A fluorescent oil detection device

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A FLUORESCENT OIL DETECTION DEVICE

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Mechanical Engineering

by

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B.S., Tsinghua University, P. R. China, 2006
M.S., Louisiana State University, 2010
May 2013
ACKNOWLEDGEMENTS

Several people have been instrumental in the completion of this project. First, I would like to specially thank Dr. Wanjun Wang, my major professor, for providing me with his extensive knowledge in microelectromechanical systems (MEMS) and microfabrication technologies. His infinite guidance, patience, and encouragement made this thesis possible. Furthermore, his academic manner and approach to problems will continue to influence me in my future studies.

I would also like to thank my fellow graduate students. Their intelligent discussions and valuable suggestions have helped me significantly throughout this project. Their friendship has also made working in the laboratory a lifetime experience for me.

Finally, I am extremely grateful to my dearest parents for helping me believe in myself and for encouraging me to pursue my doctoral degree in Mechanical Engineering. Their guidance, blessings, and love have brought me a long way in my life.
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ABSTRACT

On April 20th 2010, the largest offshore oil spill in U.S. history happened in the Gulf of Mexico. It is estimated total more than 4 million barrels oil spilled to Gulf of Mexico. More than two million gallons had been used. This had made the threat to coastal and sea ecosystem even greater and long term. Real-time monitoring is also a critical topic for oil spill response. In-situ monitoring devices are needed for rapid collection of real-time data.

A new generation of instruments for spilled oil detection is reported in this paper. The main hypothesis in this research is that the sensitivity of the new instrument based on a micro-fluidic-optic chip can be higher than its conventional sized counterparts. The adoption of the micro-fluidic-optic chip helped to miniaturize the sample extraction unit and also to integrate the optical detection on the same chip substrate. Only the monitoring and displaying unit and the power supply were external to the micro-fluidic-optic chip. In this way, the micro-fluidic-optic chip is replaceable and can be disposable. This also helps to eliminate the need for cleaning the fluidic components, which may be very difficult in micro-scales because of surface tension and flow resistances.

Liquid-Liquid extraction unit for sample pre-concentration and micro-optic components for fluorescence detection are the key microfluidic components and have been designed and fabricated on a single disposable chip.

In the Liquid-Liquid extraction system, different designs are compared and electromagnetically actuated micro-valves and peristaltic pumps have been designed and fabricated to control the aqueous sample fluid and the organic phase solution. In the micro-optic detection system, different designs are compared and an out-of-plane lens was designed, fabricated, and integrated to enhance the measurement sensitivity.
The experimental results of the integrated system have proved that the liquid-liquid extraction functioned very well and the overall measurement sensitivity of the system has been increased more than six hundred percent. An overall oil detection sensitivity blow 1ppm has been achieved. The research work presented in this dissertation has proved the feasibility of this novel oil detection instrument based on micro-fluidic-optic chip. This detection system may also be used for detection of other samples that can be measured based on fluoresce principles.
CHAPTER 1  INTRODUCTION

1.1 A historical environmental disaster in the Gulf of Mexico

In April 20th 2010, the largest offshore oil spill in U.S. history happened in the Gulf of Mexico because of the offshore oil-drilling rig explosion. Before it was capped on July 15th, oil leaked at a rate estimated between 35,000 and 60,000 barrels per day. Till the well was officially sealed in September 10, 2010 using cement, the total amount of oil spilled into the Gulf of Mexico was estimated to be about 4.9 million gallons, resulting in the largest accidental marine oil spill in world history.

The enormous amount of spilled oil spread over a large area of the Gulf, and formed large underwater plumes. Many strategies were used to help contain the leaked oil, which include removing the oil from the surface by skimmer ships, burning oil slicks at water surface, placing sand barriers at shorelines setting up containment booms to corral the spilled oil, and etc.. Among them, the primary strategy was to use dispersants to dissolve the floating oil on the surface and large underwater plumes under water.

Dispersants are chemicals used to break patches of oil into small droplets. With the help of ocean waves, these oil droplets can subsequently spread to larger area instead of concentrating in a small area. The hope was that larger area would have greater environmental self-healing capacity to expedite the recovery.

The dispersants used are of the Corexit family which is banned in the United Kingdom because of its toxicity. Though the federal government has ordered BP to limit the dispersant usage, it is estimated that more than two million gallons, a record amount of dispersants, had been used [1].
Table 1.1 presents the NOAA estimation of the percentage of spilled oil cleaned by using each of these strategies. There are three possible alternative estimations. However, there is plus or minus 10% uncertainty in the total volume. [2]

<table>
<thead>
<tr>
<th>Category</th>
<th>Estimate</th>
<th>Alternative 1</th>
<th>Alternative 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct recovery from wellhead</td>
<td>17%</td>
<td>17%</td>
<td>17%</td>
</tr>
<tr>
<td>Burned at the surface</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Skimmed from the surface</td>
<td>3%</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>Chemically dispersed</td>
<td>8%</td>
<td>10%</td>
<td>6%</td>
</tr>
<tr>
<td>Naturally dispersed</td>
<td>16%</td>
<td>20%</td>
<td>12%</td>
</tr>
<tr>
<td>Evaporated or dissolved</td>
<td>25%</td>
<td>32%</td>
<td>18%</td>
</tr>
<tr>
<td>Residual remaining</td>
<td>26%</td>
<td>13%</td>
<td>39%</td>
</tr>
</tbody>
</table>

From Table 1.1, it can be seen that there is still about 10%-40% oil still remaining in ocean.
During the two years after the April 20, 2010, the damage to the ecosystem in the Gulf of Mexico and surrounding coastal regions has been dramatic. While the ultimate impact on people and wildlife is beyond accurate account, the severity can be glimpsed from the numbers of killed wild animals reported by government agencies, which represents only a small fraction of total ecosystem damage. The ultimate toll on people and wildlife is still not fully understood.

1.2 Effect of the disaster

The accidental spilling of such large amount of oil as in the Gulf of Mexico is rare. But small spills happen frequently. The total volume annually is nevertheless quite large, and becomes a critical pollution issue. Canada and the United State have a system collecting the data of spill events. Statistically, most oil spills events reported are more than 4000L. In Canada, there are about on average 12 spills reports every day, and 100 spills reported in the US. There is 800 million tons of oil pollution worldwide each year. There are about 3 to 5 million underground chemicals and petroleum storage depots in the United States, and an annual average of about 1% of the warehouse will leak. Every year at least 500 to 10 million tons of oil get into water system through various means across the world. Oil spill offshore oil platforms operating sewage oil is estimated 50,000 tons at least a year; maritime accident oil spill volume is about 410,000 tons per year, total an estimated 100 per year to 2.6 million tons of oil into the sea of maritime transport operations and accidents [3].

1.2.1 Short term effects

This disastrous event has both short-term and long-term effects on the environment. Short-term effects became obvious quickly following the spill. Because the high concentration oil floating and underwater plume, the wildlife are directly poisoned to death, and the great number of deaths break the ecosystem chain. And it will require long time to rebuild. As reported
by the government, over 8200 birds, 1200 sea turtles, 150 marine mammals were collected. The number of dead fishes was uncountable. Experience of the similar disasters in the past indicates that mortality can be assumed to be four to 11 times higher than the number of dead bodies collected.

1.2.2 Long-term effects

The degradation of oil follows certain steps. First, when the oil initially leaked out, it would spread over the water and form a few millimeters thick layer of slick on the water surface. UV radiation in sunlight may oxidize some of the components in oil, a phenomenon called photolysis. The volatile components which were original in oil or created after the photolysis would evaporate quickly.

Some components will dissolve into seawater, known as dissolution. Most of them are low molecular weight compounds which are relatively toxic. This dissolution is small, representing less than 1% of the spilled oil. It will quickly dilute and degrade.

Most part of the oil is still dispersed into water as mentioned before, either broken up by waves or with the help of the dispersants. Normally, the waves break the oil into droplets of 0.01–1mm in diameters. With help of the dispersants, the droplets can be smaller. In such small sizes, they can be spread to large area and exist in water for a long period of time until being degraded by bacteria. The duration is affected by many factors in the environment and almost unpredictable.

Sinking is another phenomenon that usually happens. Because of the waves and ocean flow, there is large amount of clay or sand flowing in the seawater. They will carry the oil, accumulate to tar balls, and finally sink to the seabed.
Degradation of the dispersed oil depends on its concentration. It was hoped that dispersants can help the emulsion of oil spreading to larger area, and reducing the average concentration. Lower concentration means less hazard and faster degradation. But under certain sea conditions special emulsion may be formed. The droplets are incorporated into floating oil and a viscous substance called mousse will be formed. It is high concentration oil gathering with 20–80% seawater content. Mousse formation and stability normally depends on the specific type of oil. The high concentration oil of this substance means it will take a long time to degrade it and the affected area will suffer long-term ecosystem damage [4].

Only two years after the spill in the Gulf of Mexico, the long-term effect is yet to be well understood. But study of other similar spills may provide some clue, for example Exxon Valdez oil spill in 1992. Some studies still show the track of the oil remaining in the seawater after the disaster. Of course, the high temperature and sufficient sunshine in Gulf of Mexico may help the oil degradation.

The degrading rate of the oil in the water is not linear. Some studies show that only the early phases of transportation and transformation of the oil followed expectations [5]. After the accident in 1989, about 40 to 45% of the oil left on 787 km of PWS beaches; after 3-5 years, only about 2% remained in the same place [5]. It means the decaying rate of the oil was about \(-0.87/\text{year}\) (loss of 58% over a year), which fitted the expectation perfectly. And according to the expectation, the oil concentration on the oil spill spot will reduce to harmless level in 2-10 years. Of course, rebuilding the damaged ecosystem will take a much longer time. The evaluation of the recovery of the ecosystem is still controversial.

The rates of dispersion and degradation change with time. In 1992, it was estimated that 806,000 kg oil was left on PWS beaches. A 2001 survey showed that 55,600 kg still remained on
the PWS beaches. It meant that from 1992 to 2001, the decaying rate was only about 0.22 to – 0.30 per year (20-26% loss over a year). Perfect degradation process requires proper disturbance, oxygenation, and photolysis. They are all affected by many factors. Under severe conditions such as in this case, the degradation rate can be unexpectedly low.

Under normal condition in seawater, the oil usually can persist for half a year. If with favorable condition, it can be degraded to background levels much quicker. The highest concentration levels of oil are usually found in the spill center area, immediately under slicks or mussel where the oil is mixed into the water by waves or dispersants. For example, in Amoco Cadiz spill, immediately after the disaster happened, the concentration was about 3-20 g/L offshore, 2-200 g/L near shore, and up to 500 g/L in the estuaries. The spill happened on March 16th, 1978. The concentration on offshore decreased to background levels (2 g/L) by April, on near shore was about mid-May, and in the estuaries was no later than September. All were degraded under half a year. In the Argo Merchant case, the highest concentration could be as high as 250 g/L when the spill just happened. In February, two months later, samples were widely collected over Georges Bank at all depths, and the result by measuring concentration of these samples showed that the level of oil had decrease to 10-100 g/L. Measurement five months later showed continued decrease in concentration to 1-50 g/L. By winter, about a year after the spill, the concentration had fallen to generally less than 1 g/L, with occasional higher value up to 1-8 g/L in some places.

Some grained gravel shores have natural protection from the disturbances by waves with geomorphologic armoring by boulders and cobbles [6]. These places can be good sedimentary refuges for oil suppressing degradation and persisting. Some of oil was trapped in these places with mussel form. And these places happen to be where some wildlife feeding or laying eggs. By
this way, oil enters food chain with high concentration [7]. It was reported pink salmon embryos were exposed and killed through at least 1993 by the high concentration oil protected by the boulders and cobbles [8]. And other habitats including fish eggs and invertebrate predators (sea otters, sea ducks, and shorebirds) are weathered [9].

Because there are few continuing long period investigations on persistence in sediments after those critical spills, the data of the oil degradation track is scare. But there are still some data which can be taken as a small fraction of the persistence. In the Florida spill, oil was measured in sediments 12 years after the spill. In the Arrow spill, a study aimed to find out the remaining effect of the spill 6 years after spill found that the oil concentration in sediments was still as high as 10-25,000 μg/g. While death clams are average 650 μg/g of oil, living species were found to have 150-350 μg/g of oil in these sediments. For different species, the contamination of oil is different; the long-term effect by the oil is different. In the same case, Periwinkles were also found average only 12-18 μg/g. Spartina alterniflora, one kind of marsh grass, showed the surprisingly high contamination of about 15,000 μg/g from six oiled sites. Its contamination is near 70 μg/g even in well-controlled regime. In the case of Metula oil spilled in the Strait of Magellan in 1974, some researchers estimate the persistence of oil in sand and gravel beaches could be 15-30 years, and over 100 years for sheltered tidal flats and marshes. As oil last a long time in sediments and marsh, the impacts it brings to local ecosystems require to be further studied. [10]

1.3 Monitoring after spill is important

Real-time monitoring of the efficiency of dispersant application is a critical topic for oil spill response. According to the Special Monitoring Applied Response Technologies (SMART) protocol developed by U.S. Coast Guard, NOAA, U.S. Environmental Protection Agency, etc.,
when dispersants are used during spill response, the Unified Command needs to know whether
the operation is effective in dispersing the oil. In-situ monitoring devices are needed for rapid
collection of real-time data to assist the Unified Command with decision-making during
dispersant applications. According to the SMART protocol, the monitoring technique may need
to provide the concentration of spilled oil at multiple depths.

Another important issue of great concern is the long-term effects of the spilled oil to the
coastal water system. After applying the chemical dispersants, not all crude oil will be dispersed;
some oil slicks not dispersed may enter the costal water and inland water system due to tides,
winds and waves. These oil slicks tend to form ‘oil in water’ emulsion. The spilled oil tends to
dissolve slower in sediments and marsh than in seawater, because it has good protection for oil
from disturbance, oxygenation, and photolysis as mentioned before. Along the north coast of the
Gulf of Mexico, there are vast areas of marshes and wetlands with low salinity. This makes it
more difficult for any oil in it to dissipate and dissolve. It is therefore very important to keep
monitoring the leaked oil in the coastal water system, especially wetlands, and gather valuable
information not only for the evaluation of the impact of this oil spill disaster, but also for
building up a database for future studies of the long term effect of spilled oil on the wetland
ecosystem. The oil concentration monitoring in the wetlands has certain specific requirements
compared with the commonly-used in-ocean detection. First, since the oil in the wetland water
system is expected to be only a small portion of the dispersed oil and oil concentration can be
further lowered due to ecosystem restoration effects such as bio-degradation, oil detector with
ultra-low detection limit and sensitivity are required. Secondly, wetland has a more complicated
topography and is less accessible for large equipment, a low cost; in-situ, portable, system is
therefore keenly needed for monitoring oil concentration in wetland water system.
1.4 Oil components and detection technologies

The hydrocarbons in crude oil are mostly paraffin, alkanes, cycloalkanes and, various aromatic hydrocarbons; while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. The detail of each component is introduced as follows.

General formula of paraffin is $C_nH_{2n+2}$, a straight- or branched-chain molecule that can be gasses or liquids at room temperature, depending upon the molecules, for examples: methane, ethane, propane, butane, isobutane, pentane, and hexane.

General formula of Aromatics is $C_6H_5-\text{Y}$ (Y is a longer, straight molecule that connects to the benzene ring), which is ringed structures with one or more rings containing six carbon atoms, and alternating double and single bonds between the carbons. Typical examples are benzene, naphthalene.

General formula of napthenes or cycloalkanes is $C_nH_{2n}$, it is ringed structures with one or more rings containing only single bonds between the carbon atoms typically liquids at room temperature. Typical examples include cyclohexane, and methyl cyclopentane.

General formula of other hydrocarbons alkenes is $C_nH_{2n}$. It is linear or branched chain molecules containing one carbon-carbon double-bond, for examples: ethylene, butene. General formula of isobutene diene and Alkynes is $C_nH_{2n-2}$, which is linear or branched chain molecules containing two carbon-carbon double-bonds, such as acetylene and butadienes.

A wide variety of instrumental and non-instrumental techniques is currently used in the analysis of oil hydrocarbons, which includes gas chromatography (GC), gas chromatography mass spectrometry (GC–MS), high-performance liquid chromatography (HPLC), size-exclusion HPLC, infrared spectroscopy (IR), supercritical fluid chromatography (SFC), thin-layer
chromatography (TLC), ultraviolet (UV) and fluorescence spectroscopy, isotope ratio mass spectrometry, and gravimetric methods [11]. Fluorescence spectroscopy is one of the important techniques for on-site detection.

1.5 The theory of fluorescence generation

Certain chemical substances absorb and store energy from the outside, then get into the excited state. When they get back from the excited state to the ground state, the excessive energy will radiate in the form of electromagnetic radiation, i.e., emitting light. This is so called fluorescence. Fluorescence generation consists of three main processes, the molecular absorption of light energy, stimulation, and inactivation.

Absorption: When light travels through the material, certain frequencies of light will be absorbed and weakened. Because of the limited numbers and discontinuous energy levels of atoms, molecules or ions can only absorb two-level difference between the same or its integer multiple of the energy. For the absorption of light, it can only absorb photons of certain frequencies:

\[ E_i - E_0 = h\nu = hc/\lambda, \]

(1-1)

where \( E_i \) is absorbance substances in the ground state energy level, \( E_0 \) is higher energy level for the absorbance material, \( h \) is Planck (Plank) constant, \( \nu \) is the frequency of the light, \( \lambda \) is the wavelength of light, and \( c \) is the speed of light in vacuum.

Excitation: When the material absorbs the radiation of a certain frequency, the electron jumps from the ground state to the different vibrational levels of excited states, this process is known as excitation.
Deactivation of the excited state molecule: Molecule in the excited state is unstable. It will lose excessive energy and return to the ground state by the irradiative transition or non-irradiative transition deactivation process. Molecular level transition diagram is shown in Figure 1.1. When the appropriate wavelength of the excitation light is irradiated at a molecule, the irradiated molecule can absorb light and be excited to either level $S_1$ or level $S_2$. If the molecule does not undergo chemical decomposition, it usually returns quickly to the first excited states of the lowest energy level (Figure 1.1 $S_1\ V_0$ level), this process does not contain the radiation of light. The molecules on energy levels of the $S_1\ (V_0)$ are still unstable and will lose energy back to the ground state of the $S_0$ [12].

