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Short Communication

# Detection and discrimination of organophosphorus pesticides in water by using a colorimetric probe array

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ABSTRACT

Detection and discrimination of several organophosphorus pesticides in water using a colorimetric probe array containing twelve dyes has been achieved. A clear discrimination for malathion, leptophos, dichlorvos, dibrom and diazinon was observed. The array was used to determine the concentration of diazinon in orange leaves.



## 1. Introduction

Organophosphorus pesticides (OPs) constitute nowadays the most widely used class of available pesticides. They are currently employed to protect plants from disease and insect damage in agriculture, but also in home gardens and in veterinary practice. OPs are considered safer than their parent organohalide pesticides due to their faster degradation via microbial or environmental processes [1–3]. Chemically, OPs can be classified in three main groups, namely organophosphates, which contain a P═O bond (oxon pesticides), organothiophosphates, in which the oxygen has been replaced by a sulfur atom, (P═S, thions), and organophosphonates which are closely related to nerve agents such as Sarin, Soman or Tabun.

OPs are not only highly toxic to insects but also to human beings. In fact they are one of the most common causes of poisoning of humans across the world via intoxication through inhalation, ingestion or skin absorption [4–6]. The toxicity of OPs towards insects and mammals is due to their inhibition of the acetylcholinesterase enzyme by phosphorylation. This results in an accumulation of the acetylcholine neurotransmitter in the synaptic junctions causing muscle contraction, convulsions, respiratory depression, and even death by asphyxiation. The very large amounts of OPs used in fields and gardens cause their accumulation in soils, fruits, vegetables and water, increasing the risk of exposure to humans. Due to this environmental pollution and risks for human health, detection of pesticides is an issue of high interest [7–11].

Analytical procedures based on biosensing assays [12–15] or instrumental techniques such as electrochemical methods, mass, FTIR or NMR spectroscopy [16–21] have been classically used to detect these compounds. However most of these methods are complex, time-consuming, and non-portable. As an alternative the potential optical sensing of OPs using chromo- or fluorogenic probes [22–24] is particularly appealing because these methods regularly use widely available instrumentation, and in the case of chromogenic sensors colour modulations can be measured using low-cost systems, or in some cases they can be easily detected by the naked eye. In fact, there are few technologies as inexpensive as visual imaging.

Moreover, in the field of chromo-fluorogenic probes, the design of array-based systems (also known as optoelectronic

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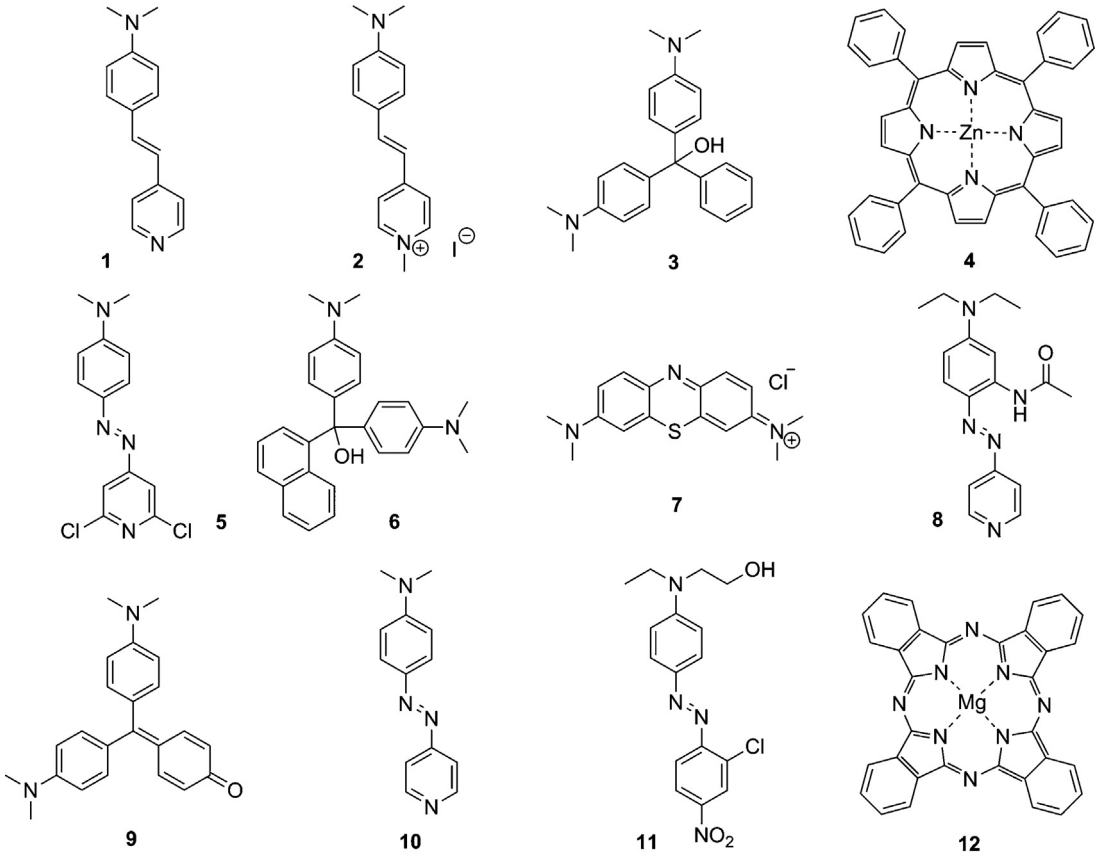


