic system at room temperature for 10 min. The detection limit was of 0.24 μg/mL. This low cost method showed an efficiency of 92% in determining chlorine ions derived from DDT, it is fast, requiring no specialized laboratory equipment.

Keywords DDT · Bimetallic particles · Potentiometry

DDT is highly stable, lipophilic and bioaccumulative in animal and human food webs. Although the production and use of DDT has been banned for some decades in most countries, it still can be used in sanitation programs to combat vectors that transmit diseases (Manirakiza et al. 2002; Dorea et al. 2001). This has led governments and researchers to be concerned with its presence in the environment (Caldas et al. 1999).

Specific and sensitive procedures for many chlorinated insecticides are available, but they are expensive and time consuming. The purpose of this study is to evaluate DDT residues using an analytical procedure requiring no specialized equipment. An emerging technology is the use of bimetallic systems for the dechlorination of pollutants (Doyle et al. 1998; Engelmann et al. 2003; Kume et al. 2008; He et al. 2009), and there are already many studies in literature indicating the success of this technology with compounds such as DDT (Zinovyev et al. 2005; Ukisu 2008; Piechocki et al. 2009; Tian et al. 2009). The use of magnesium/palladium bimetallic particles for dechlorination of DDT has been studied by many scientists in an attempt to remediate this pollutant under natural environmental conditions (Gautam and Suresh 2007). The method is based on the reduction potential of magnesium metal coupled with the catalytic activity of small amounts of palladium. This system reduces the chlorinated organic compound to its hydrocarbon skeleton and chlorine ions (Gautam and Suresh 2006, 2007; Engelmann et al. 2001). In this study, we propose a methodology for the indirect determination of DDT after dechlorination catalyzed by bimetallic particles of Pd/Mg using potentiometry with ion selective electrode for chloride.

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Materials and Methods

Metallic particles of Mg/Pd magnesium were prepared by weighing 0.5 g of magnesium (20–230 mesh, 98%, Aldrich) and washing the particles with acetone prior to use in order to remove any absorbed organic compounds. An aqueous solution of potassium hexachloropalladate (K_2PdCl_6, 99%, Sigma-Aldrich) was added to Pd metal deposits on the Mg particle surface (0.27% wt/wt Pd coverage) via the reaction

$$Pd^{4+} + 2Mg^0 \rightarrow Pd^0 + 2Mg^{2+}$$

The mixture was then shaken for 1 h. The bimetallic system was rinsed with double-distilled water quality and then put in a drying oven (140°C) for 1 h. After preparation of the catalyst, a known quantity (0.25 g) of the bimetallic system was weighed in the reaction vessel. Approximately 5 mL of the solvent system consisting of 1:1 (v/v) acetone/water was added. The vessel was continuously shaken. 50 μL of the DDT (Sigma-Aldrich) 2,000 μg/mL solution in acetone and one drop (50 μL) of glacial acetic (Merck) acid was added. Reaction vessels were loosely capped to allow the escape of hydrogen gas. The dechlorination reactions were allowed to run for 10 min at room temperature. The mixture was transferred to a volumetric flask (10 mL); a blank sample was also run.

The method was applied to fish tissue. Frozen samples of fish muscle were thawed for about 2 h in room temperature and well homogenised. Four aliquots of 2.0 g were weighed: matrix A, matrix B, matrix spike A, matrix spike B. Then 2.5 g of anhydrous sodium sulfate was added to each sample and blank, and 4.0 mg of DDT was added to matrix spike A and matrix spike B. The mixture was Soxhlet extracted with 120 mL of hexane : acetone (1:1) for 12 h. The extract was concentrated to 5 mL under vacuum in a rotary evaporator. Aliquots of 100 μL were then taken for catalysis. The dechlorination reaction was run for 10 min and the mixture was transferred to a 10 mL volumetric flask. The results were analyzed in relation to recovery of the added analyte.

The solution was added to a vial containing 200 μL of ionic strength adjuster, sodium nitrate (Merck) 5 mol/L. The vial was continuously shaken. Chlorine ions were analyzed by potentiometric measurements, using a pH/Ion-meter (pH 1100/pH 2100 Bench pH/Ion Meter) after calibration with a solution of sodium chlorine (Merck).