Therefore, the occurrence of the fluorescence has two necessary conditions: the first one is the molecule of the substance must have the same characteristic frequencies with those of the
irradiation light. Molecule’s characteristic frequencies are closely related to their structures. The occurrence of fluorescence must have an absorption structure. The second necessary condition is that the molecules must have high fluorescence efficiency. Absorbance material does not necessarily generate fluorescence if fluorescence efficiency may be too low, which is resulted from the absorbed energy consumption by collisions between the solvent molecules or solute molecules.

Excitation spectra: When an excitation monochromator is used, a fixed emission wavelength is scanned and radiated on the fluorescent material, light with different wavelengths are then excited. The fluorescence light generated by the fixed wavelength of the emission light is collected and passed to the detector to detect the corresponding fluorescence intensity. The curve of fluorescence intensity of the excitation wavelength can be recorded. Excitation spectra can be taken as identification of fluorescent material or record of appropriate choice of excitation wavelength during the fluorescence.

Emitting spectra: With the excitation light emission from the monochromator is scanned across a given range, the fluorescence intensity of each wavelength from the testing substance material corresponding to each excitation wavelength is measured and recorded. The recorded relation between fluorescence intensity and emitting wavelength is plotted and named as “the curve of the fluorescence spectra”. This property can be taken as the identification of fluorescent material.

1.6 Oil fluorescence

Almost all kinds of substances can absorb UV or visible light, but only a few compounds are fluorescent. Most of the fluorescent organic compounds contain aromatic rings, but not all of the aromatic compounds are fluorescence. Crude oil mainly contains alkanes, cycloalkanes and
aromatic hydrocarbons. Aromatics and their derivatives are oil fluorescence sources on which fluorescence spectrometry for measurement and identification is relied. Aromatic hydrocarbon is 25% to 70% of the total hydrocarbons of the oil, in which aromatic compounds containing conjugated double bond compounds are dominant. These compounds include benzene, naphthalene, anthracene, phenanthrene, fluoranthene, benzopyrene and other polycyclic aromatic hydrocarbons and their derivatives, and porphyrin compounds containing heavy metals. They all have unsaturated and π-electron conjugated structure and are the material bases of fluorescence detection for oil and its derivatives.

1.7 Current issues of fluorescence oil detection Instruments

Operators from the US Coast Guard Strike Teams have found problems during the operation of the Turner-10AU field portable Fluorometer (T-10AU) [13], which has been widely used in oil detection [14]. The device is bulky (13.39 in. × 21.65 in., weight – 34.5 lbs) and requires various accessories such as pump cables, power supply etc. The current standardization procedure for the Turner requires a standard fluoresce dye solution with large volumes. Replacement and repair of the instrument can be very expensive. The system is quite complex to operate and has poor sensitivity at lower density of oil. Because the instrument does not have an integrated sample extraction unit, sample has to be pre-processed manually using an external extraction kit (with a pipette, syringe, and additional volumetric glassware) to increase the oil density of the sample first, and then measured based on fluorescence detection principle. This increases the operation time and makes it difficult to operate, less portable, and therefore cannot be used as an in-situ detection tool. According to SMART Protocol [14], a new generation device is required.
1.8 MEMS application examples

Miniaturization and integration is the developing direction of the new generation device. Miniaturization in electrical and sensor applications brings smaller devices with stronger performance. Miniaturization and integration has become the feature of modern life. Many modern devices are the application examples of the miniaturization and integration technology.

Silicon-based micro-electro-mechanical systems (MEMS) are one of the most promising technologies in recent years. Fig.1.2 shows the major MEMS market in 2005 [15]. There are two major applications for MEMS devices, one is the actuation devices (actuators) such as Ink Jet Printer head or micro mirror device for projector, the other type includes all kinds of sensors. The market for microfabricated sensors has been growing exponentially. However each sensor application has its own specialties. Appropriate requirements, total performances of the system and the combination of other components have to be well considered depending on each application.

![Fig.1.2 MEMS market in 2005](image)

For current sensor applications, high precision and stability are limitations as the devices become ever smaller [16]. When sensor package sizes become smaller, noise density level becomes proportionally higher. Take the accelerometer as an example [15]:

\[
TNEA = \sqrt{BNEA^2 + CNEA^2},
\]  
(1-2)
where TNEA is total noise density equivalent acceleration, BNEA is Brownian noise equivalent acceleration, CNEA is Circuit noise equivalent acceleration from IC circuit.

\[ BNEA = \frac{\sqrt{4k_B T D}}{M}, \]  

(1-3)

and

\[ CNEA = \frac{\delta C}{S}, \]  

(1-4)

where T is the temperature, D is the air damping coefficient, \( k_B \) is the Boltzmann’s coefficient, \( M \) is the effective mass, \( \delta C \) is the capacitive resolution of IC, \( S \) is the sensitivity,

\[ S = \frac{2C_v M}{d \cdot K_{eff}}, \]  

(1-5)

where, \( K_{eff} \) is the effective stiffness of tether, both BNEA and CNEA are inversely proportional to effective sensor mass \( M \), the sensitivity \( S \) is proportional to \( M \). It means in theory that the smaller the size, the lower the sensitivity. Similarly for other application, if replacing the effective sensor mass with the effective sensor light source, it comes to the similar result for light sensor detection. To miniaturize the sizes while still maintaining the sensitivity of sensors to be the same, other measures have to be taken.

1.9 The research goal and my contributions

Real-time monitoring the efficiency of dispersant application is a critical topic for oil spill response as stated above. According to SMART Protocol, the new generation instruments should meet the following requirements: in-situ monitoring, with the lower detection limit in 0.1–1 ppm and upper limit at least 100 ppm, easily deployable and portable, simplicity of use,
high reliability and easier logistics, less maintenance and lower maintenance costs, and capable of being integrated with Windows operating systems and GPS.

A new technology for improved detection associated with oil spills is developed and a novel MEMS detection device is presented in this dissertation. The goal is to develop a highly sensitive and handheld instrument that can be used for in-situ detection of spilled oil. The device needs to have much higher sensitivity, lower cost, easier to operate and maintain, and with smaller size compared with the existing technologies. The applications of the instrument are not limited to oil detection and may also be used to measure any organic samples that can be measured in fluoresce detection principle.

The instrument is designed to have a built-in sample extraction/pre-concentration function to eliminate external sample preparation kit. The oil detection is based on fluoresce detection principle. In its heart is a disposable micro-sized detection cartridge with a built-in oil pre-concentration unit. It will also contain a micro-sized optic detection unit consisting of microlenses, micro-chamber for detection, and holders for optical fibers. The optic detection unit will be integrated on the same substrate as the sample pre-concentration to form an integrated micro-fluidic-optic detection cartridge. All the components on the cartridge will be passive with no power supply requirement. This micro-cartridge can be replaced easily and can be disposable. All the active components such as UV light source, photodetector, power supplies, etc., are outside the cartridge and thus, do not require replacement for each test. The micro-cartridge can be easily interfaced to these active elements. The micro-cartridge can be inexpensively fabricated through mass production using micro-replication method. It can potentially be disposable and eliminates the problem of cleaning and contamination as in permanently assembled fluidic devices. The components and test the device first on a small dimension bench top model to
demonstrate feasibility and then in the next step, assemble and design a hand held device from the tested bench top components for the implementation of a beta model.
CHAPTER 2 DESIGN OF THE MICROCHIP AND FABRICATION TECHNOLOGY

In this chapter, the general design of the proposed instrument based on fluidic microchip will be presented. The micro-fluidic-optic chip can be divided into three parts: an optical detection system, a peristaltic micropump and a liquid-to-liquid (L-L) extraction microfluidic system. All related fabrication technologies are introduced in detail in the following chapters.

From the discussion in Chapter 1, a new generation of instruments for spilled oil detection is needed. The new generation instrument should meet the following requirements:

1) With the in-situ sensing capability;

2) Satisfactory detection limits. The lower detection limit should be within 0.1 – 1 ppm and upper detection limit is at least 100 ppm;

3) Easily deployable and portable;

4) Simplicity of use. It should be simpler to operate than Turner, i.e., be easier to set up and standardize;

5) High reliability – New instrument must be robust since turner setup may vary from day to day and is sensitive to rough handling;

6) Easier Logistics – New instrument must have fewer components and must be lighter and require less logistics than the current system that requires two large boxes weighing 75-100 lbs each;

7) Requiring less maintenance and lower maintenance costs;

8) Capable of being integrated with Windows operating systems and GPS.

The key point in miniaturizing the physical sizes while still maintaining the sensitivity of sensors is to miniaturize the extraction processing and also to integrate the extraction and
detection on the same chip substrate. Only the monitoring and displaying unit, the power supply, and other parts need to be external. In this way, the sample handling and sensing units will be integrated on the chip itself and can be used as an independent and replaceable detecting head. There will only be a cable between the detection chip and the supporting unit (power supply and displaying). Another advantage is that one supporting unit can be used for several chips at the same time.

2.1 General design of the micro-fluidic-optic chip

The schematic design diagram of the in-situ oil detection instrument is shown in Fig.2.1. It includes two parts: microchip part (shown as yellow color) and supporting part (shown as grey color). The microchip is designed as a replaceable cartridge to avoid cleaning after use. The microchip can be replicated using micro-molding technology to save fabrication cost. It mainly includes three key microfluidic components, which are the liquid-liquid (L-L) extraction system, the micro optical detection system and the passive part of the peristaltic micropumps. The peristaltic micropump is specially designed and fabricated. The actuators of the peristaltic pump are designed to be right above the surface of the microchip, but not physically connected to the remaining part of the fluidic microchip. The actuators of the micro pump will have long working life. The rest microfluidic part of the pump is integrated in the microchip.

![Fig.2.1 System schematic of the oil concentration detection device](image)

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The operational principle of microchip is as follows. First the sample aqueous solution is imported into the microchip and pre-concentrated. The sample extraction/pre-concentration is based on a liquid-to-liquid (L-L) extraction principle, also named solvent extraction and partitioning. It is a technology commonly used in chemical engineering and other industries. The technology can be used to separate compounds, such as oil, based on their relative solubility in two different immiscible liquids, usually water and an organic solvent. It is therefore the most natural option for the system for extraction of the oil from the aqueous sample solution into an organic solvent, and then measured. In our design, the imported aqueous phase is extracted by an organic phase. Many researchers have proposed sandwich-structured microfluidic devices for L-L extraction applications [17-19]. In these designs, a porous hydrophobic membrane often used to separate the two flow phases. But in our application, the oil is not dispersed as solution, but emulsion. The droplet size of the oil is in the range 5μm-150μm. While the capillaries on the porous membrane are much smaller than that, it is about 1μm diameter. Therefore, a vertical fence wall is used in our design. To keep the stability of interface of the two flows, the fence wall will be selective surface modified.

The aqueous phase passed through one side of the L-L extraction continuously driven by an external pump. To increase the concentration of oil in the organic phase, it is designed flowing circularly on the other side of the L-L extraction system, so that the oil content in the organic phase can accumulate as the aqueous phase solution passes by. The peristaltic pump is almost the only option for both circular flow and separated actuators from the microfluidic system requirements. Many different designs for peristaltic micropumps have been reported [20-22]. But in these reports, the power of the actuators used is so weak that they can only drive flow in very shallow channels (5μm-10μm). In our applications, the channels are as deep as 600μm
and more powerful electromagnetic actuators are therefore needed. On the other hand, most researchers designed the micropumps on the same substrate as the microfluidic chip. The micro pumps and the microfluidic systems are therefore not separated. In this dissertation, a new design of peristaltic micro pump is presented, in which the actuators are isolated from the microfluidic system. In this design approach, the micropumps can be designed to have long working life but the microfluidic chip is designed to be disposable.

The pre-concentrated sample is then supplied to the fluorescence detection unit on the same substrate for measurement. The micro-optical detection system has an integrated microlens to boast the signal strength for improved sensitivity. Because of fabrication difficulty, most of the reported microlenses are the in-plane ones [23-25]. Fabrication of the out-of-plane microlenses is a critical problem because in most optical platforms, light transits in parallel with the substrates of the systems. A new fabrication process for the out-of-plane microlenses with controllable focal length is presented in Chapter 3. Components in grey color are supporting parts outside the microchip. The supporting components can be divided to three parts by their functions as shown in Fig.2.1. These supporting components, such as the monitoring and displaying unit, the power supply, and other parts, will be assembled using commercial products. Our goal was to develop a portable, easy to operate instrument with high sensitivity. Because the size of the microchip is much smaller than those of the supporting components, the size of the final instrument is primarily determined by the sizes of the supporting components. Sample acquisition and filtration was done in an off-chip manner. Syringe with filter was used to obtain sample from the testing point and deliver it into the on-chip sample reservoir. Other than this sample acquisition, other fluid handling procedures are finished by on-chip micro-fluidic components controlled by the peripheral electronic user interface. In the final instrument, there
will only be a cable between the detection chip and the supporting unit. The microchip and supporting parts are only connected with a pair of cable connectors. Therefore, the microchip can be independent and disposable but the supporting parts are the permanent parts of the instrument.

2.2 Fabrication technology

The fabrication of the micro-fluidic-optic oil detection chip was achieved using the combination of some of the common micro fabrication technologies, such as UV lithography of SU-8, PDMS molding process, micro cast with the PDMS intermediate mold, and PDMS to PDMS bonding. The detailed fabrication procedure is presented in the next several chapters. In this section, only the fundamental concepts will be introduced.

2.2.1 UV Lithography of SU-8

SU-8 is a negative resist commonly used in fabrication of high aspect ratio microstructures and devices. As a negative photoresist, when it is exposed to ultraviolet light, the exposed regions get cured and will remain after development while the unexposed regions are removed. It is also known for its excellent UV lithography properties and widely used in the fabrication of high aspect ratio microstructures and devices [26-28]. In addition, the exposed (and cured) SU-8 polymer has excellent physical and chemical properties, and is highly resistant to most chemicals and very stable in high temperature. Because of these advantages, UV lithography of SU-8 is one of the key technologies used in fabricating the spilled oil detection system presented in this dissertation. To explain how the technology is used, we will use the fabrication of high aspect ratio micro-columns as the example here. The basic fabrication process is as follows:

1. Wafer Cleaning. Clean up the wafer with water and acetone. After cleaning, the wafer is then heated up to 80 degree centigrade for more than 1 hour to evaporate water.
2. Resist coating. SU-8 resist, especially the SU-8 50 and 100 as used in our work, has high viscosity, therefore flows very slowly once poured on the wafer. Un-exposed SU-8 resist can be easily removed with solvents such as acetone or SU-8 developer (provided by MicroChem Corp.). The thickness of SU-8 resist depends on factors such as the viscosity of SU-8, spinning time and speed. The relationship curves between the resist thickness and these factors are readily found from the data sheets provided by the vendor of the resist, Microchem Corporation.

3. Prebake. The purpose of prebake is to evaporate the solvent from SU-8 resist. The backside of wafer needs to be carefully cleaned with acetone to prevent the wafer from to be stuck on the hot-plate during baking process. Big bubbles also need to be removed before pre-bake, otherwise air will be trapped in the resist and remain inside the resist after bake. Smaller bubbles can normally be removed during the pre-baking process. After prebaking, SU-8 becomes a solid layer on the wafer. The prebaking temperature has to be carefully controlled to prevent any residual stress in the resist and to achieve satisfactory lithography results. The relationship of temperature-time is shown in table 2.1. The only variable parameter is the dwelling time at 110°C. Generally, it is proportional to the thickness of the SU-8. For example it takes 6 hours for a resist of 600 μm and take 4 hours for resist with thickness of 400 μm. The ramping and dwelling times before and after the maximum temperature are chosen to slow down the temperature rising up and dropping down to reduce internal stress.

4. Preparation of lithography masks. The mask used in lithography is a piece of glass with desired patterns, which are normally made of a thin layer of chrome. The commonly used method of making mask is as follows: On one side of the glass, a thin layer of chrome is
deposited firstly, followed by a layer of AZ resist on the top. The AZ is a positive resist, which means the exposed part can be removed using some special chemical called developer while the unexposed parts remain. After drawing the pattern of the mask, the data file is entered into a PG (pattern generator) machine, which can then expose the AZ layer on top of the chrome according to the pattern. After exposure, the mask was placed in AZ developer for several minutes to remove the exposed parts. Then the desired AZ pattern is obtained on the mask. The mask is then placed in a chrome-etching solution to etch the chrome which is not covered with AZ resist. Finally the remaining AZ on the mask is stripped using acetone and a patterned layer of chrome is obtained on the mask.

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>Time</th>
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<tr>
<td>Ramp to 25</td>
<td>10 min</td>
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<td>2 hour</td>
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<tr>
<td>Ramp to 75</td>
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<td>75</td>
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<td>Ramp to 25</td>
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<td>25</td>
<td>2 hour</td>
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5. Exposure. Place the wafer into the UV station with the mask properly covered on it. During the exposure process, the ultraviolet (UV) light can only get through the transparent part of the mask and expose the SU-8 layer as expected. The exposure dosage is proportional to the thickness of SU-8. Further technical details related to the dosage can also be found from the user manual provided by Microchem Corporation.

6. Postbake. When SU-8 resist is exposed to ultraviolet light, it will generate an acid that will cross link the monomer, and the cross-linked resin is also named as SU-8 (which is where
the SU-8 got its name). After the UV exposure, the exposed wafer coated with SU-8 needs to be post-baked to improve the cross-link process, enhance the lithography quality, and minimize possible residual stress. The temperature set is shown in Table 2.2.

