

**SPIROPYRAN MODIFIED PDMS MICRO-FLUIDIC CHIP DEVICE FOR PHOTONICALLY CONTROLLED
SENSOR ARRAY DETECTION OF METAL IONS**

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Micro-fluidic chips are particularly attractive in biological and life sciences for analytical purposes because they provide a convenient small platform for rapid analysis and detection [1]. Using micro-fluidic devices for the determination of ions emerges as a potential solution to some of the challenges not overtaken by conventional techniques e.g. atomic absorption, inductively-coupled plasma-optical emission, mass spectrometry and ion-selective electrodes [2]. For example, these devices can integrate complex sample handling processes, calibration, and detection steps into a compact, portable system. Moreover they require small sample volumes (low μl or nL), consume little power, and are easily constructed for multi-analyte detection, either through multiple parallel fluidic architectures or by using arrays of detection elements.

Organic photochromic compounds like spiropyrans are particularly interesting targets for the development of new approaches to sensing since they offer new routes to multi-functional materials that take advantage of their photo-reversible interconversion between two thermodynamically stable states (a spiropyran (SP) form, and a merocyanine (MC) form), which have dramatically different charge, polarity and molecular conformations. Furthermore, they can be easily incorporated into membranes for improved robustness and ease of handling [3], but from our perspective, most interesting of all, they have metal ion-binding and molecular recognition properties which are only manifested by the MC form. Based on the coordination-induced photochromism characteristic of the MC form, spiropyrans have been employed as molecular probes for metal ions and organic molecules [4].

In this abstract, we show how through integrating the beneficial characteristics of micro-fluidic devices and spiropyrans photoswitches, a simple and very innovative chip configured as an on-line metal ion sensor array can be realised (Figure 1). The micro-fluidic device consists of five independent $94\ \mu\text{m}$ depth, $150\ \mu\text{m}$ width channels fabricated in polydimethylsiloxane. The spiropyran 1'-(3-carboxypropyl)-3,3'-dimethyl-6-nitrospiro-1-benzopyran-2,2'-indoline (SP-COOH) is immobilised by physical adsorption directly on ozone plasma activated PDMS micro-channel walls. When the colourless, inactive, spiropyran coating absorbs UV light it switches to the highly coloured merocyanine form (MC-COOH), which also has an active binding site for certain metal ions. Therefore metal ion uptake can be triggered using UV light and subsequently reversed on demand by shining white light on the coloured complex, which regenerates the inactive spiropyran form, and releases the metal ion. When stock solutions of several metal ions (Ca^{2+} , Zn^{2+} , Hg^{2+} , Cu^{2+} , Co^{2+}) are pumped independently through the five channels, different optical responses were observed for each metal (Figure 2), (i.e. complex formation with metal ions is associated with characteristic shifts in the visible spectrum), and the platform can therefore be regarded as a micro-structured device for online multi-component monitoring of metal cations.

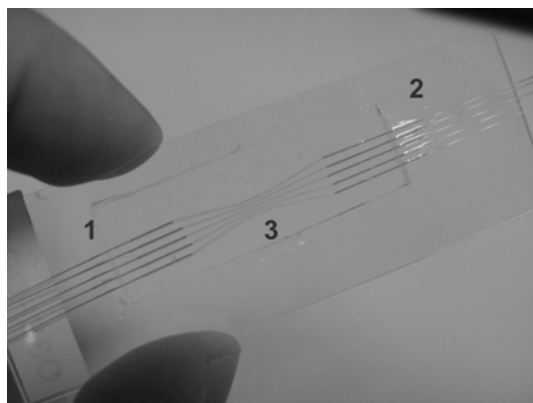


Figure 1. PDMS/glass hybrid micro-fluidic device (3.5 x 1.5 cm); **1** and **2** are the inlets and outlets respectively; **3** is the observation area.

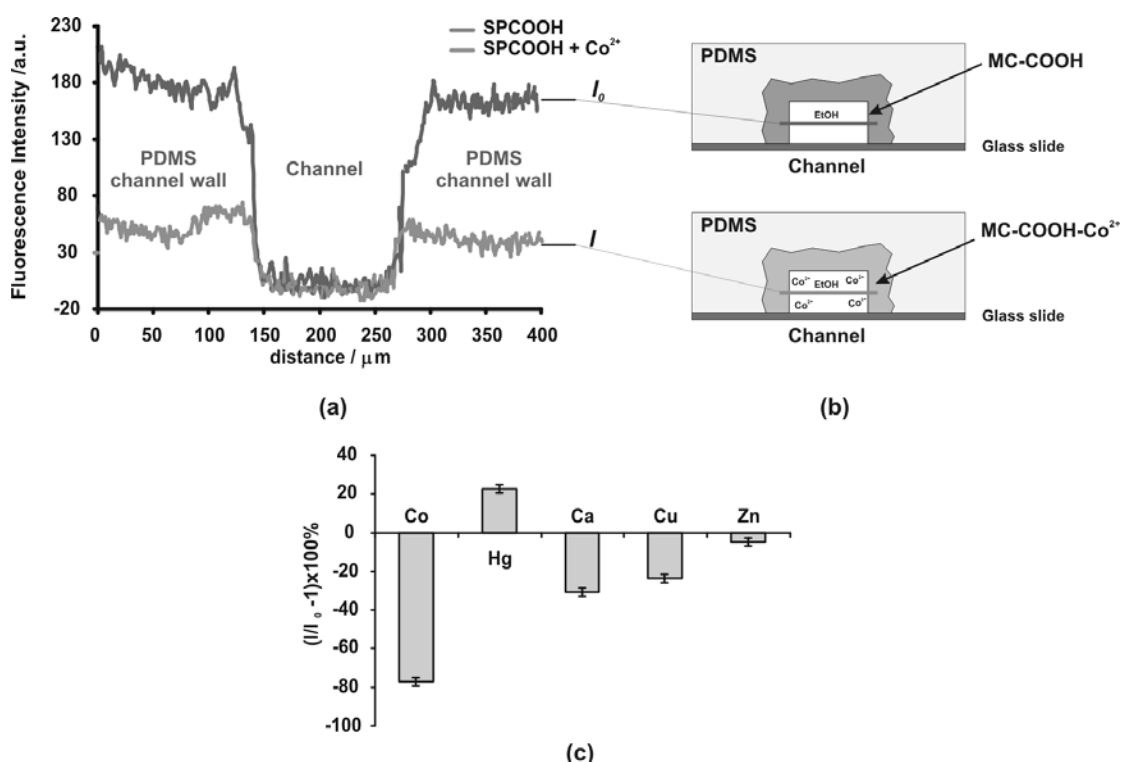


Figure 2. a) Fluorescence intensity of the MC-COOH form adsorbed in the PDMS channel walls in the presence of 10^{-3} M cobalt (II) metal ion solution in ethanol, (I) and fluorescence intensity of the MC-COOH form adsorbed in the PDMS channels walls in ethanol, (I_0). **b)** Schematic representation of a chip channel showing the MC-COOH form physisorbed inside the PDMS channel walls; lines represent the location where experiments were carried out. **c)** Relative fluorescence intensity of the PDMS channel walls in the presence of different 10^{-3} M metal ion solutions in ethanol. The experiment has been repeated three times and the fluorescence intensity error is in the range of ± 10 a.u.

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