

# Design and Development of Microfluidic Platform for Water Analysis

S. Grover\*, A. Deshpande\*, T. Ravindran\* and J.N. Krishnan\*

\*Department of Chemical Engineering, BITS Pilani, K.K. Birla Goa Campus, Goa 403726, India

[jegathak@goa.bits-pilani.ac.in](mailto:jegathak@goa.bits-pilani.ac.in)

## ABSTRACT

In this paper, a microfluidic device is designed for identifying and quantifying the amount of heavy metal ions present in water. The design consists of four modules: the sample inlet, mixing, detection and separation module. Integration of these modules into a microfluidic device provides a platform for entrapment of heavy metal ions present in the water sample. Serpentine channels with 300  $\mu\text{m}$  of width were chosen for the mixing module whereas detection module was made wider with 3 mm of width for ease of detection. The separation module consists of 'Y' shape with a width of 300  $\mu\text{m}$  so that streams could be separated and collected at the outlet. A photochromic compound, Spiropyran, is used for metal ion detection. Spiropyran changes to its polar and colored form, merocyanine, under UV light which acts as an optical switch entrapping metal ions. This research provides a powerful tool for the selective detection of heavy metal ions both qualitatively and quantitatively.

**Keywords:** Microfluidic Device, Spiropyran, Merocyanine, Photochromic compound, Heavy metal ions.

## 1 INTRODUCTION

Simple, cost-effective water analysis facilities are essential in developing countries like India. Heavy metal ion contamination is one of the major causes of chemical pollution. According to the United States Environmental Protection Agency, the permissible limits for ions like copper, arsenic, chromium and lead are 1.3, 0.01, 0.1, 0.015 ppm respectively. In general, characterization techniques such as atomic absorption spectrometry, inductively-coupled mass spectrometry involve huge machinery, inflated costs and large sample requirements for analysis of heavy metal ions. Microfluidic technologies for water analysis allow us to achieve precise environmental analysis. The advantages of microfluidic devices include the potential for on/offsite monitoring with low sample and reagent consumption and rapid detection of compounds.

Conventional metal removal techniques involve formation of complexes and ion exchange. Although these techniques are effective and well established, there are problems associated with them. Apart from the size, complexity and cost of such equipment, a major problem is that complexation requires the use of organic ligands which often cannot be reused. Hence the development of reversible metal chelation agents in which chelation can be switched on and off by exposure to light of different wavelengths is being increasingly studied.

Spiropyrans are a class of photoactivable compounds. Spiro compounds are a well known class of dyes that exhibit interesting photochromic functionality in that their structure changes reversibly with UV/visible irradiation. Spiropyrans are composed of two heterocyclic parts linked together by a tetrahedral  $\text{sp}^3$  spiro carbon atom [1]. Irradiation of a spiropyran with UV light induces heterolytic cleavage of the spiro carbon-oxygen bond, producing the open form of the ring, the intensely coloured merocyanine. The reversibility of the process offers a unique advantage that allows for the reuse of device as ion accumulation does not result in deposition or manipulation of the device.

Metal ions can also influence the change of spiropyran to merocyanine form. Metal ions have the capacity to break the C-O bond to form the open ring merocyanine form [2]. This result gives us another powerful tool which can be used to develop a sensor for heavy metal ion detection.

In this paper, a sophisticated microfluidic device which can be used as a sensor with the use of photochromic compounds like spiropyran is designed. A standard method to measure and characterize microfluidic components and fluidic properties of internal flows has not yet been established. The hydraulic resistance of a channel being a measure of its opposition to the passage of a fluid flow, is an important parameter for design of microfluidic devices that need to control the transport of fluid with high reliability and accuracy. The result is a microfluidic device that has the ability to detect heavy metal ions qualitatively and quantitatively.

## 2 DESIGN CONSIDERATIONS AND DEVELOPMENT

Here in this study, a microfluidic device which could detect heavy metal ions, perform efficient reagent mixing, facilitate ease in detection and a scope for separation is built. Many configurations have been studied in order to incorporate chaotic mixing of two or more fluids within a device. A serpentine channel along with herringbone structures incorporated within the walls of the channel, was used by Kim et.al, in their device for pre-concentration and detection of copper using copper-chelating alginate beads [3]. Usui and Fujii, fabricated a PDMS microfluidic device for measuring small amounts of Mn in seawater. The device took advantage of the catalytic properties of  $Mn^{2+}$  during the reaction of luminol with  $H_2O_2$  producing chemiluminescence which was detected using a photomultiplier tube. The device fabricated using SU-8 moulding, included a serpentine channel structure for mixing the reagents with seawater within the detection area of the PMT [4]. Kou et. al., designed a device which involved multiplexing, that is, parallelization of processes for simultaneous detection of Pd, Cu and Cd ions. The device had the inlet divided into three parallel channels, a Y-shaped micro-mixing zone followed by herring-bone integrated walls in a serpentine channel for chaotic mixing. Three different chemosensors were added through the bottom allowing for simultaneous detection of Pb, Cu, and Cd ions [5]. A device on fluorimetric lead detection using microfluidics was developed Zhao et.al. which used a selective and sensitive molecular sensor for lead. The sample and the sensor were injected via Y-shaped channels for mixing followed by mixing in a serpentine channel with herringbone patterned base. Formation of complexes leads to fluorescence that was captured by a PMT [6].