<table>
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<tr>
<th>Temperature (°C)</th>
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<td>Ramp to 25</td>
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<td>Ramp to 110</td>
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<td>Ramp to 75</td>
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<td>Ramp to 25</td>
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Development. After the post bake, the cross-link in SU-8 is almost completed, which means the SU-8 developer now can only remove the unexposed parts but not exposed parts. The development may take a longer time if the exposed wafer is placed in facing up position in developer. When the wafer is placed in the “facing-down” position (with the SU-8 side facing down vertically), the gravity helps to enhance the development process by allowing the developed chemicals to drop off and improve the circulation. The developed wafer needs to be carefully and slowly taken out from the developer to prevent them from mechanical damages caused by the developer fluid.

2.2.2 PDMS molding process

PDMS (Sylgard 184 Dow Corning) can be used in a molding process to make an intermediate negative pattern, which comes from a SU-8 master mold. The SU-8 master mold can be prepared by using SU-8 lithography process as introduced in section 2.2.1

The detailed steps of PDMS molding process are as follow:
1. Preparation of the PDMS mixture. The vendor of the PDMS pre-polymers offers two pre-polymer fluids, the base and the curing agent. They are usually mixed in a ratio of 10:1. If the base in the mixture ratio is increased, the final PDMS polymer would be softer. On the other hand, increasing the percentage of the curing agent would make the solidified PDMS harder. Therefore the exact ratio of the base and curing agent can be adjusted as needed to obtain the desired physical properties of the final PDMS polymers for different applications.

2. Stirring. The mixture of the base and curing agent needs to be stirred for several minutes to ensure complete mixing. The mixture can then be poured on the SU-8 master mold to form a certain thickness of PDMS layer. The thickness can be controlled by manipulating the weight of PDMS.

3. Eliminate the air bubbles. The wafer is then placed in a vacuum chamber for 20 minutes to eliminate air bubbles. And it also allows enough time for the PDMS mixture to flow flat and completely cover all the SU-8 microstructures on the wafer.

4. Cure the PDMS. The curing process is normally done by heating the PDMS mixture to 85°C for 3 hours or 100°C for 1 hour. The higher temperature and longer curing time are, the harder the PDMS becomes after curing.

5. Demolding Process. Peeling the PDMS off the master mold needs to be done carefully because of the vulnerable microstructures on it. Fortunately, the excellent flexibility of PDMS makes it very rare to have these structures damaged. This flexibility also makes it possible to replicate some very complicated structures and provides us opportunity to be more creative in our design.
2.2.3 Micro cast with the PDMS intermediate mold

The molded PDMS microstructures can either be used directly as functional devices, or for many times, as an intermediate mold to cast replica for batch production of microstructures or devices at a much lower cost and fast production cycle. Due to its excellent inadhesion property of the cured PDMS, almost any curable agent can be casting material. But the viscosity before curing should be low enough; otherwise it is difficult to eliminate the bubble. NOA 73 (Norland Products Inc., (Cranbury, NJ) or SU-8 are typical examples of the curable polymers. They are both low viscosity members in each of its family. The basic steps of micro-cast using PDMS intermediate mold are as follow:

1. Pour a calculated amount of UV curable resin onto the PDMS negative mold.
2. Place the sample in a vacuum chamber for 20 minutes to eliminate air bubbles.
3. Scrap off excessive resin with a clean razor blade.
4. Expose under a mercury lamp (Newport Cooperation, 9 mw at 365nm). The dosage can be checked on the menu provided by the vendor. SU-8 2 requires prebake and postbake as discussed in section 2.2.1, NOA 73 can be exposed directly.
5. Peel off PDMS negative mold to release the replicas.

Because the PDMS mold is reusable, multiple replications can be done using the same negative mold.

2.2.4 PDMS to PDMS bonding

In general, it is difficult to achieve good bonding between PDMS and PDMS. However, strong bonding is desired for some special applications. Bonding strength between PDMS and PDMS or PDMS and glass can be increased using oxygen plasma assisted method. The detailed steps are as follows:
1. First, prepare two pieces of PDMS to be bonded together. It is always best to do the bonding as soon as the PDMS structures are just peeled off from the master mold, so that the PDMS surfaces are clean. If it is hours or days after peeling off, the surfaces may become dirty. It can be compensatory cleaned by sticking plastic tape on and then striping it off several times.

2. Put the PDMS bonding side up into the Bransen Plasma Asher. Set on 600W for 30s.

3. Put two pieces face to face together, carefully aligned if required. The pressure needs to be maintained for a while to squeeze out possible bubbles. With this process, certain bonding force is achieved between them. However, they can still be separated if necessary by physically pulling them apart.

4. If a better internal bonding is needed, the sample can be heated up to 100°C for 1 hour to enhance the bonding strength.

2.3 Summary

In this chapter, the general design of the instrument is introduced and the fabrication technologies used in this research work are also discussed. The whole microchip can be divided to three parts: an optical detection system, a peristaltic micropump and a liquid-to-liquid (L-L) extraction microfluidic system. The detection function of the device all depends on the optical detection system. The peristaltic micropump drives the fluid flowing in the microfluidics system. And the liquid-to-liquid extraction part is used to pre-concentrates the sample and improves the sensitivity of instrument. The extraction and detection units are integrated on the same chip substrate. Only the monitoring and displaying unit, the power supply, and other parts need to be external. In this way, the sample handling and sensing units will be integrated on the chip itself and can be used as an independent and replaceable detecting cartridge. In addition, three parts are all made of PDMS structures and integrated in multilayers. Each layer is simple structure
fabricated by reversing SU-8 mold. All three parts of the microchip are then bonded together with PDMS bonding technology. The detailed design and fabrication process will be presented in the following chapters.
CHAPTER 3 MICRO OPTICAL DETECTION SYSTEM

In this chapter, the design and fabrication of the optic detection unit is presented. The optical detection unit is an important part of the in-situ oil detection system. The feasibility of the optical detection unit needs to be proved and the sensitivity of the optical detection unit needs to be high enough for it to be used in the proposed oil detection system.

The background knowledge of fluorescence spectroscopy will be introduced. Then the detailed design of the optical detection unit, its mathematical modeling, and experiments will be provided in detail.

3.1 Background Introduction

The technology of microfluidic systems has been developing very fast in the past decade. It is widely used in engineering, physics, chemistry, biology and other fields because it has many unique advantages, such as small size, low energy and low material consumption, micro scale effects. With the help of this technology, researchers not only can miniaturize the sizes of the systems, but also achieve higher sensitivities, faster response times, and multiplex functions for the microfluidic systems. The common method is to integrate all analytical process steps into a single micro-fluidic chip, including steps such as sample acquisition, sample pretreatment, detection, signal acquisition and processing etc. The commonly used detection technologies in micro-fluidic chips include optical, electrochemical, mass spectrometric (MS) and nuclear magnetic resonance (NMR).

Optical detection is widely used because of its good compatibility with microfluidic technologies. In particular, the optical detection technology provides a non-contact detection option in which light passes through the microfluidic system and the optic detection unit such as photodiode does not have to have physical contact with the fluids in the microfluidic system. In
addition, optic signals can be easily transferred by optical fibers, which provides unique design flexibility. Conventional optical devices can incorporate well with the microfluidic systems through an optic fiber. It greatly simplifies the interaction of the microfluidics detection chip and outside supporting devices, and widely extends the useful fields of each single chip. However, the optical detection also has a critical drawback. The signal of optical detection in microfluidics is relatively weak and sensitivity is low due to the small amount of sample detected at a small area in the micro channels. Many pre-treatments such as pre-concentration and pre-reaction and proper supporting devices are required to enhance the signal quality.

The optical detection can be divided into absorbance detection [29-30], fluorescence detection [31-32], chemiluminescence, and bioluminescence detection according their operation principles [33-34]. Absorbance, chemiluminescence, and bioluminescence detection have many limitations respectively. The absorbance detection usually has large error and easily affected by background factors. Chemiluminescence and bioluminescence detection can only be used for special fluid solutions that can emit light themselves. Fluorescence detection is the dominant optical detection technique used in microfluidics due to its high sensitivity and easy incorporation into microfluidic devices. [35-36].

3.2 Introduction of fluorescent properties

3.2.1 Fluorescence effect and molecular structures

Fluorescent molecules usually have π-electron conjugated systems, most of which are aromatic organic compounds or complexes with metal ions. A large conjugated π bond, rigid planar structure, and the electronic substituent are beneficial for fluorescence. Molecules with at least one aromatic ring or multiple conjugated double bonds can emit fluorescence. Molecules with saturated or only isolated double bonds compounds do not have significant fluorescence
properties. There are four types of relationships between fluorescence and molecular structure: transition effects, conjugate effect, structural rigidity effects, and substituent effects.

The most fluorescence are caused by $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition, and then the excited state deactivation, $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transition. The transitions of $\pi^* \rightarrow \pi$ has higher quantum yield than that of the transition of $\pi \rightarrow \pi^*$. The molecular absorption coefficient of $\pi \rightarrow \pi^*$ transition is more than 100 to 1000 times of that for the $n \rightarrow \pi^*$ transition. The fluorescent substance molecules contain conjugated double bonds (\pi) system. When the conjugated system is larger, then fluorescence becomes stronger. Most of fluorescent substances have aromatic rings or heterocyclic aromatic rings, the greater the rings are, and the stronger the fluorescence will be. For structural rigidity effect, molecule with rigid structure tends to be fluorescence. fluorescent dye is attached on solid surface, due to additional rigidity provided by solid surface enhancing fluorescence. Additional the molecular plane rigid structure affects the fluorescence of many metal complexes. Fluorescence spectra and fluorescence efficiency often change with the substituent for the aromatic hydrocarbons and heterocyclic compounds. Substituent on the benzene ring causes the displacement of the maximum absorption wavelength and the corresponding change of the fluorescence peaks. Typically, $-\text{NH}_2, -\text{OH}, -\text{OCH}_3$, and similar electron donating groups enhance fluorescence; carbonyl, nitro electron withdrawing groups and $-\text{NHCOCH}_3$ heavy atoms (generally refers to halogens Cl, Br, I), decrease the fluorescence, and enhance phosphorescence. Ortho-substituents, para-orientating groups enhances fluorescence, while meta-substituents inhibit the fluorescence.
3.2.2 Background factors on the fluorescence

Background factors on fluorescence include influence of solvents, temperature, fluorescence quenching, pH, hydrogen bonds, scattering and Raman light.

Influences of solvents can be divided into general solvent effect and special solvent effect. General solvent effect is immanent, referring to the influence of solvent refractive index and dielectric constant; special solvent effect depends on the chemical structure of the solvent and the fluorescent substance. It refers to the special chemical reaction of the fluorescent substance and solvent molecules, such as solvents and fluorescent substances reacting to compounds or solvents changing the ionization state of the fluorescent substance. Fluorescence spectral shift value caused by special solvent effect is often greater than the value of general solvent effects.

When temperature increases, fluorescence quantum yield decreases because the probability of external transition increases due to the collision frequency increasing as temperature rises. Therefore, fluorescence detection in low temperature conditions improves the sensitivity of the analysis and reduces the thermal noise of the detection system.

Interaction between fluorescent molecules and solvent or other solute molecules decreases fluorescence intensity a phenomenon called fluorescence quenching. Excitation of fluorescent molecules and quencher fluorescent molecules collide, transitioning back to the ground state without radiation and is called fluorescence dynamic quenching (oxygen is a common collision quenching agent). When fluorescence molecules and quencher form a non-fluorescent complex, it is called fluorescence static quenching. In fluorescence measurements, the concentration of fluorescent material should not be too high.

When fluorescent material is weak acid or weak alkaline, the changing of pH of the solution will have a dramatic influence on fluorescence spectra and fluorescence intensity. Weak
acid or weak base molecules are different from their ions in the electronic configuration. For fluorescence properties they can be regarded as a different type, and they will have totally different fluorescence quantum yield, fluorescence spectra, and fluorescence intensity. For fluorescent complexes of metal ions and organic reagents, the pH value changing will affect the stability and composition of the light-emitting complex, thus affecting their fluorescence.

There are two types of hydrogen bonds exiting between fluorescent material and solvent or other solute: one is fluorescent substance bond with solvent or other solutes in the ground state of the molecules before excitation to be the hydrogen bond complexes. In this case, absorption and fluorescence spectra are all influenced by hydrogen bonding; The other type is the fluorescent substance molecules bond with the solvent or other solute molecules in the excited state after excitation to be hydrogen bonding complexes; in this case, only the fluorescence spectra is affected by hydrogen bonds.

When molecules absorb lower energy photons, the energy of these electrons is no longer enough to transit the electrons in the molecules to the excited state, and can only transit them to other higher vibration levels in the ground state. If the electron energy does not drop after being excited and returned to the original level immediately, it will emit light with the same wavelength as excitation light in all directions; this radiation is called Rayleigh scattering light. The Rayleigh scattering of light intensity is inversely proportional to the biquadratic of its wavelength. Molecules in excited states in a solution are of a small number, but molecules excited to higher vibrational level of the ground state and scattering Rayleigh light are much more; and other solvent and solute molecules are also scattering.

When electrons excited to higher vibrational levels of the ground state electronically return to the slightly higher or slightly lower than original vibrational levels, they will emit light
with wavelength slightly longer or slightly shorter than that of the excitation light. This is known as the Raman scattered light. The intensity of the Raman scattered light are much less than fluorescence intensity and Rayleigh scattering light, almost less than one-thousandth of the fluorescence intensity. Fluorescence spectra have a certain peak, and the wavelength of the Raman band changes with the wavelength of the excitation light. But there is a certain frequency difference between the excitation light, and this frequency difference is not related to the frequency of the excitation light, but only to the different features of molecular structure. Scattering of light and Raman scattered light affect fluorescence analysis, and often become the main limitation of fluorescence analysis sensitivity. Its effect can be reduced by selecting the appropriate measurement wavelength, using lower excitation intensity, and other measures.

3.2.3 Fluorescence parameters

a. The average life of the fluorescent molecules

The lifetime of the excited state is defined as the average time the number of molecules in the excited state decay to the original 1/e. When a molecule is in $S_1$ (As mentioned in section 1.5, $S_1$ is the excitation state, $S_0$ is the ground state.) states, its average lifetime ($\tau$) can be

$$\tau = \frac{1}{k_f + \Sigma K}, \quad (3-1)$$

Where $k_f$ is the rate constant for fluorescence emission, $\Sigma K$ is the sum of the rate constant of a variety of single-molecule non-irradiative deactivation process.

The fluorescence emission is a random process, only a small number of excited molecules emit photons at the time of $t=\tau$. The fluorescence decay is usually a single exponential decay process, 63% of the excited molecules have decayed before $t=\tau$, the rest 37% of the
excited molecules decay when $t > \tau$. The relationship between the average life of the fluorescent molecules and a certain transition is as follows,

$$\tau \approx 10^{-5} / \varepsilon_{\text{max}}, \quad (3-2)$$

where $\varepsilon_{\text{max}}$ is the molar absorption coefficient of maximum absorption wavelength. If $S_0 \rightarrow S_1$ is the certain transition, generally, the value of $\varepsilon_{\text{max}}$ is approximately $10^3 \text{m}^2/\text{mol}$, thus the average life of the fluorescent molecules is about $10^{-8}$ s.

If non-irradiative deactivation process does not exists, the life of the fluorescent molecules is called as the inner life, represented by $\tau_0$,

$$\tau_0 = \frac{1}{k_f}, \quad (3-3)$$

Attenuation of the fluorescence intensity follows the equation:

$$\ln I_0 - \ln I_t = -t / \tau, \quad (3-4)$$

where $I_0$ is the fluorescence intensity at $t = 0$ and $I_t$ is the fluorescence intensity at time $t$.

Measure $I_t$ values corresponding to different time $t$, the relationship curve of $\ln I_t$ vs. $t$ can be obtained. The resulting relationship will be a straight line; the value of the fluorescence lifetime can be obtained as the slope of the line.

b. **Fluorescence efficiency**

The fluorescence efficiency can be represented by the fluorescence quantum yield. The molecular fluorescence efficiency is not high for some materials that can absorb light. The absorbed energy is consumed on colliding with solvent molecules or other solute molecules, and it may not present fluorescence. Fluorescence efficiency is generally the fluorescence quantum yield ($Y_F$).
The deactivation processes of excitation molecules include irradiative transition and non-irradiative transition. The fluorescence quantum yield can be calculated as,

$$Y_F = \frac{k_f}{k_f + \Sigma K}.$$  \hspace{1cm} (3-5)

If the non-irradiative transition rate is much smaller than the irradiative transition rate, \(\Sigma K << k_f\), the fluorescence quantum yield values will be close to 1, usually under the \(Y_F\) value and less than 1. The greater the value of the fluorescence quantum yield is, the stronger the fluorescence of the compounds is. For non-fluoresce material, its fluorescence quantum yield value is zero or close to zero.

**c. Fluorescence intensity and spectral shape, bandwidth, peak position**

According to the Beer–Lambert law, the relative fluorescence intensity of the fluorescent substance in a certain concentration range solution can be expressed as,

$$I_f = KY_F I_0 (1 - e^{-\varepsilon cl}),$$  \hspace{1cm} (3-6)

in which fluorescence intensity, \(K\) is instrument constant, \(Y_F\) is fluorescence quantum yield, \(I_0\) is the excitation light intensity, \(\varepsilon\) is the fluorescent molecules molar absorptiv efficient, \(C\) is concentration of fluorescent material in the solution, and \(l\) is thickness of the fluorescent pool.

When the concentration is very low (\(\varepsilon cl \ll 0.05\)), for instance \(e^{-\varepsilon cl} \approx 1 - \varepsilon cl\), the equation can be simplified as,

$$I_f = KY_F I_0 \varepsilon cl.$$  \hspace{1cm} (3-7)

For dilute solution of a fluorescent substance exposed in a certain frequency and a certain intensity of light, the fluorescence intensity produced by the solution is proportional to the
concentration of the fluorescent substance. This is the theory basis of quantitative analysis of concentration by fluorescence.

