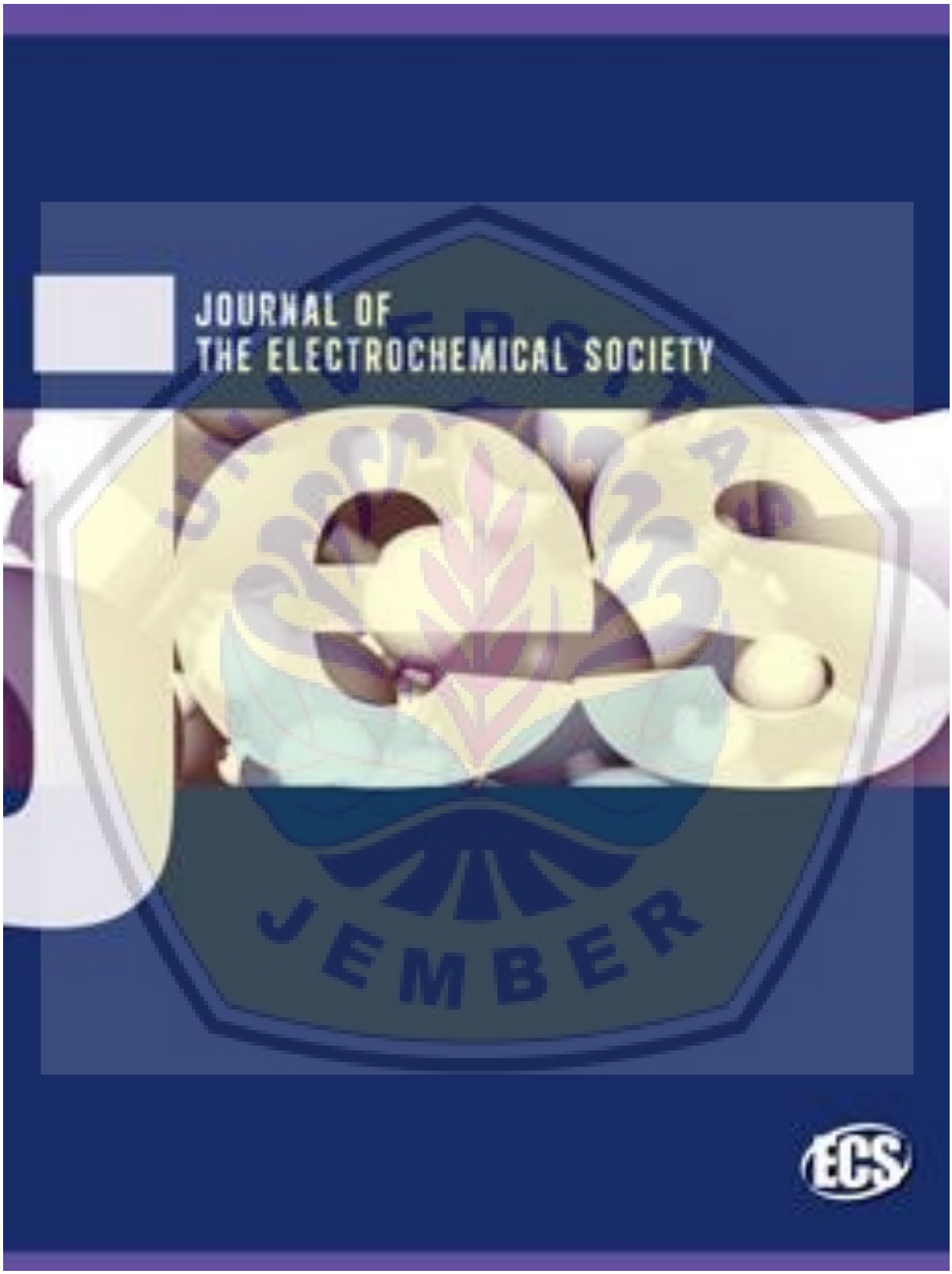

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Communication—An Optical Fiber Biosensor Based on a Lab-on-a-Tip Approach for User-Friendly Carbosulfan Detection in Vegetable Samples