Although efficient mixing can be achieved using other passive mixing techniques such as construction of weirs; such techniques require increased sensitivity and precision for fabrication thereby increasing the cost. Therefore the most efficient way of performing mixing would be using two (or more) channels that converge in a Y-shape. This may be followed by a serpentine channel that would increase the overall length of the channel on the chip

providing more passage for better diffusion. Additionally, as demonstrated by Usui and Fujii, dividing an input stream into two parts which then merge to meet another input stream perpendicularly is also a good design to initiate

mixing. All such designs can be incorporated for efficient mixing of the sample and reagents.

Based on the literature survey discussed previously, the common dimensions in conjunction with the operation expected and size limitations were chosen. It was decided to fix the depth of the channel as  $100\mu m$ . The width of the channel was fixed at an intermediate  $300\mu m$ . Following the logical sequence of operations in the laboratory, it was expected that the first operation to be performed on the chip after injection of the various reagents would be effective mixing. Numerous examples [3]-[6] have been discussed before that suggested the usage of serpentine channels. One of the designs [4] even utilized the initial division of the inlet fluid into two streams which simultaneously merge with the second input for better mixing. Both these designs were incorporated to form mixing section of the channel. The inlet diameters were set as 1mm. After the mixing zone, the detection region is needed for optical detection of ions in the sample dependent on the reagents used for their reaction. The Y-shaped separation region was designed in which the upstream fluid is divided into two channels kept at an angle of 60 degrees (figure 1).

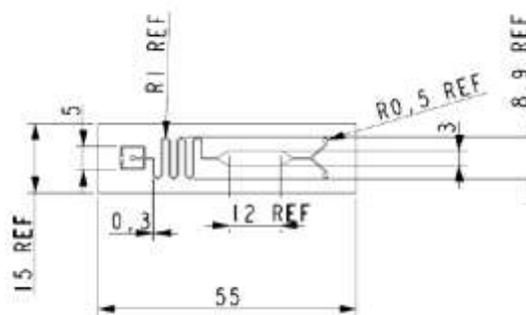


Figure 1. The 2-D design of the microfluidic device

The hydraulic resistances for each part of the device are important as they offer information on the resistance to internal flow [7]. These were calculated using the equation (1) given below:

$$R = (f Re) \mu L / 2D^2 A \quad \text{----- Equation (1)}$$

Where R is the hydraulic resistance, f Re is the friction constant and D is the hydraulic diameter. The microfluidic devices were made using CNC micromilling in PMMA using appropriate end mills.

### 3 SIMULATION STUDY

Simulation studies were conducted for obtaining the velocity and pressure profiles using COMSOL Multiphysics®. These were performed to understand the type of flow in the channel and verify occurrence of any efficient mixing. These would also provide us information on the chance of leakage in the device due to high pressures. Figure 2 shows the velocity profile of the flow when fluid is injected at 10 µl/min. Navier-Stokes Equation and Fick's law was used with boundary conditions being injection velocity and 'no slip' at the walls. Figure 3 exhibits the concentration profile of copper ions.

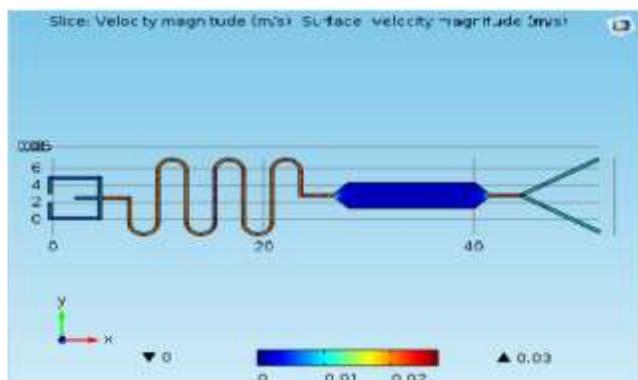


Figure 2. Velocity profile of the fluid flow

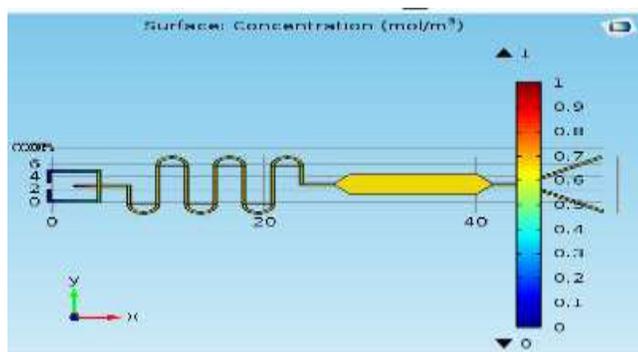


Figure 3. Concentration profile of Copper ions (mol/m<sup>3</sup>)

### 4 DETECTION SCHEME

The method that is used in this paper involves the use of the photochromic compound Spiropyran. Metal/UV induced activation of Spiropyran is considered for use with the device. Figures 4 and 5 below shows the changes that take place in the device.