3.2.4 A model of oil fluorescence in water

The mathematical model of oil in water needs to be developed and studied for better design of the fluorescence oil detection system in this research. Fluorescence is the $S_1 \rightarrow S_0$ state irradiative transition and associated with light. A fluorescence spectrum is directly related to only two energy levels, which simplifies the electron model of molecular to a two-level model. It is assumed that during light pulses only two energy levels of particles change: level 2 representing the excited state energy, and levels 1 representing the ground state. The changing rate equation of the excited state particle density $M_2$ can be expressed as:

$$\frac{dM_2}{dt} = M_1(t)(\omega_{12} + S_{12}) - M_2(t)(\omega_{21} + S_{21} + A_{21}) - \omega_{12} - \omega_{21}. \quad (3-8)$$

In the equation 3-8, $\omega_{12}$, $\omega_{21}$ are molecule absorption and emission rates when stimulated, $M_1(t)$ is ground state particle density, $S_{12}$ and $S_{21}$ are respectively the excitation rate and eliminate excitation rate by molecular collision, and $A_{21}$ is the spontaneous emission probability.

Set two-level statistical equal weight:

$$\omega_{12} = \omega_{21} = \omega.$$

Generally, $S_{12} \ll \omega_{12}$.

Then the equation can be simplified to:

$$\frac{dM_2}{dt} = M_0\omega - M_2(2\omega + S_{21} + A_{21}), \quad (3-9)$$

where $M_0 = M_1 + M_2$ is the overall quantity of particles.
When it is stable,

\[ M_2 = \frac{M_0 \omega}{2 \omega + S_{21} + A_{21}}. \]  \hspace{1cm} (3-10)

Photon number of the total fluorescence emitted by the fluorescent substance in unit time:

\[ m_f = M_2 A_{21} V = \frac{M_0 \omega A_{21} V}{2 \omega + S_{21} + A_{21}}, \]  \hspace{1cm} (3-11)

where \( V \) is the volume of the fluorescence substance.

Assuming the angle of the condenser system received from the fluorescent substance is \( \Omega \), the number of fluorescent photons a detector receives per unit time is then calculated as

\[ m_d = \frac{m_f \Omega}{4\pi}. \]  \hspace{1cm} (3-12)

Assuming the detector’s quantum efficiency is \( \eta_d \), the fluorescence signal intensity detected by the detector is \( I_d \):

\[ I_d = m_d \eta_d = \frac{m_f \Omega \eta_d}{4\pi}. \]  \hspace{1cm} (3-13)

This equation shows all factors affecting the signal received by a detector. This is the theoretical basis of the fluorescence oil detention method. It shows the optical signal is proportional to the density of oil in water. Fluorometry is the standard and most effective oil detection method used in the field [14][37-38]. The techniques to increase the signal sensitivity are to increase the fluorescence source volume, increase the receiving angle of the fiber, and increase the size of the fiber.
3.3 Select supporting parts of the optical detection system

In this dissertation, the fluorescence oil detection system integrated on the micro-fluidic-optic chip as stated in Chapter 2. It is connected with the supporting parts outside the microchip by a cable. The supporting parts include fibers, an optical source and an optical detector.

![Diagram of microfluidic device](image)

**Fig. 3.1** Schematic diagram of a microfluidic device integrated with fluorescence optical detection system

**Fig. 3.1** shows the schematic design of the optical detection unit. It is connected with the supporting parts though fibers. Optical supporting components, such as excitation light sources, detectors, and filters are external to the chip, will be off-shelf commercial products. This makes it easy to change them. It is especially important because the microchip may be used to detect other types of oil solution, which may requires different excitation lights and detectors with different spectrum responses. Since the fluorescence characteristics of crude oil may vary depending on the different geographic locations it is from, different types of excitation light sources, detectors and filters can be chosen for the specific measurement requirements. The oil sample used in our research was provided by BP Company. Crude oil typically absorbs light of
wavelength between 300 nm and 400 nm, and emits light in the range from 450 nm to 650 nm [13][39].

In theory, the thicker the fiber is, the better the performances are. With thicker optic fiber, both excitation and emitting light can be increased. For example, in theory both excitation and emitting light signal for 600μm fiber are 36 times greater than that of a 100μm fiber. Consider both excitation and emitting light amplification together, the total amplification of system is 1296 times. Experiments have been done to compare the performances of 100μm and 600μm fibers. With all other experimental conditions maintained to be the same, the experimental results showed that 100μm fiber had no measurable signal but 600μm fiber produced well measurable signal. Thicker fiber (600μm) was therefore preferred and used. Design effort has also been made to make sure the transmit distance is short for the optical fiber to reduce signal loss. A greater NA (numerical aperture) value of fiber means a greater angle to receive signal. Greater NA value is therefore preferred. Consider suitable wavelength range of the fiber. Optical fiber BFH48-600 (Thorlab) was therefore chosen in our experiment. Its NA value is 0.48.

The two optical fibers must be arranged perpendicularly as shown in Fig.3.1. The wavelengths of excitation light source and emitting light are different. The intensities of excitation and emitting light would be shown on one graph. There would be two different peaks on the result diagram by using a spectrometer as the detector and the selecting light source and filter properly if the two fibers are arranged in the same line. However, the intensity of excitation light is much stronger than that of the emitting light. No matter how properly to select the light source, the relation between the intensity and wavelength is a Gaussian distribution. It means that there still exists light in emitting light wavelength in excitation light, although its intensity is much less than the peak intensity, it is still strong enough to affect the output result. The
excitation light would disturb the emitting light signal significant. To minimize this effect, we must reduce the possibility of the excitation light entering emitting fiber. The arrangement of two fibers is therefore selected to be perpendicular to each other.

There are three optional selections for the light source: laser, LED (light-emitting diode), or broadband spectrum light source. We target to develop a new device that is highly portable with a physical size much smaller than these on the market. The light source must be physically small and energy efficient. Thanks to the micro-scale of our design, the excitation fiber and emitting fiber can be arranged very close to each other. The Gaussian beams can be considered as parallel lights. The laser is not necessary as in other applications. Broad spectrum light source can be as small as LED, such as small xenon lamp. Through proper filter, the broad spectrum light source can be used similarly as the narrow bandwidth wavelength LED. It can easily provide several wavelength excitation lights through several switchable filters, and give several emitting spectrum diagrams on different excitation lights. It can provide more information for oil components identification. One of the disadvantages is that it consumes more energy. For simply oil concentration detection purposes, it is not necessary. Particular wavelength LED is the best option for this particular design.

The fluorescent efficiency is different for the excitation light with different wavelengths. In theory, the wavelength of the light source with the highest fluorescent efficiency should be chosen, which is about 300 μm. However, LEDs with shorter wavelengths tend to become more expensive. Another more important factor is that the output power of commercial LED drops dramatically as the wavelength decreases. Even if the fluorescent efficiency is high, much low excitation output power brings much low emitting power, and this would eventually limit the sensitivity of the entire detection system.
Comparison has been done between 290nm LED (Spectra Ecology) and 360nm LED (Thorlab). The power of 290nm LED is 20mw, for 360nm LED, the power drops to 3 mw. The set of experiments is shown in Fig.3.1. Optical fiber used is 600 μm, the detector used is a spectrometer (Ocean Optics) with the Integra Time of spectrometer adjusted to be 100ms. Sample is 1000ppm oil sample. The result is that 290 m LED has no signal but 360nm LED produced clearly measurable signal. LED with light wavelength of 360nm was therefore selected.

Two types of detectors can be used, one is to use a spectrometer, and another option is to use a photo-multiplier tube (PMT) as reported in many literatures. Spectrometer can provide the fluorescence spectra of the sample; it can therefor provide more information about oil components while PMT only can provide a voltage value that is dependent on the light signal intensity. Spectrometer already has an integrated circuit with it and ready for use, but PMT requires a signal analysis circuit designed built by ourselves and no commercially available circuit for this purpose. The drawback of spectrometer is its physical size; it is much bigger and more expensive. However, the research work reported in this dissertation targets to prove the feasibility of the proposed instrument. A commercial spectrometer is therefore chose. At later stage for commercial product development, special integrated circuit with the basic function of a spectrometer can always be developed with less cost and smaller sizes. PMT is potentially available when signal analysis circuit is solved.

Therefore, Optical fiber (Thorlab BFH48-600), 360nm LED (Thorlab M365f1) and a spectrometer (Ocean Optics USB4000-UV-VIS) were chosen as the supporting parts for the optical detection system in the microchip.
3.4 Design and fabrication of micro-optical detection system in the microchip

Design and fabrication of micro-optical detection unit in the microchip is presented in this section. The most critical part is the out-of-plane microlens. The relationship between pressure applied during the fabrication and surface profile of the microlens is well studied both numerically and experimentally. There are two options to fabricate an out-of-plane microlens in this system, one-membrane lens and two-membrane lens. Experimental results have shown that the first one is better for our system.

3.4.1 General design of micro-optical detection system in the microchip

The micro optical detection unit includes the optical fiber holders, a microfluidic channel and a vertical microlens. As shown in Fig.3.1, after L-L extraction, pre-concentrated oil is dissolved in organic solvent and passing through a micro channel. Optical components such as micro lenses and optical fibers are integrated onto the micro channel.

Two optical fibers perpendicular to each other are inserted into the PDMS chip through pre-aligned optical fiber holder. One optical fiber is used to deliver excitation light from a LED light source (360 nm) to the fluid sample and the other one is used to output fluorescence signal (470nm) to a detector. An optical filter is placed between the output optical fiber and the detector to separate the collected fluorescent light from the scattered light. To enhance the light collection of the fluorescence signal, a three-dimensional (3D) out-of-plane microlenses is directly integrated onto the microfluidic device at the end of the optical fiber. There are two potential positions for the microlens as shown in Fig.3.1.

The microlens, optical fiber holder and the microfluidic channel are fabricated with the same process. The microfluidic system for sample pre-concentration and manipulation can be fabricated entirely on a PDMS chip using molding technique. The pattern of the microlens, the
optical fiber holder and the microfluidic channel are fabricated in SU-8. It is then used as the master mold for the subsequent PDMS molding step. In this step, the PDMS pre-polymer is directly poured onto the mold and then peeled off after complete curing. Both the microlens and optical fiber holders can be fabricated with the fluidic channels in a single platform and molded using PDMS. This molding technique provides an integrated solution, reduces the final cost, and makes it possible to have a disposable microfluidic-optical cartridge.

3.4.2 General fabrication process of the vertical microlens

In the integrated optical detection system, the most critical part is the fabrication of the 3D microlenses. The general fabrication process of the microlens is presented in this section. Some detailed processing parameters will be discussed in the next sections. For the on-chip optical detection, the microlenses need to be in the out-of-plane orientation, i.e., with their optical axes parallel to the substrate. A fabrication of a controllable out-of-plane microlens has been developed for it. It is completely compatible with soft-lithography technique, which makes it possible to integrate microlens into various microfluidic chips with minimum conflict with the fluidic chip design and fabrication process. Fig. 3.2 shows a close-up image of the microlenses and fiber holders with optical fibers inserted. There are two options to fabricate an out-of-plane microlens for this system. We call them “one-membrane microlens” and “two-membrane microlens” respectively. Schematic diagrams of one membrane lens and two-membrane lens integrated with the coupling optical fibers are shown in Fig.3.3. Fig.3.4 shows the focusing images of the one-membrane lens and two-membrane lenses respectively. Both of them meet our requirements for the focusing purposes.
Fig. 3.2 Cured out-of-plane microlens filled with NOA 73
Micro lens (between receiving fiber and fluid)

Fig. 3.3 Schematic diagram of no lens, one-membrane lens and two-membrane lens integrated with the fiber at position 1 and 2

The general steps to fabricate the two-membrane lens and one-membrane lenses are schematically shown in Fig. 3.5. First, the fabrication process of two-membrane lens is presented as follows (Fig. 3.5a):

1. Make SU-8 master mold
2. Soft lithography. Pour and cast PDMS to make the basic structures to be used for lens
fabrication. The two vertical membranes and a small channel between them were fabricated.

3. Seal the top of the microfluidic channels with a PDMS membrane. Then the small chamber between two vertical membranes was made, with only a small channel connecting them.

4. NOA73 fluid was injected through the micro channel into the chamber while the pressure was maintained. Because the PDMS membrane is not gas proof, the air trapped inside the chamber after injection would leak out under pressure. The pressure was maintained until all air leaks out. The chamber was therefore completely filled with NOA73 fluid and the membrane deformed to be a lens shape under the pressure.

5. Flood expose with UV light while the pressure was maintained stable. The NOA73 would be solidified to hold the lens shape. This completed the in-situ fabrication of the microlens with the desired focal length.

The process to fabricate the one-membrane lens is similar as shown in Fig. 3.5b, is as follows:

1. Make SU-8 master mold;

2. Soft lithography;

3. Seal the top of the microfluidic channels with a layer of PDMS membrane. The right side of the vertical membrane is wide open;

4. Insert the fiber carefully to a proper position;

5. NOA73 was injected through the micro channel. NOA 73 filled up the entire gap between the fiber and the channel wall. The channel can be fabricated a little smaller than the diameter of the fiber. When the fiber is inserted, the channel is sealed and it can support the pressure following applying;

6. Apply pressure and flood expose. The one member lens is fabrication. The disadvantage of the one member lens is that the fiber was fixed.
The precise position of the micro lens can be defined during mask design stage and no alignment or post-fabrication assembly is required.

Fig. 3.4 Light beam focused by one-membrane lens (a) and two-membrane lens (b)

Fig. 3.5 Schematic diagram of micro lens fabrication process
The pressure used during the fabrication process is applied through a small channel as shown in Fig. 3.3 and Fig. 3.5. Fig. 3.6 shows the schematic diagram of the set-up used to apply the pressure to the PDMS chamber to create the lenses. This set-up was connected at the other end of the pressure channel. The syringe’s (BD 3ml syringe) shoulder was fixed on the frame. A flat thin plate, which is only free to move vertically, is put on the top of putter. The tube connects the needle and inlet of the micro channel on the fluidic chip. When the system becomes static, the fluid pressure is uniform and determinate by the standard iron weight on the plate. The diameter of BD 3ml syringe is 8.66 mm.

The pressure is \( P = \frac{4mg}{d^2} \). (3-14)

Each pound of weight corresponds to about 75kpa.

![Fig.3.6 Schematic diagram of the experimental set-up used to apply pressure to the PDMS chamber to create the microlenses](image)

**3.4.3 Simulation of lens surface profile**

From the fabrication process, it is obvious that the applied pressure is the primary factor determining surface profile of the fabricated lenses. Numerical simulations with finite element
analysis (FEA) were conducted to study the relationship. The numerical analysis was used as a guide to fabrication and design of microlenses.

In general, the deformation of the PDMS membrane can be simulated using a simplified model. Assume the PDMS membrane is thin enough so that thin membrane model can be used. The four sides of the square membrane are fixed as shown in Fig.3.7. The pressure is assumed to be applied uniformly on one side of the membrane.

The deformation can then be analyzed using the following equation, [40]

\[ z = d - R + (R^2 - r^2)^{1/2} \]  \hspace{1cm} (3-15)

\[ R = \frac{a^2 + d^2}{2d}, \]  \hspace{1cm} (3-16)

where \( z \) is the deflected height at \((x,y)\), \( a \) is half of the edge length, \( d \) is the center deflection, \( r \) is the distance from the center, \( R \) is the radius of curvature of the deflected membrane, \( t \) is the thickness of the membrane, and \( P \) is the pressure applied.

![Fig.3.7 Schematic diagram of PDMS membrane deformation](image)

The Young’s modulus and Poisson ratio of PDMS are referred from publication [41] and set as 30MPa and 0.50 respectively.

The dimension of the presented rectangular membrane is 600 μm wide, 600 μm long and 120 μm thick.
To study the elastomer membrane deformation under pneumatic pressure and visualize the potential surface profile of our proposed micro lens, a finite element analysis (FEM) software package (Stress analysis and grid deformation modules in CFD-ACE+, ESI Groups, France) was used.

The results are shown in Fig.3.8 and Fig.3.9. When the pressure is low, the profile of the PDMS membrane is approximately sphere. The lens can be approximately considered as a sphere lens, especially the central part of the membrane. However, if the pressure is too high, the deformation can no longer be approximated as a sphere any more. Two different size lenses are simulated, which are 600 μm diameter and 100 μm diameter lens. The pressure range for 100 μm is about 0-1400kPa and for 600 μm is about 0-400kPa.

Fig.3.8 Simulation result of a 600 μm rectangular PDMS film deformed under 250kPa
3.4.4 Experimental results

a. Calibrate the relation between pressure and focal length of lens by experiments

The relation between pressures of lens’ surface profile was also experimentally studied. The pressure $P$ is the main factor which determines the deflection $d$ and the focus length of the lens $L$.

As shown in Fig.3.4, the optical fiber is held on one side of the lens. Another side is filled with fluorescence fluid. The microlens was placed under fluorescence microscope. The optic fiber was connected to excitation light source with proper wavelength. A filter was used to allow emitting light pass through and get into the microscope but block all other excitations. The emitting light shows the deflection of light beams through the lens. The focal length $L$ can be estimated from the picture. However, the light beam was not perfectly focused to a point during the experiment. The focal length was only approximately measured.
Microlenses with both 100 μm and 600 μm diameters had been fabricated and tested. As stated in lens fabrication process, vertical membranes of the microlens were bonded with a horizontal membrane on the top. The adhesion at top is not as good as at the bottom. Because the adhesion was not very good, when the pressure was applied, the bonding broke off occasionally and caused fluid leakage. The lens fabrication failed sometimes.

If the vertical membranes are thicker, the adhesion can be better. But thicker membranes would absorb more optical signal in the detection process. Therefore, the membranes are intended to be as thin as possible as far as they are thick enough to satisfy the adhesion requirement. A series of experiments were conducted and the results had demonstrated that for 100 μm diameter lenses, the minimum membrane thickness is 10 μm; for 600 μm diameter lenses, the minimum membrane thickness is 120 μm.

From the results of the numerical simulations, it had been found that if the applied pressure is too high, the deformation cannot be approximately considered as spherical. In the experiments, the deformation can be observed through microscope as in Fig.3.2. The maximum pressure for lens fabrication can be estimated. The maximum pressure for a 100 μm diameter lens was found to be about 1.1 MPa, and for 600 μm diameter lens was found to be about 0.4 MPa. Every connecter requires sealing enhancement with super glue. And it is almost the maximum limit for the syringe pump.