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The use of a disposable pipette tip was studied to create a lab-on-a-tip approach. The configuration of a pipette tip, fiber optics, and paper-based biosensor show the compatibility of creating a novel one-shot optical biosensor for carbosulfan as carbamate pesticide. Under optimal experimental parameters, the lab-on-a-tip could detect carbosulfan in the linear range value of 10–22000 μg l^{-1} with a detection limit value of 10 μg l^{-1}. The results show good agreement with the HPLC method.
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The search for new materials or platforms to be integrated into sensing design and devices is an interesting topic in sensor development, particularly a user-friendly and integrated device that no need for sample treatment and expertise. For this purpose, a pipette tip can be used as a novel approach in sensor development. For example, a pipette tip was developed as a pool optode for Hg (II) ions sensing.[1] A pipette tip containing amine-functionalized sol-gel to enrich and purify phosphopeptides called a "lab-in-a-pipet-tip" was employed for mass spectroscopy measurements.[2] Furthermore, a pipette tip was used as a lab-on-a-tip to create an electroanalysis system for Cu(II) ions detection.[3] Here, a pipette tip can provide a sensing system for field application. Furthermore, it can be combined with other materials, such as paper and cotton. Generally, like lab on a chip (LOC),[4,5] lab-on-a-tip (LOT) can be presented as a sensing platform where one or several tools integrated on a miniaturized single tip,[6] and detection can be done by electrical, optical, or mechanical techniques. However, LOT is in infancy and typically developed for a single analyte, but its potential to be developed for multiple analytes is promising that can be integrated with imaging, diagnostics, and therapeutic function.[6]

In the case of a paper-based sensor, it allows providing portable devices that are simple, flexible, and low-cost.[7] This low-cost technology employs hydrophilic paper to create hydrophobic channels by patterning.[8] It is introduced to the device to examine a sample solution and flowed through a sensing zone by capillary without external power.[9,10] Among these techniques, the most widely used is colorimetric detection. Since a color change can be detected via ligand-analyte interaction.[11,12] The main advantages of the paper platform are (i) adsorption properties; (ii) capillary action; (iii) high surface to volume ratio; (iv) suitable with various samples; (v) allow immobilization of biomolecules (e.g., enzyme, proteins, and antibodies),[13,14] very light and readily available.[15] Moreover, paper allows to transport and absorption of reagents within its substrate, without the need for reagents handling, and simple disposal by incineration, and simple fabrication (e.g., wax printing) at a low-cost.[16]

In this work, we propose a novel concept in fiber optic sensors employing a pipette tip, by adopting as the optical cell, where the paper-based biosensors attached inside a tip wall to perform optical detections via optical fiber. The LOT is highly portable, and allowing both to load a sample and to react with the biosensor inside the tip, and provides the user a laboratory system. Furthermore, it allows using very low sample volume to be detected, reducing the waste that is often produced in the automatic detection, such as flow analysis.[17,18] Herein, the carbosulfan as carbamate pesticides were selected as an analyte. Compared to the other optical biosensors for pesticides, such as biosensor based on the recovered fluorescence of carbon dots-Cu(II) system,[19] lab-on-a-drop,[20] colorimetric and phosphomimetic dual signaling strategy,[21] and GQDs-MnO2 based assay with turn-on fluorescence,[22] this approach offers simple and user-friendly pesticide detection in real samples, such as vegetable samples. Moreover, it can easily be suited to other platforms (e.g., polymeric membrane), other analytes, or different sensing techniques, such as electrochemical[3] or mechanical techniques.[6]

Experimental

Paper-based biosensor fabrication.—The paper-based biosensor was fabricated using filter paper (Whatman, cat no 1001–150) and shaped into a circle paper (7 mm diameter). The paper was then impregnated with polyvinyl alcohol (1%) for overnight to increase the bonding of paper with enzyme and reagent used, and to enhance enzyme activity in the immobilized phase[23,24] Afterward; the impregnated paper was completely dried at room temperature. The paper was then firstly immobilized with 2 μl acetylcholinesterase/AchE (EC. 3.1.1.7, Electrophorus electricus, 518 IU mg^{-1} solid, 1 mg AchE in 1 ml tris-buffer 7.5 mM, at pH 7.5), and left for dry at room temperature (25 °C). Secondly, 2 μl bromothymol blue (6000 mg l^{-1} at ethanol-water mixture (25% v/v)) was immobilized on the enzyme-paper to create a paper-based biosensor. After the biosensor was completely dried at room temperature (25 °C), it was ready to be integrated into the LOT or stored in chiller condition (~4 °C) for further use.