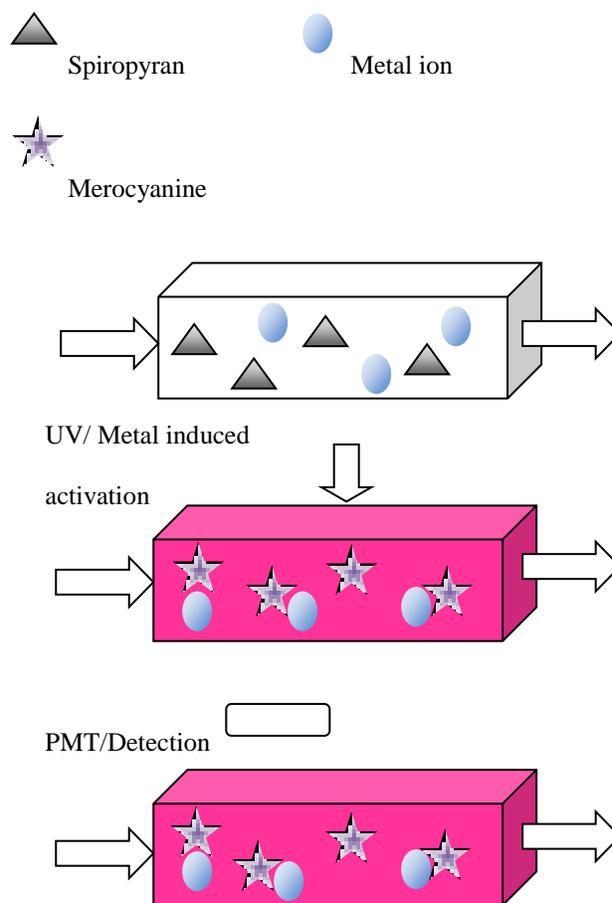


Figure 4. Schematic of the detection channel

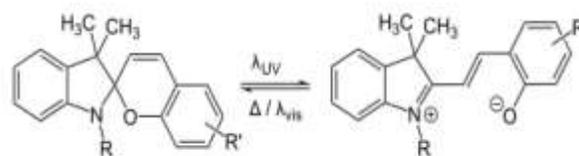


Figure 5. Scheme for Spiropyran to Merocyanine form

### 5 EXPERIMENTAL ANALYSIS

The experimental setup consists of a programmable syringe pump obtained from Braintree Scientific which can hold two syringes upto 60 ml each, and can dispense continuously at pumping rates ranging from 6 µl/hr to 1200

ml/hr. The fluids from the pump are directed to the device through tubes for analysis under the optical microscope STEMI 2000C, which was obtained from Carl Zeiss.

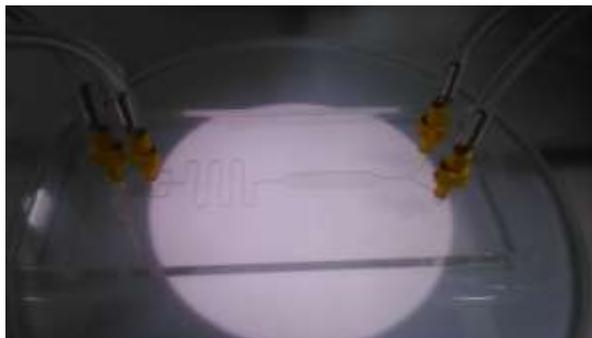


Figure 6. The image of microfluidic device

The concentrations of spiropyran and copper sulphate were prepared according to the study done by Nordin et al.[2]. All these solutions were stored in dark environment. The pumping flow rate used for both sample and reagent was kept the same at 10  $\mu$ l/min. The microscope is focused on the detection section. Figure 7 shows the experimental setup.



Figure 7. Experimental setup

## 6 RESULTS AND DISCUSSION

In this study, a device that can successfully detect heavy metal ions has been developed. The device designed is easy to use and portable which gives it significant advantage over the other conventional methods. It also has the potential to be used to quantitatively measure the ion concentrations. The simulation studies show that the velocity at the centre of the detection section is 0.0252 m/s which confirms that there will be no stagnation. The pressure profile confirms that there will not be any leakage

and bubble formation. The concentration profile in figure 6 shows the variation in concentration of Cu ions ( $10^{-3}$ M).

The experiments conducted showed that there was a colour change in the presence of copper ions. The colourless spiropyran changed to the intensely coloured merocyanine form for solutions with ion concentration  $10^{-2}$  M and  $10^{-3}$  M. Using a similar technique, presence of other ions in water can also be detected. Quantitative analysis is under progress. Photo multiplier tubes may be used for quantitative analysis as used in the study by Zhao et al. [6]. Thus, the device has the potential to detect, quantitatively as well as qualitatively the presence of heavy metal ions and separation of ions can be made possible in the near future.

## ACKNOWLEDGEMENT

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