Table 3.1 Experiment result of micro lens (diameter d =100 μm, membrane thickness t= 10 μm)

<table>
<thead>
<tr>
<th>Pressure (kpa)</th>
<th>Deformation d (μm)</th>
<th>Focal length L (two members, μm)</th>
<th>Focal length L (one members, μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>375</td>
<td>40</td>
<td>200</td>
<td>350</td>
</tr>
<tr>
<td>750</td>
<td>65</td>
<td>130</td>
<td>200</td>
</tr>
<tr>
<td>1125</td>
<td>105</td>
<td>70</td>
<td>150</td>
</tr>
</tbody>
</table>
Table 3.2 Experiment result of micro lens (diameter d = 600 μm, membrane thickness t = 120 μm)

<table>
<thead>
<tr>
<th>Pressure (kpa)</th>
<th>Deformation d (μm)</th>
<th>Focal length L (two members, μm)</th>
<th>Focal length L (one member, μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>165</td>
<td>1200</td>
<td>--</td>
</tr>
<tr>
<td>225</td>
<td>215</td>
<td>750</td>
<td>1300</td>
</tr>
<tr>
<td>375</td>
<td>325</td>
<td>450</td>
<td>800</td>
</tr>
</tbody>
</table>

Table 3.1 and table 3.2 show the relationship between the pressure and lens shape for 100 μm and 600 μm lens respectively. This experiment can also be treated as a calibration process of the lens fabricated for a desired focal length. A vertical microlens with controllable focal length is very useful in other micro optical systems.

When the deformation is too small, the light scatters and cannot focus to one point. The focal length cannot be measured when the deformation is too small. As show in the table, the deformation and focal length increase with the pressure with some nonlinearity. The experimental results match the predictions of simulations quite accurately.

b. Experimental results of the microlenses

Some experiments were also conducted to find out the best focal length of the microlenses at position 1 and position 2, and compare one membrane lens and two-membrane lens using in the optical detection system.

In our application, the diameter of the lens is designed as 600 μm. Firstly, the microlens was tested at position 1. The two membranes lens was tested. From the calibration results in 3.54a, the focal length range is 450 μm-1200 μm.

The set of experiments are shown in Fig.3.3. We used an optic fiber of 600 μm diameter and a spectrometer (Ocean Optics) as detector, the Integra time of spectrometer was adjusted to be 100ms. The oil sample was mixed at 1000ppm. The best focal length is found, which is the membrane had no deformation. The signal intensities with and without the lens were measured
and compared. The results had demonstrated that the signal intensity received with the lens was only about 50% of the signal without the lens. It means the lens reduced the intensity of the signal to about 50%.

The reason is that the light beams transmit through too many interfaces, and there is reflection attenuation on each interface. The more important factor is that the fiber was cut and polished by hand. The interface was not perfectly flat, and increased scattering attenuation when light beams transit the air gap between fiber and lens.

We tested the single-membrane microlens with the same experimental conditions as for the two-membrane lens. The optic fiber of 600 μm was used and the same spectrometer (Ocean Optics) as the detector. The Integra time of spectrometer was again adjusted to be 100ms. The same 1000ppm oil sample was used. The best focal length is found, which is again when the membrane had no deformation. The result obtained was that the intensity of signal received after the fluid is injected and the lens is fabricated was about 140% of the signal in comparison with the one with no lens. This means that the improvement efficiency of the lens is about 140%.

One-membrane lens is better compared with two-membrane one. It reduces the total number of surfaces the light beam has to pass. The advantage of the lens fabricated using one membrane is that it only has two interfaces, less than those made with two-membranes. This helps to reduce the reflection attenuation when the light beams pass through. What is more important is that the deflection index of NOA73 is much closer to the core material. Comparing with the air gap in two-membrane lens situation, the scattering caused by the non-flat of the fiber head is much less as shown in Fig.3.3.

Another set of experiments was conducted to test the effectiveness of the microlens in position 2. For two-membrane lenses, the best focal length was found to be about 1200 μm. The
signal intensities with and without using the lens were measured and compared. The results had demonstrated that the signal intensity received with the lens was only about 80% of the signal without the lens. For one-membrane lens, the best focal length was found to be about 1200 μm. After the fluid was injected with the lens integrated, the experimental results showed that the intensity of received signal almost doubled in comparison with the one with no lens. This means that the improvement efficiency of the lens is about 200%. The reason is that our light resource is the LED has a glass spherical cover that would scatter the light. The microlens can focus the scattering light, increase the intensity of light passing through the excitation fiber, and increase the intensity of final signal. This result has proved that using one-membrane lens can help to improve the sensitivity of the detection.

From theoretical and experimental study, we can conclude: 1) the deformation of the membrane, in other word, the focusing of the microlens didn’t enhance the signal; 2) one-membrane lens is better than the two-membrane one. Because in one-membrane lens, the air gap between the fiber and membrane is filled by NOA73. The reflection index of NOA73 is much closer to the core material of the fiber. This would reduce the scattering of the signal in the small gap significantly. Therefore, the design in position 1 was selected. The gap was filled with NOA73, similar to the case of fabricating one-membrane lens, but the membrane remained flat without deformation. The following conclusions can be made based on the experimental results with the lens in position 2: 1) the best focal length of the microlens is about 1200μm; 2) one-membrane lens is better than two-membrane one. Therefore, the design in position 2 was selected with the one-membrane lens with the focal length of 1200μm as the preferred one.
c. Feasibility test of the optical detection unit

![Experimental results of the micro-optical detection system for different oil densities.](image)

Fig.3.10 Experimental results of the micro-optical detection system for different oil densities. a) 1000 ppm; b) 500 ppm; c) 100 ppm; d) 50 ppm; e) 10 ppm; f) 1 ppm; g) measured response vs. oil density.

We have conducted some experiments to test the optical detection system and calibrate the signal by using standard oil samples. Crude oil sample was provided by BP Company. The samples were prepared using nonane as solvent with oil densities at 0 ppm, 1 ppm, 10 ppm, 50 ppm, 100 ppm, 500 ppm, and 1000 ppm respectively. The integration time of the signal (amplitude) has been adjusted correspondingly. As stated in section 3.4.4a, the optimal focal length of the microlens was selected to be about 800 µm, and with the one-membrane lens used in our system.

The wavelength of the excitation light supplied through optical fiber is around 365 nm. The fluorescence signal was received using a spectrometer (USB 4000 Spectrometer, Ocean Optics Inc.). The response spectrum of the fluorescent signal has two peak wavelengths. One peak is around 420 nm and the other one is around 480 nm. Fig. 3.10 shows the results with filter. Filter used is a 400 nm long pass filter (Thorlabs). Because of the absorption of the filter, the integrated time with filter is 4 times as much as integrated time without filter. As can be observed, at a density of 10 ppm, the signal was still easily measurable without pre-concentration.
The experimental results have therefore proved the feasibility of the fluorescence detection idea. The intensity of the signal is approximately proportional to the concentration of the oil. The lower range is below 10ppm.

### 3.5 Conclusions

In this chapter, a fluorescence detection system for microfluidic system is presented as a part of the in situ oil detection system. The theory of the fluorescence and fluorescence oil detection is introduced. The optic detection system is well designed and its fabrication process is presented.

An out-of-plane microlens was used to improve the signal of the system. The microlens was fabricated due to the pressure applying in the fabrication process. The relation between the pressure and lens surface shape was studied using numerical simulations. The experimental results matched the predictions of simulations quite closely.

The key hypothesis of the optic detection unit is that fluorometry detection principle can still be effectively used when the measurement system is dramatically reduced in its physical size. As the device size is scaled down in micro-size, both the sample volume and light intensity are significantly reduced in comparison with their conventional sized counterparts. To validate this hypothesis and prove the feasibility, we have conducted some experiments to test the optical detection system and calibrate the signal by using standard oil samples. The experimental results show that the optic detection system can measure the concentration of crude oil very well. The intensity of the signal is approximate proportional to the concentration of the oil. The lower range is below 10ppm. The experimental results have proved the feasibility of the system.
CHAPTER 4 THE PERISTALTIC MICROPUMP

As stated in Chapter 2, the peristaltic micropump is one of important components in the microfluidic system. It provides the energy and drives the fluid flowing in the system.

In this chapter, the design and fabrication of a peristaltic micropump are presented. The actuators used in the pump are isolated from the fluidic parts. The peristaltic pump consists of three electromagnetic valves and the synchronized operation of the valves is achieved by electronic control. The flow-handling part of the pump is integrated on the micro-fluidic-optic chip and can be used in biological/medical/chemical analyses. The pump can be used for relevant large size in microfluidic system, where in this dissertation it works for 600 μm×600 m channels. The flow rate of the pump was found to be about 3 l/min with the step time set at 0.1 s and the most appropriate operational frequency of the valves was set at 10Hz.

4.1 Background and introduction

The microfluidic systems develop very fast and are widely used in biology, chemistry and other areas. The microfluidic systems have many unique advantages compared with their conventional sized counterparts: much less quantities of samples consumption, shorter reaction times, and lower cost. Microfluidic systems using channels with dimensions of tens to hundreds micrometers have been developed for a wide variety of applications in the last decades. Typical examples of such systems are the so-called Micro Total Analysis Systems (μTAS) [42-43]. Other common applications for microfluidics technologies include implantable drug delivery systems [44], portable fuel cells [45], and controlling blood flow in biomedical detection systems [46]. The fluid flows in the micro channels in general require a suitable power source and one or several micro pumps with appropriate output and a suitable size for integration in the microfluidic system.
In many applications, the fluids travel through a series of mixing and reactions. One problem with these micropumps is that they are difficult to clean up once used. As the microfluidic chips with no active components such as pumps are often made using replication methods, many microfluidic chips are designed to be disposable. Because fabrications of most micropumps are normally complicated, they are designed for long working life. Therefore, it is preferable that the microfluidic system is designed in such way that the actuators for valves and micropumps are separated from remaining parts of the disposable microfluidic system. In such designs, the microfluidic chips are replaceable and the actuators for valves and micropumps or any other active components are separated from the microfluidic chip and are the permanent parts of the instrument.

One option is to design the micropump as completely external one and with inlet and outlet connectors to fit with the disposable part of the micro-fluidic chip. The other option is to integrate all the passive components of the micropumps on the microfluidic chip and only have the actuators with all other active components of the system, such electrical signal processing and display. In our application, the pump is required to drive the fluid flowing circularly inside the microchip. Therefore, only the second option can meet the requirement.

Many different types of micro pumps have been developed. Generally, these pumps can be divided into two categories: mechanical and non-mechanical [47], based on whether the energy of the fluid flowing comes from the mechanical energy or non-mechanical energy. Non-mechanical micro pumps usually do not have a mechanical actuation part. The actuation is instead based on the properties of the pumping fluids. Typical examples include flexural planar wave pumps [48], capillary-force driven [49], electrochemical micro pumps [50], and osmotic type [51]. The design and fabrication of non-mechanical pumps in general are simpler compared
with the mechanical ones because no moving mechanical components are needed. Because the energy is transduced from either electric or magnetic field and in most cases it can be achieved in non-contact fashions, the energy source can be easily separated from the micro fluidic part. These pumps are ideal ones for disposable microfluidic system. However, there are two limitations for the non-mechanical micro-pumps. First, the types of fluids that can be delivered are limited by their energy transferring mechanism. For example, EHD (Electro hydrodynamic) pumps require the fluids with appropriate electrical properties solution (permittivity and conductivity), and electro-osmotic pumps require solutions with certain pH level. Secondly, most non-mechanical micro pumps can deliver very small volume flow rates and very low driving pressures, and they tend to have very slow response times.

Mechanical pumps can be further divided into dynamic pumps and positive displacement pumps. For the hydrodynamic pumps, the force is applied directly onto the fluid continuously. The hydrodynamic pumps are usually centrifugal pumps [52], and rotary pumps [53], and normally have to be imbedded inside the fluid channels so that their actuators can continuous pushing the fluid. It is almost impossible to design these pumps separated from the disposable micro fluid chips.

The majority of reported micropumps are displacement ones. Various kinds actuation methods have been used for the displacement pumps, such as electrostatic [54], electromagnetic [55], piezoelectric [56] and pneumatic [57] forces. In displacement type of micro pumps, energy is periodically supplied by applying a force to one or more movable boundaries of fluid-containing volumes. Volume changes resulting from this action produce a direct pressure increase to overcome flow resistance of the channel and valves. By controlling various valves, the fluid is pressed by the pressure and flow to the designed direction. Some researchers use
passive one-way valves that open when a certain level of pressure is applied on it. The valves have to be imbedded in the micro fluid channels. They usually require multiple layers fabrications. The other choice is to use active valves that are controlled with external power. The micropump functions as these valves were open and close in synchronized fashion. This type of micropump is called the peristaltic micropump. For the active valves of the peristaltic micropump, their actuators are separated from fluid by the membrane while the external actuation force is applied on the “dry side” of the membrane. This design option for valves is therefore suitable for the application that it requires separating the active and passive components of the fluidic system and making the microchip with all passive fluidic components on it disposable.

Peristaltic pump was first invented in 1881 and has the unique advantages of pumping biological or chemical fluids that need to be isolated from the mechanical components of the pump. It can be classified as either linear or rotational, depending on the actuation mechanisms used. The conventional or miniature sized peristaltic pumps have been widely used for many biological, medical, and industrial applications. In microfluidic systems for biological, chemical, or medical analyses, biological/medical samples are often needed to be isolated from the environment or the mechanical components of the pumps to avoid cross-contaminations. From fabrication point of view, using a peristaltic pump in a microfluidic chip may help to avoid complicated structures as commonly seen in using other type of positive displacement micropumps. Without the complicated structures of valves and pumps, the remaining parts of the microfluidic chips only have micro channels, chambers, etc. This means that the fluidic part of the pump can be easily integrated on micro-fluidic chips and feasible to replicate the entire micro-fluidic chips to reduce the fabrication cost of the entire MEMS chips.
Many peristaltic micropumps are also reported [20-22]. But in the current publications, the power of these actuators is small, so that they can only drive very shallow channels (5μm-10μm). In addition, most researchers still take the microfluidic chips as substrate to fabricate the micro pump for fabrication convenience. The active valves were imbedded on the micro fluid channels as those positive valves, and the actuators and the microfluidic systems are not separated.

In this chapter, we report a new design and fabrication of a peristaltic micropump. In our applications, the pump can be integrated on micro-fluidic chips for biological/medical/chemical analyses. More powerful electromagnetic actuators are used and designed to be isolated from the fluidic part. In this case, the fluid channel can be as deep as 600μm.

4.2 Design and fabrication of the peristaltic pump

The fabrication process of the valve will be presented first. The fabrication of the peristaltic pump is similar to the valve fabrication process, other than that three valves were fabricated at the same time. Some experiments were conducted to test the valves. An optimal size of the flow channel and cuboid was studied to maximize the flow rate of the pump by both simulation and experiments.

4.2.1 General principle and design of the peristaltic pump

As we mentioned before, the peristaltic pump is constructed by using three same electromagnetic valves synchronized electronically. Each valve has two separated parts, the actuator part and the flow channel part. The actuator part is designed to have a long working life while the flow channel part is replaceable and disposable. A powerful electromagnetic solenoid is chosen as the actuator. The size of the flow channel is studied by simulation. When these three valves were open and close in synchronized fashion, the fluid in the flow channel would be
driven forward, therefore pump the fluid to flow in the micro-channel. The direction of the flow can also be reversed easily by electronically control the order of the valve operations.

The requirements for a peristaltic micro pump include enough achievable pumping rate, low flow rate fluctuation, and low power consumption. The peristaltic micro pump in our design is basically a linear one. As shown in Figure 4.1, it consists of a horizontal flow channel covered with a flexible membrane and three electromagnetic micro-actuators (marked as A, B, and C). The electromagnetic microactuator is separated from the underneath flow channel by the flexible membrane. Each actuator and the flow channel beneath it form one valve. When a pressure is applied on the membrane, a mechanical deflection is generated to close the fluidic channel. A peristaltic pump can be built with three such valves working in a synchronized fashion. The operation principle of the peristaltic pump is schematically shown in Figure 4.1. In step (1), valve A is closed and valves B and C are open with the fluid filled up the micro-chamber. With valve A closed, valve B is closed down in Step (2) the fluid in the microchamber is forced to flow to the right side. In Step (3), after valve B closed down, the downward motion of valve C forces the fluid in the microchamber to flow to the right side as in the step (2). When the valve A opened up, the elasticity of the PDMS membrane helps it to move up and the fluid is sucked to fill the left channel of valve B. In step (4), both valve A and valve B are open, the elasticity of the PDMS membrane helps it to restore to the original flat position. With the valve C closed, as the membrane restores to its equilibrium position, a pressure difference is generated to suck the fluid into the microchamber to fill it up again. A new cycle starts after the previous one is complete. This process is repeated as the operations of valves A, B, and C are controlled in synchronized fashion to pump the fluid from the left side to the right side continuously.
Fig. 4.1 (a) Schematic diagram of the peristaltic pump working principle; (b) Schematic diagram of the valve design

To conduct a simple analysis of this peristaltic micropump, we can assume the total time of completing one cycle of pumping operations is $T$, the fluid displacement of the peristaltic pump in one cycle is $V$. In theory, $V$ is the total volume displacement of fluid driven forward by the downward motions of valve B and valve C when they were closed. Then the flow rate $F$ of the peristaltic pump can be known as $F = \frac{Vf}{2}$, where $f$ is the operation frequency of the valves.

The displacement $V$ is determined by the size of the cuboid fixed at the tip of the actuator as shown in Figure 4.1. As physical size of the actuator limited in our design, the actuator force is small and design compromise must be made. The fluidic pressure force is consistent and it is very small compare with the elastic force, therefore it can be negligible here. The cuboid pad cannot be too big; otherwise the elastic force of the membrane may be too large to overcome in closing the valve. However, the cuboid pad cannot be too small either; otherwise the flow rate of the micropump may become too low.