LOT set-up.—The experimental set-up consists of a pipette tip (100-μl plastic tips) containing a paper-based biosensor and micropipette (10–100-μl, Socorex, Germany). A circle piece of the paper-based biosensor (7 mm) was attached inside the pipette wall using double tape (Fig. 1A). Afterward, the sample was loaded into the tip and direct detected with the biosensor. This procedure allowed for sample delivery and detection of an analyte with increased reproducibility as the sample volume loaded in the fixed volume and fixed position when the analyte interacts with the biosensor membrane.

The reflectance measurements were acquired in the visible wavelength between 400–800 nm using a fiber optic portable spectrometer (USB 2000, Ocean Optic, USA). The inhibition measurement of carbosulfan was carried out by calculating the reflected intensity response according to Eq. 1. For simple measurement, the LOT was employed as a disposable, as it does not need for regeneration of the inhibited enzyme in this case. Moreover, the

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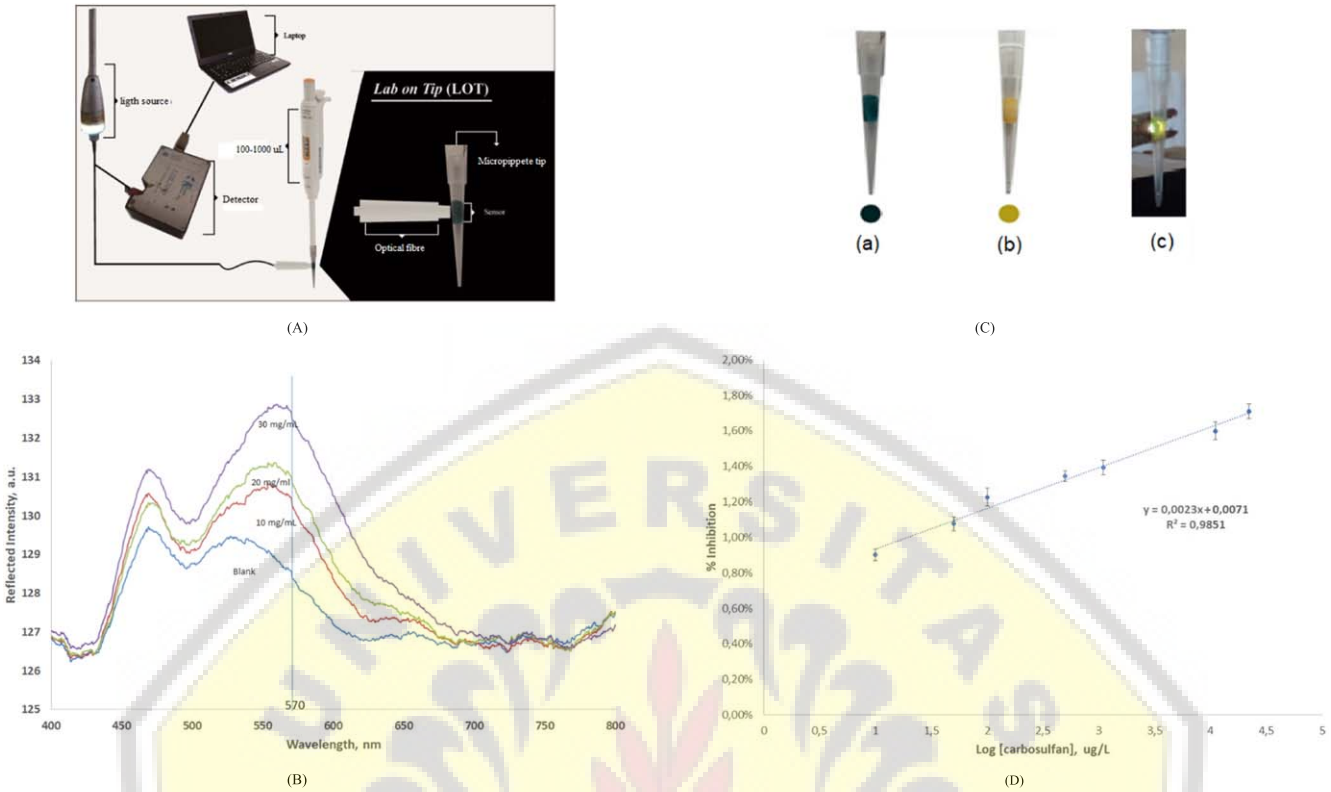


Figure 1. (A) The LOT set-up for carbosulfan detection in food samples. (B) Tthe spectra of LOT toward the substrate (acetylcholine), where the maximum wavelength was at 570 nm. (C) the color change of the paper-based biosensor, before (a) and after reaction with a substrate (b), and under fiber optic light (c). (D) Calibration curve of the carbosulfan concentrations (10–220 μg l^{-1}) vs % inhibitiom performed by LOT biosensor.

transparent plastic tip helped in the detection of the color change of the biosensor inside the LOT by a nude eye.