**Scheme 1.** The 12 dyes used in the chromogenic array.

noses) is becoming increasingly popular due to their capability of multianalyte sensing and versatility and the possibility to be applied in complex systems [25–27]. In fact, optoelectronic noses, based in relatively simple arrays of dyes have been applied for the detection of different volatile compounds (VOCs) including odorants, volatile amines [28–31], or drugs [32,33] via simple colour modulations.

Based on the above issues, and following the general interest of us and others in developing colorimetric probes for toxic organophosphonate derivatives [28–31] we report herein a prospective study of the use of an array of chromogenic indicators which we have applied to the detection and differentiation of several pesticides in water.

## 2. Results and discussion

Optoelectronic noses are usually based on the use of chromofluorogenic probes displaying a large cross-reactivity and use a full range of different intermolecular interactions. In our case, inspired by our own experience in the field and in previously reported optoelectronic noses, a total of 12 dyes were selected (see Scheme 1) including push-pull chromophores containing reactive sites such as pyridine, alcohol and amine groups (able to be phosphorylated) and compounds capable of coordinate with the studied pesticides or with their possible hydrolysis products.

The array was prepared by placing 2 μL of the corresponding dye solution in a 5 cm × 5 cm silica gel plate (see Supporting Information for details) and the response of the colorimetric array was tested in the presence of 12 analytes including thions (chlorpyriphos, diazinon, parathion, azinphos-methyl, methidathion and malathion), oxons (dichlorvos, dibrom), phosphonates (leptophos, glyphosate) and two non-organophosphorus pesticides (atrazine and pirimicarb). The chemical structures of these studied pesticides are shown in Scheme 2.

In a typical sensing experiment, a drop (2 μL) of a solution containing the corresponding pesticide (in $H_2O$:MeOH 95:5, v/v) was deposited on each probe of the colorimetric array, and then the array was dried in air for 5 min. The sensing array in the absence of the tested pesticides was used as control, which showed minor colour variations. Five completely independent experiments for each pesticide were performed with the aim of checking the reproducibility of the chromogenic array response. A scanner was used to obtain pictures of the array (see Supplementary data) and, from the photographs, Lab coordinates were measured using image processing software (Photoshop). Difference maps were obtained from the absolute values of the differences of Lab coordinates for each dye before and after reaction with the corresponding pesticide.

Colour differences were analysed using principal component analysis (PCA), which is a powerful linear unsupervised pattern recognition procedure and a simple suitable method to project data onto a two-dimensional plane. PCA decomposes the primary data matrix by projecting the multi-dimensional data set onto a new coordinate base formed by the orthogonal directions with data maximum variance. The eigenvectors of the data matrix are called principal components (PCs). PCs are ordered so that PC1 displays the largest amount of variance, followed by the next largest, PC2, and so forth. In our case (see Fig. 1) the first principal component contained 58.60% of the variance of the data. The first two components represented 72.86% of total variance, whereas seven PCs were needed to account for 95% of variance. A clear clustering of the data was found for the pesticides malathion, leptophos, dichlorvos, dibrom and diazinon and this was not confused with the presence of other pesticides (see Supplementary data for details).