The flow rate of the micropump is limited by the driving power. A powerful actuator is needed. The electromagnetic actuator is a good choice because of its power capacity.
The electromagnetic actuators from Tubular Company were selected for our design. A similar valve was reported [58]. The solenoid coil (Tubular, Push Type) is a hollow cylinder with a pole inside. The cylinder has a diameter of 0.38"(9.7 mm) and a length of 0.69"(17.5 mm). There are different duty cycle types of solenoid coil for selection, where duty Cycle is defined as the ratio of on-time to the sum of on-time and off-time in each cycle of the operation. For different duty cycle type, the internal wire gauge for winding is different. If the on-time in one cycle is shorter; the electromagnetic force provided by the solenoid coil is generally greater.

The duty cycle for the valve in our design is 50%. The solenoids with 50% duty cycle were therefore chosen. The force capacity for the solenoids is 7.9 Oz (2.20 N) at stroke of 0.01" (0.3 mm), 2.1 Oz (0.58 N) at a stroke of 0.05" (1.3 mm), and 0.4 Oz (0.12 N) at a stroke of 0.09" (2.3 mm). Therefore the available electromagnetic force is over 2.2N when the solenoid has the stroke of 0.01” and the valve is completely closed.

4.2.2 Design of the flow channel

The flow channel and the size of the cuboid pad are studied by using numerical simulations. The maximum electromagnetic force delivered by the solenoid coil is over 2.2N. Considering the fact the normal operation of the valves is always within this limit, a normal operation force of 2N is assumed in our design. The cross-sectional area of the flow channel is chosen to be rectangular. The numerical simulation results for different channel sizes and corresponding pressure required to close the channels are shown in Figures 4.2 and 4.3. The cuboid pad was designed to be 400 m wider than the flow channel, because if the width of cuboid pad is the same or smaller than that of the channel width, the cuboid pad may not completely close the flow channel because the deformation of the channel may make it wider in operation.
The cross-section of the channel was designed to be 600 μm×600 μm as shown in Figure 4.2. The electromagnetic force was assumed to be 2N. The pressure required to just close the flow channel was calculated to be about $4\times10^5$ Pa. The length of the cuboid was calculated to be about 4mm. By maintaining the height of the channel at the same size while increasing its width to 1000 μm as shown in Figure 4.3, the pressure required to close the flow channel was $3.8\times10^5$ Pa. The length of the cuboid pad was calculated to be about 4.2mm. From the simulation, the pressure of just closing the channel is almost not related with the width of the channel. Therefore, increasing the width of the channel is a good method to increase the volume of the valve once closing driving, and increase the flow rate of the pump.
But in many cases, the channel size is determined by other parts connected to the pump. In this dissertation, the channel and the L-L extraction system, which will be introduced in the next chapter, are fabricated in the same process. The channel in L-L extraction system is 600 μm×600 μm. To simplify the fabrication process and avoid dead volume, the cross-section of the channel was designed to be 600 μm×600 μm and the length of the cuboid was chosen to be 4mm long. This pump is a good option in other applications. In other applications, wider channel may be a good design.

4.2.3 Fabrication of electromagnetically actuated valve

Figure 4.4 shows the fabrication process of the magnetically actuated micro-valves. Figure 4.4a shows the fabrication process for micro-channel. The master mold of the flow channel was first fabricated using ultra violet (UV) lithography of SU-8. A soft lithography was done to create a negative PDMS pattern. When the PDMS is solidified, it was then peeled off from the SU-8 master mold. A thin layer of PDMS membrane was then sealed onto of it to seal the channel.

Figure 4.4b shows the fabrication of cuboid holder. Similar to the fabrication of the micro channel, the master mold for the cuboid was fabricated using UV lithography of SU-8. A negative pattern of the SU-8 master mold was then produced using soft lithography technology with PDMS. SU-8 cuboid was fabricated in such way that its cross-section is slightly bigger than that of the micro-channel.
A negative PDMS pattern was then generated using a PDMS soft lithograph process. Finally the molded structure was peeled off and the bottom was sealed with a thin layer of PDMS. After the channel and cuboid holder were fabricated, they were bonded together. Since the channel is designed disposable. The bonding is temporary, which required the channel part to be easily removed after used. The plasma treatment meets this requirement. Before bonding plasma treatment was applied on two bonding faces that can provide appropriate adhesion, without difficulty for potential separation. Only after being heated up to 100°C for one hour, the
bonding would be permanent. Because the sizes of both parts are not too small, the alignment can be done by hand. The bonding process was helped significantly by making a few alignment marks on both parts in mask design.

Figure 4.4c shows the fabrication process for the frame of the solenoid coil. The solenoid coil is a hollow cylinder with internal diameter of 5.3mm and external diameter of 9.7mm. In Step 1, a SU-8 cylinder with a diameter of 5.3 mm was fabricated lithographically. In Step 2, the solenoid coil was occluded on the SU-8 cylinder. Because the internal diameter of the solenoid coil and the diameter of SU-8 cylinder were designed to have the same sizes, this can be done easily. Because the position of the SU-8 cylinder was accurately controlled in the lithography fabrication, the positions of the solenoid coils were also accurately controlled. Because the solenoid coils were occluded on the SU-8 cylinders, they are therefore resistant to possible physical disturbances in the following assembly process. In Step 3, a PDMS to PDMS soft lithography process was used to produce a negative pattern with enough thickness to be physically strong to serve as the frame for coil. In our experiment, the thickness was chosen to be 2 cm and the baking temperature in PDMS soft lithograph process was over 100°C to increase its rigidness. The solenoid coil was removed from the frame in Step 4. The solenoid coil has screw thread on its external shell. A negative screw thread was therefore created in the PDMS frame structure. The solenoid coil therefore had to be screwed off from the PDMS frame. Finally the PDMS frame was peeled off from the wafer.

Process shown in Figure 4.4d was used to fabricate the elastic cuboid pad. The cuboid pad was designed to be slightly wider than the flow channel. The SU-8 mold was made in Step 1 by UV lithography of SU-8. A negative PDMS pattern was made with a soft lithograph process in Steps 2 and 3. In Step 4, a UV curable resin was then poured onto the PDMS negative mold to
obtain the cuboids. In our experiment, both NOA 73 and SU-8 were tested. Finally, the UV curable resin was exposed, and then removed from the PDMS mold after solidification. Due to the low adhesion and flexibility of the PDMS, the casted replicas of cuboids were easily removed.

With the flow channel, the solenoid frame, and the cuboids fabricated separately, they were then assembled to form the magnetic valve as shown at the bottom of Figure 4.4. Because there is screw thread on the frame, the solenoid coil was carefully screwed onto the frame. When the voltage is applied on the solenoid coil, the magnetic force would pull the meter pole down to push against the cuboid. The PDMS membrane was then forced to deflect and block the flow channel as shown schematically in Figure 4.1, the valve is therefore “closed”. When the control voltage is turned off, the electromagnetic force disappears, the elasticity of the membrane helps to restore it to the horizontal position to permit fluid to flow through the channel. The valve therefore returns to the “open” state.

4.2.4 Experimental results of the electromagnetically actuated valve

Experiments were conducted to study the leakage of the valve under different flow pressures and with different materials for the cuboid pads. In the experiments, different pressures were applied on the inlet side of the valve while the valve was closed. The flow rate on the other side of the valve was continuously measured. Because the flow rate was very low and difficult to measure, a simple scheme was designed to measure the flow rate. The outlet of the valve was connected to a precision syringe whose minimum measurement range is 0.02ml. By operating the valve for long period and measuring the time it took to fill up 0.1ml in the syringe, the flow rate can then be calculated based on the time and the fluid volume. The flow rate of leakage measured using this technique is therefore an averaged value. In general, the lower the flow rate of the leakage, the better the valve is.
The cross-section of the channel was designed to be 600 μm × 600 μm while the cross-section of the cuboids were designed to be 1 mm × 1 mm. Different lengths of the cuboids were used in our study to find the optimal length. Two different materials, NOA73 and SU-8, were used and compared. It was found that as the length of the cuboid becomes longer, the pressure produced by the electromagnetic force of the actuator on the cuboid is reduced, and therefore the leakage of the valve becomes higher. However, as the length of the cuboid increases, the fluid volume displaced by the valve in each downward operation is higher, and so does the flow rate of the micropump. A design compromise therefore needs be made in designing the cuboid length. The simulation results show that 4 mm is an optimal length for the cuboid.

The experiment results using different cuboid designs and materials are shown in Table 4.1 and Table 4.2.

From the experiment results, it can be observed that the cuboid pads made of NOA73 performed better than the SU-8 ones under any conditions. The main reason for this performance difference is that NOA73 polymer is much softer than the SU-8 and permits the needed deformation to close the rectangular flow channel completely. The softer material can compensate the error and fit the dead area and small gaps caused by the deformation of the flow channel made of PDMS. NOA73 was therefore selected as the cuboid material. The length of the cuboid was chosen to be 3 mm. The length is shorter than the simulation. The reason is first because of fabrication error; the magnetic force cannot be perfectly applied on the center. Secondly, the armature size is made a little longer than the idea design to make sure the valve can be completely closed, it would reduce the force it apply. The final design for the cuboid was therefore chosen as 1 mm × 1 mm × 3 mm cuboid made of NOA73.
<table>
<thead>
<tr>
<th>Pressure</th>
<th>SU-8 2mm</th>
<th>SU-8 3mm</th>
<th>SU-8 4mm</th>
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<tbody>
<tr>
<td>150kpa</td>
<td>0μl/min</td>
<td>20μl/min</td>
<td>40μl/min</td>
</tr>
<tr>
<td>225kpa</td>
<td>20μl/min</td>
<td>50μl/min</td>
<td>80μl/min</td>
</tr>
<tr>
<td>375kpa</td>
<td>80μl/min</td>
<td>100μl/min</td>
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<thead>
<tr>
<th>Pressure</th>
<th>NOA73 2mm</th>
<th>NOA73 3mm</th>
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<td>150kpa</td>
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<td>375kpa</td>
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4.3 Experimental results of the prototype peristaltic pump and discussions

A peristaltic pump consists of three electromagnetic valves as schematically shown in Figure 4.1. In operation of the micropump, the three electromagnetic valves need to be turned on and off in a synchronized fashion to suck in the fluid from one side of the flow channel and pumped out from the other side. This synchronized operation of the valves is achieved by electronic control.

One of our design targets was to be capable of being controlled in Windows environment. The commercial software package, LabVIEW (National Instruments, Austin, TX), was used in the experiment. There is no text-based code as such, but a diagrammatic view of how the data flows through the program. The National Instruments USB-6008 was used in the experiment. UDB-608 is a low-cost, multifunction data acquisition device (DAQ). It has eight analog inputs,
two analog outputs, and twelve digital input/outputs. In our application, three outputs are needed to control the three valves in the pump. Figure 4.5 shows the flow chart of the program: 1) First, set the step time \( t \), the step time can be entered when the program was running; 2) Set a counter which counts number \( n \) from 1 to infinite; 3) After each step time \( t \), the counter was reset to \( n=n+1 \); 4) When \( n \) is changed each time, some logical judgment would be done. If \( n+3 \) divide by 4, the remainder is 0, then valve 1 is closed and valves 2 and 3 are open. Otherwise if the remainder of \( (n+2) \) divided by 4 is 0, then valve 1 and valve 2 are closed while valve 3 is open. Otherwise if the remainder of \( (n+1) \) divide by 4 is 0, then valve 1 is open while valve 2 and valve 3 are close. Otherwise valve 1 and valve 2 are open while valve 3 is close. By this logic, the pump function can be achieved.

![Flow chart of the controlling program](image)

The data acquisition board Ni 6008 only has two analog outputs but there are three valves. Three digital I/O outputs were therefore used to control the valves. The maximum output voltage of the digital I/O is 5V with the maximum current at 0.6mA. The operational voltage of the
valves is 12V and the current is 40mA. An amplifying circuit was therefore designed and built to boast the outputs of the I/O board to the operation voltage and current of the valves.

If the step time is set too long, the flow rate of the pump may become too low. If the step time is set too short, it may cause the temperature of the solenoid to increase significantly and potentially damage the devices. Though PDMS is stable at the over 100°C, the sample fluid inside the flow channel may be negatively affected. After many experiments, the optimal step time was found to be 0.1 s.

The peristaltic pump was tested with free load. The input side was connected to a water pool; the other side was connected to a precision syringe with resolution of 0.02ml. The prototype peristaltic micropump was tested and the flow rate was obtained by measuring the fluid volume accumulated in the syringe and the total operation time. The flow rate of the pump was found to be about 3 l/min with the step time set at 0.1 s and the operational frequency of the valves was set at 10Hz.

4.4 Summary

A peristaltic micro pump with three electromagnetically actuated valves was designed, fabricated, and tested. The major advantage of the prototype peristaltic micropumps reported in this chapter is that the flow channels are separated from the electromagnetic actuators. In this design, it can dramatically reduce the complexity of the microfluidic chips by removing the active components from them. The microfluidic chips therefore include only passive components with simple structures and can be molding replicated and disposable. In this design approach, the overall cost of the microfluidic chips can also be significantly reduced.

The pump in this chapter can be used to handle the micro channel with cross-sectional size of 600 μm×600 μm. From the simulation results, it was found that to increase the width of the
flow channel significantly increases the flow rate of the pump. The sizes and material of the closing cuboid pads of the valves are both important to avoid leakage of the valves. Numerical simulations and experiments have proved that cuboid pads made of NOA73, which have dimensions of 1mm×1mm×3mm, provide the best results. The operations of these three valves were synchronized using a control program written in Labview. It was found that the optimal operation frequency of the valves was 10Hz; the flow rate of the pump was measured to be about 3 l/min.
CHAPTER 5 LIQUID-LIQUID EXTRACTION SYSTEM AND EXPERIMENTS RESULTS OF FINAL INTEGRATED DEVICE

In this chapter, the fabrication process of the Liquid-to-Liquid extraction part is presented. As stated in chapter 2, the Liquid-to-Liquid extraction part is the key point to miniaturize the physical sizes while still maintaining the sensitivity of the oil detection instrument.

Experiments were conducted on the integrated micro-fluidic-chip consisting of the extraction and optical detection unit. Different sizes of the fence-wall designs were compared. The experimental results have showed that the best design of the micro-fluidic chip achieved as high as 7 times concentration after 15 mins extraction. The experimental results show that the liquid-to-liquid extraction unit functioned as expected.

5.1 Background

Although liquid-liquid extraction has been a sample pre-concentration technique widely used in chemical and other industries, conventional set up is often laborious and requires multiple-equipment, it is therefore not suitable for in-field applications. Similar to the conventional liquid-liquid extraction systems, micro-chip for liquid-liquid extraction also utilizes the difference of analyte solubility in sample solution and the extraction solution to extract analyte from sample solution to the extraction solution. Because the extraction solution is generally selected as having higher solubility for the analyte, higher concentration of the analyte can therefore be achieved in the extraction solution. With microfluidic technology, not only the liquid-to-liquid extraction unit can be integrated into the same microchip with the detection unit, the liquid-liquid process can be accomplished automatically on chip, thus faster and higher efficiency extraction can be achieved due to the higher surface-volume ratio and shorter diffusion length. In addition, the oil droplets, which are of our particular interest in this research
work, are very likely dispersed (droplet size 20\(\mu\)m-150\(\mu\)m), emulsified (5\(\mu\)m-20\(\mu\)m) and dissolved oil droplets (<5\(\mu\)m) [59]. Therefore the droplet sizes are in the same scale as the feature size of microchannels in the microfluidic chip, which gives microfluidic chip the intrinsic advantages in the manipulation and separation of oil droplets.

In the past decade, many efforts have been made in field of microfluidics for design of liquid-liquid extraction devices. Many researchers have proposed sandwich-structured microfluidic devices for L-L extraction applications [60-62]. In these designs, a porous hydrophobic membrane is often used to separate the two flow phases and mass transportation can only be accomplished through micro-pores in the membrane. Capillary pressure and interfacial tension prevent both flows from leaking into each other, but solute in the aqueous phase can easily pass through these pores by wetting the membrane surface. Although these designs are generally more robust due to the extra pressure balance force resulting from the capillary pressure, alignment of top and bottom fluidic layer and the bonding among three layers make fabrication process much more complicated. And most importantly, the size of the capillaries in the membranes commonly used in these designs is much smaller than oil droplets. Therefore, these designs are good options for solution extraction, but not for dispersed oil in water application, emulsion extraction. Some other designs did not use membranes, and instead, utilized the laminar flow interface between two immiscible solvents. In these designs, the pressure difference between two flow phases is balanced by interfacial tension [63-64]. Because no physical separation was used, the L-L interface can only be stabilized in certain flow conditions and selective channel modification is often required [65-66].

We use a design similar to the one mentioned by Ryan et al. [67]. In our design, the aqueous solvent and organic solvent flows are separated by micro-sized intermitted walls formed
by array of micro-posts. The small gaps between the micro-posts have the function similar to the pores in the porous membrane previously mentioned, and can be fabricated together with the fluidic channels and other components.

5.2 Design and fabrication of L-L extraction system

5.2.1 Principle and general design of the L-L extraction system

The design of the L-L extraction system for sample pre-concentration is schematically shown in Fig.5.1 and Fig.5.2. The L-L extraction system consists of three functional layers: the electromagnetic control layer, the fluid handling layer and the L-L extraction layer. The sample enters the system from aqueous sample reservoir to the L-L extractor (made of PDMS) through the vertical hole 2. The wastewater then flows through the vertical hole 3 and peristaltic pump, and then flows out of the system. With valve B open and valve A closed, the organic solvent enters the circulating system through valve B, flows through vertical hole 1 into the L-L extractor, and then splits into two channels, one in the left side of the sample channel, and the other in its right side. The solvent flows (with oil in it) in both channels and then recombines. In the pre-concentration stage, the valves A and B are closed; the solvent flow keeps circulating in the L-L system. After the pre-concentration is done, valve A is open; the solvent flow with oil is then supplied to optical detection unit for measurement. With the control signal from peripheral electronic system, the pneumatic stop valves and peristaltic pumps in the pneumatic control layer work in a synchronized fashion to deliver sample and also control the circulation and output of the organic solvent. The fluid handling layer provides microfluidic channels for the sample aspiration and delivery to the L-L extraction layer. The SU-8 layer consists of three fluid channels, two organic solvent channels are at both sides of the aqueous sample channel and are
separated by a porous channel wall between aqueous flow channel and each organic flow channel.