Results and Discussion

Reaction catalysis on the surface of bimetallic systems is a rapid and complete method to achieve DDT dechlorination. This system reduces the chlorinated organic compound to its hydrocarbon skeleton and chloride ions in a reaction that takes place at room temperature in 10 min. The Pd and Mg concentrations and the reaction time were varied. Studies were conducted in an acetone/water (1:1) phase to determine the rates of dechlorination of 100 μg of DDT as a function of: (a) reaction time and (b) percent (wt/wt) of palladium deposited on the magnesium particles. According to the results presented in Table 1, we conclude that the best reaction conditions for DDT dechlorination are an acetone/water (1:1) solution with DDT reaction with a 0.27% (wt/wt) palladium/magnesium bimetallic system at room temperature for 10 min.

In order to use as little catalyst as possible, studies were conducted varying the quantity of the bimetallic system. These results are presented in Table 2, and they suggest that the reaction is not completed up to 1 mg of the bimetallic system. Furthermore, to reach stabilization of the chlorine ion concentration more than 3.5 h are necessary. The same was observed for 2.0 mg and 1.5 g of catalyst despite 100% of recovery, leading us to consider 2.5 mg of catalyst to be the ideal quantity for the most efficient reaction.

Gautam and Suresh (2007) studied the effect of varying ratios of acetone/water on the extent of DDT dechlorination by Pd/Mg bimetallic system. According to these authors, the highest conversion of DDT (86%) was obtained using the 1:1 ratio, while a 19:1 ratio only resulted in 40% of dechlorination.

Using stock solution of DDT, it is possible to construct an analytical curve for the quantification of total DDT content from chlorine ion selective electrode response (Fig. 1). These results reflect the reproducibility of the dechlorination reaction. The detection limit was of 0.24 μg/mL calculated according to Miller and Miller (1989).

The results in Table 3, shows the recovery of the concentration of DDT in spiked fish samples. It is worth noting that the concentrations of Cl^- are 2.18, 4.24, 6.14 and 7.94 mg/L, which represent recoveries of 109.0, 106.0, 102.0 and 99.4%, respectively, for DDT in fish muscle.

The chlorine ions derived from pesticides can be quantified by potentiometry with ion selective electrode by using the Pd/Mg bimetallic system for the complete dechlorination of the compounds. Advantages of the presented method are its low cost compared to other analytical methods, its speed and the ease of the analytical procedure

Table 1 Experimental conditions and recovery of DDT dechlorination reaction

[DDT] (μg)	% Catalyst (wt/wt)	Reaction time (min)	Recovery %
100	0.05	10	80
100	0.10	10	80
100	0.27	10	100
100	0.27	20	100
100	0.27	30	100
Average	–	–	92

Table 2 Recovery of DDT dechlorination using varying quantities of catalyst

[Pd/Mg] (0.27% wt/wt) (g)	Recovery %
0.25	100
0.20	100
0.15	100
0.10	80
Average	95

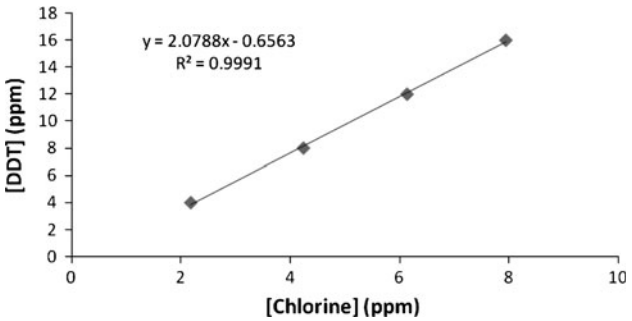

Fig. 1 Analytical curve of Cl^- from the dechlorination of DDT

Table 3 Chlorine data obtained from the dechlorination of DDT

DDT stock solution (2 mg mL^{-1}) (μL)	Amount of added DDT (μg)	[DDT] (μg mL^{-1}) 10 mL final volume	[Cl^-] (μg mL^{-1}) from the dechlorination of DDT
20	40	4	2.18 ± 0.71
40	80	8	4.24 ± 0.34
60	120	12	6.14 ± 0.20
80	160	16	7.95 ± 0.40

which requires no specialized laboratory equipment. Because of the ease of this method dechlorination may find wider use in analytical procedures. Nevertheless, there are numerous reports in the literature that have used ISEs to monitor important anions such as chlorine in environmental analysis. An additional advantage to the proposed analytical method is to minimize errors due to interference of chloride from other organic compounds. The use of dechlorination methods may, in some circumstances, lead to false results caused by the contribution of chlorides arising from sources other than DDT, especially in plant matrices. As an example, the quaternary salts of lecithins present in plant tissues can increase the concentration of chloride when using analytical methods based on stoichiometric [DDT]/[Cl^-] (Gunter et al. 1966).

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