

# Fluorimetric Determination of Carbamate Pesticides in Host-Guest Complexes

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**Abstract:** From the effect of  $\beta$ -cyclodextrin and hydroxypropyl- $\beta$ -cyclodextrin on the UV-visible and fluorescence spectra of carbaryl and carbofuran, the values of association constants were determined. The ratio of the fluorescence quantum yields for the bound and free substrates indicated an enhanced fluorimetric method of detection.

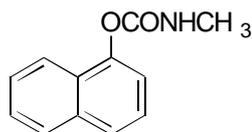
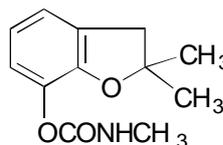
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## Introduction

The study of organized systems has proved to be very useful for analytical purposes.[1] These microheterogeneous systems can be classified into: molecular aggregates (micelles, vesicles, monolayers, etc.) and polymolecular species (polysilicates such as zeolites; polysugars such as cyclodextrins (CD); polyethers such as crown ethers ). The cavities or pores with defined sizes in these permanent molecular systems favour inclusion or complexing small molecules leading to high selectivity of these molecules. In these complexes, known as supramolecular species, are produced specific interactions that play an important role in the modification of physical and chemical properties of the substrates included.[2] Several photochemical and photophysical studies have been done with these receptors to investigate inclusion with substrates that have, for example, luminiscent properties. A remarkable increase of these properties was found.

The molecular luminiscent spectrometry and in particular molecular fluorescence has become a routine technique with many analytical applications [3] that offers a lower detection limit and with higher selectivity than the absorption spectroscopy.

Some pesticides from the carbamate group ( $-OCONH_2$ ) derived from fluorescent nuclei such as naphthalene, for example carbaryl (1-naphthyl-N-methylcarbamate, **CY**), or such as benzofuran, for example carbofuran (2,2-dimethyl,2-3-dihidro-7-benzofuranyl-N-methylcarbamate, **CF**) are widely used for plant protection against insects. However, the high toxicity of these pesticides requires sensitive and reliable methods to detect their presence in fruits and seeds. Therefore, an improved determination of these pesticides in presence of certain receptors is here proposed.

**CY****CF**

## Experimental [4]

UV-Visible absorption spectra of **CY** and **CF** (analytical grade commercial reactives) were performed in neutral aqueous, acid or basic medium in absence and in presence of 10 mM  $\beta$ -CD (cyclic oligomer with 7 glucose units) or HP- $\beta$ -CD (CD derivatized). The two carbamates **CY** and **CF** showed decomposition at alkaline pH so pH=7 was selected for the determinations. The presence of  $\beta$ -CD and HP- $\beta$ -CD produced changes in the UV-Visible spectra. The excitation wavelengths ( $\lambda_{\text{ex}}$ ) chosen for the fluorescent measurements were the  $\lambda$  where the substrate and the complexed substrate presented the same molar absorptivity ( $\epsilon$ ); it being 280 nm for **CY** and 273 nm for **CF**. Fluorescence emission spectra of the aqueous solutions were taken from each substrate at absorbance concentrations lower than 0.050 at the  $\lambda_{\text{ex}}$  chosen in each case with 10 nm excitation and emission widthbands, at low gain for emission spectra. The spectrofluorimeter cell was thermostated at  $25.0 \pm 0.1$  °C. The areas below the curves (F) and the fluorescent intensities at different  $\lambda$  ( $F_{\lambda}$ ) were recorded. All measurements were performed using a substrate solution at pH=7 as reference, to check the response of the apparatus.

## Results and Discussion

The association constants ( $K_{\text{ass}}$ ,  $M^{-1}$ ) could be determined by UV-visible and fluorimetry obtaining values of 190 and 123 for **CF** and 350 and 644 for **CY** with CD and HP- $\beta$ -CD respectively. The values of the quantum yield ratios ( $\Phi_{\text{complexed}}/\Phi_{\text{free}}$ ) were 1.30 for **CY** but 7.02 and 9.48 for **CF**. The detection limits expressed as a limit concentration ( $C_L = \text{ng/mL}$ ) were determined employing the corresponding analytical and statistical methods. Notable enhancement of these limits was achieved for the compounds studied.

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## References and Notes

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2. Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Great Britain, 1991.
3. Li, S.; Purdy, W.C. *Chem.Rev.* **1992**, *92*, 1457.
4. Partial results obtained by Pablo A. Hocsman and Fernanda Bresina during their professional training.