Fig. 5.1 Schematic Diagram showing the multi-layer structure for L-L extraction and fluidic control for in-situ detection

Without any oil content in the sample, the aqueous sample flows in two channels on both sides of the channel for organic solvent and flows at the direction opposite to the organic solvent flow. The immiscible aqueous sample and the organic solvent are separated by the fence-walls. As long as the hydro-pressure difference between two immiscible flows is within the interfacial tension limit, the interface is stable and both fluids shall not pass through the hole and mix into each other. On the other hand, if there is oil content in the aqueous flow, oil droplets should be able to pass though the gaps between the fences and dissolve into the organic solvent because interfacial tension between oil and the corresponding organic solvent is much lower, and there is little resistance to prevent oil from entering the organic solvent flow. Because the organic solvent circulates in the system and new aqueous sample is continuously supplied into the system, oil concentration in the organic solvent phase can accumulate and reach a much higher level than that in the sample flow.
In comparison with the conventional static balance procedure, the organic solvent in this design continuously circulates in the system and fresh aqueous sample is continuously supplied to the system. The oil concentration of aqueous sample exiting is far from exacting balance, but oil concentration in the organic solvent phase can accumulate, for any controlled time period, until the maximum concentration is achieved, i.e., the equilibrium of the concentrations of oils in the aqueous sample solution and organic phase is reached. For a portable device as targeted in our design, the operation time shall be controlled in an acceptable period. The best approach is to calibrate the relation between oil concentration of fresh aqueous sample and oil concentration of organic solvent when the system operated for a given time period. Because the fenced walls provide much higher diffusion efficiency in comparison with porous membrane and counter-current flow (higher efficiency than that of the co-current design), the required operation time for L-L extraction unit can be much shorter.
After L-L extraction, the organic solvent with the extracted oil is then controlled by pump and valves to flow through a microfluidic channel and enter the optical detection unit. The detailed design and operation principle for the optical detection unit are shown in Chapter 3 and Chapter 4. The optical measurement unit is integrated on the same chip as the microfluidic L-L extraction unit, as well as microvalves and micropumps for flow control to form an integrated micro-fluidic-optic cartridge. Optical fibers are used to supply and receive light from the measurement chamber. Other optical components including light emitting diodes (LEDs) as excitation light sources, spectrometer as detectors, and filters, are external components of the instrument and not integrated with the micro-fluidic-optical cartridge. Because the fluorescence characteristics of crude oil may vary depending on where the crude oil was from geographically, this design allows different types of LEDs, detectors and filters to be chosen for the specific oil sources and independently of the microfluidic chip.

For the L-L extraction layer, the depth of all channels is 600μm. The aqueous phase channel in the middle is 600 μm wide. The organic phase channels on the two sides are 300μm wide each. The diameter of the vertical hole is 1mm. The length between two vertical holes is 3cm. The size of the fence wall will be discussed in later sections. The cross-sections of channels in the electromagnetic control layer and the fluid handling layer are all 600μm×600μm.

5.2.2 Counter-current and co-current flow configuration of the L-L extraction layer and interface stability

There are two design options for L-L extractors. The first one is the so-called co-current design in which the aqueous and the organic phases flow in the same direction. The second design is the counter-current one in which the aqueous and organic phases flow in the opposite
directions as shown in Fig.5.3. Numerical simulations and experiments were used to compare the extraction efficiencies of two designs.

For co-current flow design, the flow interface stability has been extensively studied, especially for the conventional sized ones widely used in chemical industry. In micro-flow L-L extractor, interfacial stability can be easily maintained with co-current design because the flow is generally laminar. The main disadvantage of the co-current design is its lower extraction efficiency because as the organic solvent flows out the system, the difference of the sample concentration between the two flows drops significantly. As the result, there may be significant amount of sample still left in the aqueous solution. In the counter-current flow design, a high concentration gradient can be maintained as the organic phase flow from the downstream of the aqueous phase and it is expected to obtain high solvent extraction.

![Schematic diagrams of the liquid-liquid extractor in counter-current (a) and co-current (b) flows with physical separation](image)

Fig.5.3 Schematic diagrams of the liquid-liquid extractor in counter-current (a) and co-current (b) flows with physical separation

In theory, co-current fluids in micro flow channels are laminar. They will not mix into each other even if no physical separation is used if the pressure differences in the flow channels are carefully controlled. In reality however, some separation wall and surface modification are obligatory for both designs. Numerical simulations were performed to study the extraction efficiencies of both counter-current and co-current flows with a two-dimensional model. Fig.5.4 illustrates the distribution of concentration and mass flux of the solutes in both cases. As the
aqueous phase flows through the channel, the solute penetrates the fence wall and reaches the organic phase because of the concentration difference. The result confirms that the concentration decreases faster in the counter-current flow than that in the co-current flow along the channel. In the co-current extractor, uniform concentration is immediately established so that the solute is prevented from transferring between the two phases. On the contrary, a high concentration difference is maintained during the extraction in the counter-current flow extractor, which drives solute to move from the aqueous phase to the organic phase. Thus, higher extraction efficiency can be eventually achieved.

![Fig.5.4](image.png)

Fig.5.4  Comparison of mass flux and concentration distribution of the solute in the extractor in co-current and counter-current flows

Fig.5.4 shows that comparison of mass flux and concentration distribution of the solute in the extractor in counter-current flow and co-current flow. The extractor is 1.2mm in width and 2mm in height. The thickness of the porous wall is 0.2mm. The velocity of the organic phase and aqueous phase is 0.6mm/s. Inlet concentration of solute is 1mol/m³. The diffusion coefficient is $1e^{-8}$ m²/s. The parameters of the model have been adjusted to show the difference between co-current and counter-current flow more significant. These parameters used in numerical simulations are in the same order of magnitude but not exactly the same sizes as used in our
design. The numerical simulation results show that the extraction efficiency of the counter-current flow is always higher than co-current flow as expected.

The counter-current design is chosen for its high efficiency and because the fabrication technology to be used provides us with the design flexibility. Two pressure values are considered in the flow interface stability analysis. One is the pressure difference, $\Delta P_{\text{flow}}$, between two phases with different viscosity and velocity. The other is the Laplace pressure $\Delta P_{\text{Laplace}}$ caused by the interfacial tension between the two phases. At very low Reynolds number (as in microchannels), the pressure drop can be considered linear (Fig.5.5). The maximum $\Delta P_{\text{flow}}$ is located at the tips of the transfer region. When $\Delta P_{\text{flow}}$ exceeds $\Delta P_{\text{Laplace}}$, the interface cannot sustain the pressure drop and break down.

![Pressure profile of the two-phase flow along the channel](image)

According to Young's law, the relationship between the contact angle and surface tension is expressed as:

$$\gamma_{AO} - \gamma_{AS} = \gamma_{OS} \cos \theta,$$

where $\theta$ denotes contact angle. A is aqueous phase; O is the organic phase and S is the substrate surface. $\gamma_{AO}$, $\gamma_{AS}$ and $\gamma_{OS}$ are the surface tensions between the corresponding interfaces, respectively. Additionally, the Laplace pressure across the interface in a pore can be evaluated as:
where $R$ is the curvature radius of the interface and $d$ is the size of the pore. The major goal here is to achieve higher $\Delta P_{\text{Laplace}}$. Eq.5-1 indicates that the contact angle is submitted to the characteristic of the substrate surface (i.e. $\gamma_{OS}$ and $\gamma_{AS}$), meanwhile $\Delta P_{\text{Laplace}}$ relies entirely on the contact angle at a given flow condition. Ideally $\Delta P_{\text{Laplace}}$ reaches maximum at $\theta=0^\circ$ or $180^\circ$. This relationship implies that selective surface modification is a valid method to control the extraction process. Much work has been devoted to this technique [68-70]. Arata etc [63] detailed a theoretical model to analyze the pressure balance. A typical process is to form a hydrophilic-hydrophobic pattern modification. The surface of the aqueous phase side is hydrophilic, while that of the organic phase is hydrophobic (Fig. 5.4). The range of the contact angle is between the peak contact angle of organic phase $\theta_{\text{org/philic}}$ and the hydrophilic surface and that of the aqueous phase and the hydrophobic surface $\theta_{\text{aq/phobic}}$. On the basis of Eq.5-2, it can be written as:

$$-4\gamma_{AO}\sin(\theta_{\text{org/philic}} - 90^\circ)/d < \Delta P_{\text{Laplace}} < 4\gamma_{AO}\sin(\theta_{\text{aq/phobic}} - 90^\circ)/d.$$  

The selective surface modification provides wider range of $\Delta P_{\text{Laplace}}$. It allows the extractor operates at larger velocity difference between the two-phase flows. Consequently, the extraction efficiency is improved.

Fig.5.6 (a) the shape of the interface when the organic phase moves to the hydrophilic surface; (b) the shape of the interface when the aqueous phase moves to the hydrophobic surface.
5.2.3 Material selection for L-L extraction layer: SU-8 or PDMS

The structure of L-L extraction layer is shown as green part in Fig.5.1 and dash part in Fig.5.2. It is the most important layer in three layers of the L-L extraction system. Both the electromagnetic control layer and the fluid-handling layer are fabricated with PDMS for ease of fabrication. The L-L extraction system material can be selected between PDMS and SU-8. The advantages and disadvantages of PDMS and SU-8 are compared.

a. Comparison of SU-8 and PDMS surface modification

In order to obtain high liquid-to-liquid extraction efficiency and two-phase counter flow stability, large wettability difference on two opposite sides of the fence wall is highly desired. The wall on the aqueous phase channel side is highly hydrophilic while the one on the organic phase channel side is highly hydrophobic. To reach this goal, two different surface modification techniques (hydrophilic on aqueous side and hydrophobic on organic side) on the same fence wall are implemented.

Generally, Surface modification on SU-8 is easier than PDMS. Because of low adhesion property of PDMS, it is always a problem to do surface modification on PDMS. For PDMS, hydrophobic treatment is rare. But there are plenty of well-studied hydrophilic methods [71-74]. For a SU-8 substrate surface, both hydrophilic and hydrophobic surface treatments in microfluidic channels are well known techniques.

The PDMS is hydrophobic naturally. Its contact angle of water is about 108°. There are some methods to improve its hydrophobic property. But they are either not significantly enough or lasting very short. In fact, PDMS is naturally hydrophobic enough for our requirement. On the other hand, some treatments can improve hydrophilic property of PDMS surface significantly. Many techniques for hydrophilic treatments are reported, such as plasma treatment, UV
treatment, CVD, coating with metals and metal oxides, and many other wet chemical methods [75]. The effective period is still a problem. Most of these treatments can only last several days or several weeks. Our target is to make a commercial device. The shell life of the device should last as long as possible. Therefore, a treatment of long life is chosen. It is reported that it can last about two months. The details of the treatment are introduced in later section. Many types of monomer can be deposited on the surface of PDMS, AA (anionic acrylic acid) is used in this dissertation. Our experimental results show that the water contact angle can approach 40° after using AA surface modification. ZW (zwitterionic [2-(methacryloyloxy)-ethyl] dimethyl (3-sulfopropyl) ammonium) may be better and can be used in the future. Some research shows that the water contact angle can be as low as 15° after using surface modified by ZW.

Cured SU-8 itself is relatively hydrophobic, with a water contact angle of 70°-80° [76-77]. To date, many hydrophilic surface modification techniques have been reported, including oxygen plasma treatment, reaction with ethanolamine, or UV-initiated graft polymerization etc. [71-72][74]. If only the surface of selected area (fence on the aqueous channel side only) needs to be modified, UV initiated graft polymerization is proven to be more effective due to its ability of micro-patterning surface with the aid of a mask [74]. UV-initiated graft polymerization of SU-8 relies on the residual photoacid generator within the SU-8 matrix after being cured. With the presence of a monomer solution and UV light, the remaining photoacid generator initiates the polymerization of the monomer onto the SU-8 surface [78]. A wide range of water-soluble monomers, such as poly(acrylic acid), poly(ethylene glycol) methyl ether acrylate and 2-(dimethylamino) ethyl methacrylate, could be successfully photografted onto the surface of the SU-8 photoresist surface. Two monomers candidates have been tested in our research: the first
one is poly(ethylene glycol) methyl ether acrylate with water contact angle 45°, and the other one is 2-(dimethylamino) ethyl methacrylate with water contact angle 13°.

SU-8 can be made hydrophobic by coating with octadecyltrichlorosilane (OTS) [79-81]. After aqueous channel side of the fence have been hydrophilic modified, silanization (coated by a covalent binding of octadecyltrichlorosilane (OTS) was then carried out on the organic phase channel side. After the treatment, fence on the organic channel half (not covered by grafted polymers) and the organic channels are silanized. A water contact angle of 110° can be achieved.

b. Comparison of SU-8 and PDMS fabrication

There are two design options for the fenced wall structures for L-L extraction separation, one is the array of micro-posts, and the other is the porous fence. The fabrication of SU-8 porous fence can be accomplished with multiple steps of normal lithography and tilting lithography technique. The fabrication process of the wall with micro-pores to separate the input sample fluid with the organic solvent is illustrated as following. The SU-8 layer is exposed twice, one at 45°, another at -45°. An aligned normal exposure is then conducted to define the fluid channels [27][82]. The size of the pores can be well controlled. Smaller these pores are, greater the surface tension is. The flow rates of both phases are allowed to rise up. Since SU-8 is harder, the frame can be thin and the total contact area between two phases can be larger. The extraction efficiency would increase. The porous wall structure can only be achieved by SU-8.

However, the fabrication process of the porous wall is more complicated than that for the fenced wall formed with array of the micro-posts.

The L-L extraction system consists of three functional layers: the electromagnetic control layer, the fluid handling layer and the L-L extraction layer. The electromagnetic control layer and the fluid handling layer were fabricated by PDMS. If the L-L extraction layer was fabricated
by SU-8, the rest two layers are bonded to the Su-8 layer in the top and bottom sides. If the L-L extraction layer is fabricated with PDMS, the L-L extraction layer and the fluid handling layer can be combined to be one layer. Both of them are fabricated in the same layer and then bond with the electromagnetic control layer. As stated in section 5.2.3a, if it is made of PDMS, there is only once surface modification needed. But if it is made of SU-8, it requires surface modifications on both sides.

Bonding is another issue for SU-8. Bonding strength between PDMS and PDMS can be achieved with oxygen plasma assisted method. Bonding strength between PDMS and SU-8 structures is a challenge. Direct oxygen plasma treatment has only resulted in a weak bonding between PDMS and SU-8. Chueh et al., [83] proposed a leakage-free PDMS to polymer bonding technique that used a thin layer of PDMS pre-polymer as a glue layer for the PDMS bonding to various polymer surfaces. However the bonding strength is still weaker and the bonding process is more complicated.

c. Summary of comparison

PDMS and SU-8 have their own advantages for the L-L extraction layer material. Firstly, the surface modification of SU-8 can be easier than PDMS. For SU-8, the water contact angel after hydrophilic treatment is 13° and hydrophobic is 110°. For PDMS, the water contact angel after hydrophilic treatment is 40° and hydrophobic is 108°. The surface tension of the SU-8 is greater, which means higher flow rate in the channel and more stability of the flow. The hydrophilic on the PDMS can only last about two months; the hydrophilic and hydrophobic treatment on SU-8 can last longer.

Secondly, with micro-molding process of, the separation wall between the aqueous phase and organic phase can only be the fenced wall formed with array of micro-posts because the
walls with microholes cannot be molded. If SU-8 is used as the structural material for the device, not the molded PDMS, then both the fenced wall formed with array of microposts and the wall with micro porous can be used. The micro porous wall may improve extraction efficiency significantly.

However, the molding fabrication process of PDMS is simpler and may reduce the overall cost of the device significantly. The L-L extraction layer and the fluid handling layer can be combined as one layer. On the other hand, bonding strength between PDMS and PDMS is better than PDMS and SU-8.

Both of PDMS and SU-8 have their advantages and disadvantages respectively for L-L extraction layer material. PDMS is chosen in this dissertation, but SU-8 is still a potential option for future work.

5.2.4 Surface modification of the PDMS L-L extraction layer

The following procedure was used for surface modification of the PDMS samples: 1) to immerse PDMS sample in acetone solution containing 10wt% benzophenone (Sigma Aldrich) for 40s, and then blow it dry with nitrogen. Benzophenone can be excited photochemically with UV irradiation. The purpose of immersing PDMS in it is to diffuse some benzophenone into the PDMS surface and to use it as a photoinitiator in the UV-induced reaction later; 2) Prepare a solution with 5 wt% in water monomer, 0.5 mM NaIO4 (Sigma Aldrich), and 0.5 wt% benzyl alcohol (Sigma Aldrich); 3) Coat the solution on the PDMS; 4) Prepare a UV-transparent glass slide and clean it up in a 5:1 mixture of Milli-Q water and 35wt% hydrogen peroxide for 10 min at 80°C; 5) Load the glass slide carefully onto the PDMS to contact the solution coated on the PDMS sample. After completely contact with the solution, the PDMS is adhered below the glass because of the surface tension as shown in Fig.5.7; 6) UV exposure.
The temperature needs be controlled in this process. If the temperature rose up because of the UV exposure in later processing step, a phase transition may happen and polymer chain may aggregate. To control the temperature, a frame is made to support the PDMS so that the lower surface of the substrate is maintained to contact ice water in the dish. Finally the sample was placed under the UV lamp for exposure. The UV intensity was about 8 mW/cm². The Exposure took about 40 min. After the exposure, the PDMS sample was removed from the glass slide and washed with deionized water and ethanol for 15 mins, then incubated in deionized water overnight to eliminate the loosely deposited but not covalently attached monomer and polymer from the PDMS surface.