Inhibition measurement.—Initially, 100 μl of the substrate (ACh) at a tris-buffer solution (pH 7.5) was loaded into the LOT to determine the enzyme initial activity, i.e., absence of inhibition (*Eo*), and drained out. The carbosulfan solution (100 μl) was loaded into the LOT. After optimized inhibition time, the sample solution was drained out, and the residual enzyme activity was obtained by a substrate (ACh) loaded into the LOT, and the percentage inhibition (%*I*) was calculated according to the following equation:

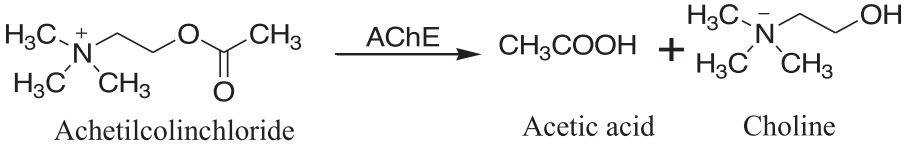
$$\text{Inhibition}(\%I) = (Eo - Ei)/Eo \times 100\% \quad [1]$$

where *Eo* and *Ei* are the reflected signal intensity for substrate and inhibitor plus substrate, respectively.

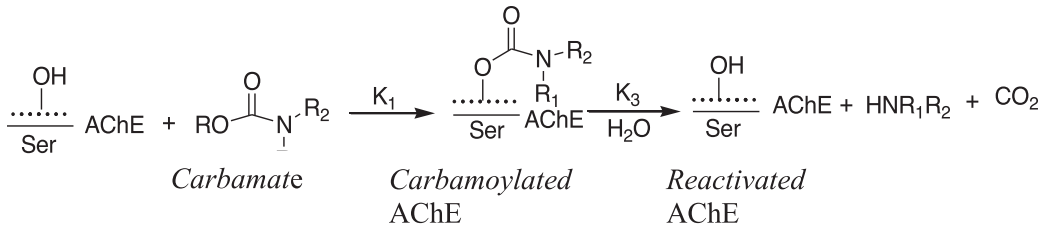
Real sample preparation.—The vegetable samples (lettuce, cabbage, and tomato) and rice samples (organic and non-organic rice) were collected from the traditional market at Jember-Indonesia. Each sample was prepared according to Kuswandi et al.,[25] with slight modification. The sample was crushed using a mortar and a sample portion (0.5 g) was taken for pesticide extraction. Then distillate water was added to the sample until the volume was 10 ml. Afterward, the mixture was ultrasonicated for 15 min followed by centrifugation at 3000 rpm for 15 min. The filtrate was taken for carbosulfan detection using the LOT. While for HPLC protocol, the crushed sample (0.5 g) was added with methanol until the volume was 10 ml. Then, the solution mixture was ultrasonicated for 15 min, then centrifuged at 3000 rpm for 15 min. The filtrate obtained needs to be filtered by the filter membrane (PTFE, 47 mm, pore size 0.20 μm, Shimadzu, Japan) before it can be injected into an HPLC system.[26] Shimadzu HPLC system used consist of SPD 20 A UV–vis detector, an LC 20AD isocratic pump, and a C18 column (4.6 × 250 mm, 4 μm, 100 Å), controlled by LC software.

Results and Discussion

The biosensing scheme obtaining from a paper-based biosensor towards carbosulfan can be described below. In the uninhibited biosensor, a pH change caused by the acetic acid produced during the enzymatic reaction as given in Eq. 2 was measured as the blank signal. While the inhibited biosensor, a pH change is inhibited by carbosulfan, was measured as the inhibited signal. As a complete pesticide detection, a net of pH change before and after inhibition of the AchE was calculated. Here, the AchE inhibition corresponds to the acylation of the serine–OH in the AchE active site by pesticides.[25,27] The biosensing scheme using AchE is similar to the enzyme-substrate reaction, whereby a Michaelis enzyme–pesticide complex is first formed, then followed by the transfer of the pesticide acyl groups to the serine–OH of the enzyme, along with the side product (HNR_1R_2) release.[27] Thus, the AchE inhibition by carbosulfan is presented as Eq. 3:



[2]



[3]

According to the scheme, to create the sensitive biosensor response toward carbosulfan, the paper-based biosensor needs to be well constructed, including acetylcholine used as a substrate, the maximum wavelength used for the reflectance measurement, and inhibition time used in the LOT need to be optimized. Using various substrate concentrations, the spectra measurements were performed. According to Fig. 1B, the maximum wavelength was found at 570 nm. To select optimum substrate for biosensing process via enzymatic reaction, the various concentration of acetylcholine was tested in the range 10,000 −50,000 μg ml^{-1}, where the substrate concentration was optimum at 40,000 μg ml^{-1}. Moreover, this color change could also be detected visually by the naked eye (Fig. 1C), so it is open-up for using another detection, such as colorimetric analysis using a smartphone via the App. (e.g., imageJ,[28] and color grab[29]). To detect a very low concentration of carbosulfan as an inhibitor, the low carbosulfan residue (100 μg l^{-1}) was tested. Here, the inhibition time was tested between 5–25 min, and 15 min was found to be optimum.

In order to detect carbosulfan at trace concentration (μg l^{-1} or ppb), it was tested at low carbosulfan concentration (10–22000 μg l^{-1}) using the optimum parameters, and the calibration curve was given in Fig. 1D as a log [carbosulfan] vs %I (percentage of inhibition), where the linear equation was %I = 0.223 log [carbosulfan] + 0.0071, with the correlation coefficient (r) value of 0.993. Based on this linear curve, the limit of detection (LOD) was calculated to be 10 μg l^{-1}. This LOD values was lower than previously reported work[25,27] and allowed pesticide detection within the maximum pesticide residue (50 μg l^{-1}) allowed by the Indonesian Government.[30]

Based on this calibration, the reproducibility for three consecutive days toward 100 μg l^{-1} carbosufan was found at 99.35 μg l^{-1} with reproducibility was 5,17% (RSD), and this value fulfils the required reproducibility value (RSD <11%).[31] While the recovery value (%) was found to be 91.79%, that meets the recovery value needed (80%–110%).[31] While for interference studies, it was focused on the compound that presents in food sample that may interfere the biosensing, i.e., quercetin and amylum, as they present at high concentration in the food sample, such as vegetables, and rice respectively. Herein, it was found that no interference from these compounds up to a ratio of 1: 100, since the interference was <5%. The biosensor lifetime can be used up to three days when it is stored at room temperature, as it retained 85% of its activity. It produces reproducible measurements for up to 1 month when it is stored in a chiller (4 °C) and up to two months when it is stored in cold storage (0 °C). Afterward, it gradually deteriorates due to the biosensor activity was reduced by more than 20% of its response.

Table I. Results of carbosulfan detection in the food samples between the LOT vs HPLC.

Sample	*Lab on Tip* (μg l^{-1})	HPLC method (μg l^{-1})
Lattice	980 ± 4.04	1010 ± 1.82
Cubbage	1330 ± 2.31	1368 ± 1.03
Tomato	510 ± 5.21	530 ± 1.04
Organic rice	870 ± 3.51	752 ± 1.05
Non-organic rice	710 ± 4.64	680 ± 1.20

The LOT applicability was tested toward vegetable samples and rice samples, then the results were compared with the HPLC as the reference method. The HPLC was performed using methanol as a solution, with acetonitrile: H_2O (80:20) as eluent using flow-rate at 1 ml min^{-1} and UV detector at 275 nm.[32] The samples were spiked with carbosulfan at five different concentrations, 500, 750, 1000, 1250, and 1500 μg l^{-1}, and the results are summarized in Table I with three replicate measurements. The linear regression analysis provided the correlation data indicates a good agreement between the two methods (R^2 = 0.964).

Summary

The use of a disposable pipette tip to create the novel approach of lab-on-a-tip has been developed. The proposed biosensor shows the compatibility of creating a novel one-shot optical fiber biosensor with simple operation. The simple procedure involves sample loading into the tip, and reacted 15 min as inhibition time, then added with the substrate. In this biosensing scheme, the indicator color change from blue to yellow will depend on the carbosulfan concentration as an inhibitor. The color change in the tip can be detected by fiber optic using a reflectance mode. The lab-on tip applicability can be used for other types of optical sensor membranes, such as PIM (polymeric inclusion membrane), etc., and various target analyte.

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