There are a few options for the monomer, such as cationic dimethylacrylamide (DMAA), anionic acrylic acid (AA), and zwitterionic [2-(methacryloyloxy)-ethyl] dimethyl (3-sulfopropyl) ammonium (ZW). AA is used in this dissertation. Some studies show that the water contact angle can approach 40° after using AA surface modification. Some research shows that the water contact angle can be as low as 15° after using surface modified by ZW [84]. ZW may be better and can be used in future work.

Fig.5.7 Schematic diagram of the PDMS surface modification
5.2.5 Fabrication of L-L extraction layer

The design of L-L extraction layer is shown in Fig.5.1, and its operation principle has been introduced. The schematic diagram of fabrication procedure for the L-L extraction layer is shown in Fig.5.8. Step 1 was to fabricate the SU-8 mold. The thickness of the SU-8 was 600 μm. The side length of the vertical rectangle holes was variable and can be well controlled. In Step 2, a negative PDMS pattern was created using a soft lithograph process. In Step 3, the cast-molded PDMS structure was carefully peeled off the SU-8 master mold. Because the micro-posts were thin and fragile, the peeling process needs to be carried out carefully and from one side to the other. The micro-posts need to be peeled off the master mold one by one. After peeling off, the sample was placed on a clean wafer. In step 4, SU-8 photoresist was poured onto the PDMS and excessive SU-8 was scraped off with a clean razor blade and then placed in a vacuum chamber for 20 minutes to eliminate air bubbles. Low viscosity SU-8 was better for filling in to the microstructures and quickly eliminating air bubbles. SU-8 50 was used in this research. After Step 4, the following was standard SU-8 lithography process, prebake, exposing, post bake and developing. It is worth noting that the photomask was aligned onto the PDMS substrate and SU-8 after prebake by using Quintel UL7000-OBS Aligner and DUV Exposure Station. The SU-8 was exposed on selected area as shown in Step 5. After development, only selected area remained as in Step 6. Step 7 was used to carry out the surface modification for the PMDS sample. Because the coated SU-8 layer protected the selected regions, only the unprotected regions were surface modified. The detail surface modification process was introduced in section 5.2.4. After the surface modification, the SU-8 protective layer was removed. Thanks to the low adhesion property of PDMS, SU-8 protective layer could be easily removed mechanically with
the help of a needle. In Step 8 the top of the L-L extraction channel was sealed with a layer of PMDS membrane. This completed the fabrication of the L-L extraction channel.

Limited by the molding process, the sizes of the rectangle micro-posts of the fence wall cannot be too small. In Step 1, the rectangle holes were not through holes. Thus, it was difficult to completely clean the bottoms of the holes by developer if the sizes of these holes are too small, and would negatively affect the following processing steps. Especially after PMDS molding, the PDMS micro-posts might become shorter than the sidewalls, and therefore could not be bonded to the top membrane when the entire micro-fluidic-optic chip was integrated in bonding process. Even if they were bonded together, there would be gaps between micro-posts and the top membrane, and if the gaps were big enough, the aqueous and organic phase solutions might easily flow through them with little pressure. If the size of the micro-holes made on SU-8 was too small in Step 1, the molding process with PDMS might become impossible because the molded PDMS micro-posts might be too small and fragile, and could be easily broken during the peeling off process in Step3. After many experiments, it was proved the size of the rectangle poles must be bigger than 150 μm×150 μm.
Fig. 5.8 Schematic diagram of the fabrication process for the L-L extraction layer
5.2.6 Simulation of L-L extraction layer extraction efficiency

A numerical simulation was performed to study the extraction efficiency of the L-L extraction layer in counter flow with a 2-dimensional model. Similar simulations were reported by other researchers [85]. The only difference in our mold is the fence wall structure. The model was built and the fluid in the fence wall was considered as static layer of fluid. For the entire organic phase channel that forms a loop, cross-section area is 600 μm×600 μm. The flow rate of the peristaltic pump is 3μl/min. The total length of the looped channel for the organic phase is about 8cm. Therefore, the total time for organic phase flowing one circle is therefore calculated to be 9.6 mins.

The L-L extraction layer is symmetric, thus we can simulate half of it. As shown in Fig.5.3a, we can assume the oil concentration of aqueous phase on the entrance is $C_0$ and the oil concentration of organic phase on the exit is $C$. In theory, if the thickness of the fence wall is smaller, the extraction efficiency is better, because the traveling distance for oil is shorter as it diffuses from the aqueous phase to organic phase. Limited by the fabrication process, the achievable minimum size of the poles’ cross-section was found to be 150μm×150μm. The cross-section of the micro-posts was set to be 150μm×150μm in simulation and the gaps between the poles were also set to be 150μm. The flow rate of the aqueous phase was set as 150 l/min.

Fig.5.9 shows the simulated results of $C/C_0$ as a function of time. For the first circle, $C/C_0$ has an equilibrium state as shown in Fig.5.9a. After 3 minutes, $C/C_0$ reached over 90% value of the equilibrium state. To simplify the simulation of the system, assume that there is no diffusion after the organic fluid leaving the L-L extraction layer. It means when it leaves the exit of the L-L extraction layer, the oil concentration distribution of the organic phase is the same as it enters the entrance in the next round of circular flow. From this assumption, the relation between $C/C_0$
and time of the second circle is shown in Fig.5.9. C/C₀ also has an equilibrium state. After about 14 minutes of virtual operation, C/C₀ has reached over 90% value of the equilibrium state.

**Fig.5.9** The relation between C/C₀ and time in the first (a) and second (b) flow circle

**Fig.5.10** Oil concentration distribution of both organic and aqueous phase in the first and second flow circle

Fig.5.10 illustrates the equilibrium state distribution of concentration and mass flux of the solute in the first and second circle. As the length of both phases is 3cm while the width is only 300μm, the length is 20 times smaller in the figure to give a better view. Figs. 5.10a and b are the oil concentration distribution of the organic phase and aqueous phase in the first circle; Fig. 5.10c and 5.10d are the oil concentration distribution of the organic phase and aqueous phase in
the second circle respectively. The simulation results show that the oil concentration magnitude of the organic phase after 15mins extraction operation can be as high as 7 times of concentration in aqueous sample without extraction.

5.3 Experimental results of the integrated system and comparison of different fence size designs

The design of the integrated micro-fluidic-optic chip was shown in Section 5.1. The optical detection unit was designed and presented in Chapter 3. The peristaltic pump was designed and discussed in Chapter 4. The size of the micro-posts forming the fence wall as the physical separation between the organic phase and aqueous sample solutions in the L-L extraction layer and the gaps between the poles need to be studied. In theory, the smaller the size of the micro-posts is, the higher the extraction efficiency can be because the thickness of the fence wall is thinner and it is easier for oil passing through. Several different sizes of microposts were tried to prove this theory. As discussed in Section 5.2.5, limited by the fabrication process, the minimum cross-section of the micro-posts’ is 150μm×150μm. In this dissertation 150μm×150μm×600μm, 200μm×200μm×600μm and 250μm×250μm×600μm poles were tried. To keep the contact area between organic and aqueous phases the same for different designs of the micro-posts, the gaps between the poles were set to be 150μm, 200μm and 250μm respectively.

The organic phase was driven to circulate in the micro-channel by a specially constructed peristaltic pump. As mentioned in Chapter 4, with a step time of 0.1s, the flow rate of the peristaltic pump was found to be about 3 μl/min under free load condition. When the integrated micro-fluidic-optic chip operates, the flow resistance of the organic phase must be greater than free load. Thus, the flow rate of the peristaltic pump may be slightly lower than 3 μl/min. The
aqueous phase was designed to be driven with an external pump. In our experiments, it was driven by the syringe pump (NE-4002X Syringe pump), which can control the flow rate accurately.

The surface tension is an inherent physical property of a fluid. For the aqueous, and the organic phase fluid, how hard for these two fluids to flow across the fenced wall formed by the array of micro-posts depends heavily on the gaps between the neighboring micro-posts. When the gaps are smaller, higher pressure difference is required to drive the fluids to flow to the opposite sides of the fence wall. This means that the flow rate of the organic phase can be higher with no concern for leakage to the opposite side of the fence wall.

In our experiment, while the peristaltic pump continues to operate, the aqueous phase sample was supplied into the system with an external syringe pump. The aqueous and the organic phase solutions flow in counter-directions. The flow rate of the aqueous phase was gradually increased to find the maximum flow rate while the stable interfacial surface still maintained. The maximum flow rate of the aqueous phase flow rate was measured for different sizes of micro-posts in the fence wall. If the flow rate of the input aqueous solution was higher than the maximum rate permitted, the interface between the two phases would be broken through and two phases would mix together.

The maximum aqueous phase flow rate was measured for three different designs of fence wall formed with the micro-posts and gaps. The result was that the maximum of the aqueous phase flow rate of for the fence wall of 150μm×150μm×600μm micro-posts and 150μm gaps design was about 150μl/min. The maximum of the flow rate for the fence wall of 200μm×200μm×600μm micro-posts and 200μm gaps was about 50μl/min. And for fence wall
with $250\mu m \times 250\mu m \times 600\mu m$ micro-posts and $250\mu m$ gaps, the interface was not stable at any aqueous phase flow rate.

We have conducted some experiments to test the integrated system using fence walls with the two different designs of the micro-post and gap sizes using standard oil samples. Crude oil was provided by BP Company. The samples with 1ppm, 50ppm concentrations were prepared with nonane as solution. A commercial spectrometer was used to measure the output spectrum of the photodiode signal. The integration time of the signal (amplitude) in the spectrometer was adjusted correspondingly. The extraction time was set to be 15 minutes. The flow rate of the aqueous phase was set to be close to maximum. Fig.5.11 shows the experimental results. Fig.5.11a shows the output signal obtained by the spectrometer for the 1ppm concentration sample without using the L-L extraction unit. Without extraction, the sample with 1ppm oil concentration was undetectable. The same sample of 1ppm oil concentration was also used experiments shown in Figs.5.11b, c, and d respectively. In Fig.5.11b and c, fence wall in the L-L extractor was formed by array of micro-posts with cross-sectional area of $200\mu m \times 200\mu m$ with height of $600\mu m$ and $200\mu m$ gaps. In the experimental results shown in Fig. 5.11b, counter flow scheme was used, i.e., the aqueous and organic phase solutions were flowing in opposite directions. Fig.5.11c shows the results obtained with the aqueous and organic phase solutions in co-current flow. The result shows that the sample with 1ppm oil concentration is detectable after L-L extraction unit was used. However, the difference between counter flow and current flow is not significant. This observation is different from the results obtained in numerical simulations and analysis. In experiment shown in Fig.5.11d, the fence wall consists of array of micro-posts with sizes of $150\mu m \times 150\mu m$ and height of $600\mu m$ and gaps of $150\mu m$ was used in counter-flow scheme. The resulting signal is greater than in Figs.5.11c and d.
Fig. 5.11 Experimental results of the integrated system a) 1 ppm sample without L-L extraction; b) 1 ppm sample with fence wall of 200 μm by 200 μm micro-posts and gaps and counter flow L-L extraction; c) 1 ppm sample with fence wall of 200 μm by 200 μm micro-posts and gaps and co-current flow L-L extraction; d) 1 ppm sample with fence wall with 150 μm by 150 μm micro-posts and 150 μm gaps in counter flow extraction.

Fig. 5.12 shows another group of experimental results. Fig. 5.12a shows the experimental results of the standard sample of 50 ppm oil concentration with no L-L extraction. Samples with oil concentration of 50 ppm were also used in experiments shown in Figs. 5.12b, c and d. In Fig. 5.12b and c, fence wall formed with micro-posts of 200 μm × 200 μm cross-section and height of 600 μm and gaps of 200 μm was used in the L-L extraction unit. In Fig. 5.12b, counter-current flow scheme was used in experiments shown in Fig. 5.12b, and co-current flow scheme was used in the experiments shown in Fig. 5.12c. The difference in results between counter-current flow and co-current flow was still not significant. In the experiment shown in Fig. 5.12d, fence wall formed with array of micro-posts of 150 μm × 150 μm cross-section, height of 600 μm and gaps of 150 μm was used in the L-L extraction unit. The aqueous and organic phase flows were controlled in counter-current flows. The two significant fluorescent peaks of the oil are clearly observed in Figs. 5.12b, c and d. The peak of 480 nm is far away from the excitation light wavelength and in theory least affected by it. The value of 480 nm peak is taken to count the magnification of extraction comparing with the results obtained without using L-L extraction. In
Fig. 5.12b and c, the magnification ratios are close to 2 times, and in Fig. 5.12d it is about 7 times.

The experimental results agree well with the predictions from numerical simulations.

These experimental results have proved that the L-L extraction is useful and the sensitivity of the device is significantly increased. The measurement sensitivity of the instrument was improved to be better than 1 ppm. It was also found that the optimal design for the separation fence wall is the design with a cross-sectional area of 150 m x 150 m, the height of 600 m, and gaps of 150 m between the neighboring posts. The reason is that the static fluid in the gaps is shorter for the oil passing through, the extraction between two flowing phase should be faster. And the aqueous phase flow rate is faster in the design with the array of micro-posts of 150 m x 150 m with height of 600 m and gaps of 150 m, the quantity of emulsified oil passed through the channel is much more, therefore the accumulation of oil in organic phase is faster.

No significant difference is observed between the results for the counter-current and co-current flows. The main reason may be that the flow rate of the peristaltic pump is very low, only at 3 l/min under free load. The flow rate might have become even lower in our experiments with
load while the flow rate of the aqueous phase is much greater. Thus, the flow rate of the organic phase is so low that there is not much difference between the counter flow and co-current flow.

5.4 Conclusions

In this chapter, design and principle of the Liquid-to-Liquid extraction unit has been introduced. The liquid-to-liquid extraction consists of three layers. Both cured SU-8 polymer and PDMS are used in fabrication of the L-L unit. Both materials have their own advantages and disadvantage. The L-L extraction unit presented in this dissertation has been built using PDMS as the main material. SU-8 can be taken as another option in future depends on the specific applications. The separation fence wall surface of the L-L extraction unit was selectively modified to stabilize the two liquid phases in the microfluidics system. The detail technology and processes of the surface modification process have also been presented. The experimental results show that the hydrophobic and hydrophilic properties of the selected surfaces of the fence walls have been significantly improved.

The numerical simulation results of the extraction efficiencies of two fluid phases have proved that the counter-current flow scheme is better than that of the co-current flow one. Prototypes of the micro-fluidic-optic chips have been fabricated. The optical detection system, the peristaltic micropump and the liquid-to-liquid (L-L) extraction microfluidic system were integrated together. Experiments were conducted to test the prototypes of the microchips. The experimental results have shown that the L-L extraction layer function very well and the sensitivity of the entire system have been enhanced in comparison with those without L-L extraction as shown in Chapter 3. The resolution of the entire system has been improved to blow 1ppm. The study has also found that the optimal design for the fence wall is to use array of micro-posts with cross-sectional area of 150 μm×150 μm and height of 600 μm, with the gaps
between the neighboring posts to be 150 μm. The experimental results have shown that the sensitivity has been improved as high as 7 times after 15 mins extraction. The experimental results agree well with the predictions of numerical simulations. The experimental results have also shown that no significant difference was observed between the results by using co-current flow and the counter-current flow schemes, in contrary to what has been expected based on theoretical analysis. The main reason for is may be that the flow rate of the organic phase is too low, which made the difference of the flow velocities of the organic phase and the aqueous phase flows are negligible. To overcome this problem, better micro-pumps should be designed and built to increase the flow rate, and therefore to increase the flow velocity of the organic phase solution. Therefore, to improve the flow rate of the micropump is one of future research tasks.

In conclusion, our study has proved the feasibility of the design and fabrication of an integrated micro-fluidic chip based instrument for in-situ detection of spilled oil in water. Further work is still needed to improve the sensitivity of the system.
CHAPTER 6 CONCLUSIONS

A new generation of instruments for spilled oil detection is highly desired for applications for in-situ measurements. Specifically, the new generation of instruments should meet the following requirements: 1) In-situ sensors should be the priority; 2) with the lower detection limit in 0.1 – 1 ppm and upper detection limit at least 100 ppm; 3) easily deployable and portable; 4) simplicity of use, be simpler to use than Turner, that is, be easier to set up and standardize; 5) Reliability – Turner setup may vary from day to day and is sensitive to rough handling. New instrument must be robust; 6) Easier Logistics – New system must have fewer components and must be lighter and require less logistics than the current system that requires two large boxes weighing 75-100 lbs each; 7) require less maintenance and lower maintenance costs; 8) Must be capable of being integrated with Windows operating systems and GPS. From the experiment results of the integrated system, these requirements are meted.

The research work presented in this dissertation targeted to develop a new generation of spilled oil detection instruments to meet these requirements. The key point in miniaturizing the physical sizes while still maintaining the sensitivity of sensors is to miniaturize the extraction processing and also to integrate the extraction and detection on the same chip substrate. Only the monitoring and displaying unit, the power supply, and other parts need to be external. All the external parts are well selected. Multiple designs of the micro-optic detection systems were tested and compared, and an optimal design was then selected. The output signal without extraction was calibrated by standard density samples. The detection limit without extraction was found to be between 1ppm and 10ppm.

An out-of-plane lens was designed and fabricated to enhance the sensitivity of the optical detection unit. The fabrication process and the property of the lens were studied both
theoretically and experimentally, and eventually a lens design with one-membrane was and selected and constructed to integrate with the optical fiber.

Both the co-current and counter-current designs of the liquid-liquid extraction system were studied and compared. A peristaltic pump was designed, built, and used to deliver the flow for the micro-fluidic chip. The pump was controlled using a Labview program. The controlling program can be integrated with any operating systems. Different designs of the pumps were also tested and compared. The maximum flow rate of the prototype micropump was found to be about 3 l/min. The experimental results showed that the best design of the L-L extraction unit can increase the oil density in the organic phase solution by as much as 7 times of the oil density in the aqueous phase. Therefore the detection limit is improved by 7 times. The final oil detection resolution was found to be lower than 1ppm. Besides the computer and the monitor, the rest part of the device can be controlled under 10cm×10cm×10cm cubic and the weight can be less than 5 lbs.
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