CHAPTER 4

CONCLUSIONS

In the present work, there are three part, the first part involves development of a flow injection analysis with univariate optimization for Ni(II) determination. In the second part, a mini-CNC machine was modified with diode laser for fabrication of a PMMA chip and fabrication of a PMMA chip using CO_2 laser for Zn(II) determination. All works are focus mostly on reduction of reagents and sample consumption in all the steps of the analytical procedure leading to be "Green Analytical Technique" .These inspected works are as follows**:**

4.1. Fabrication of a simple FIA analyzer for nickel(II) determination

The home-made software programmed in our laboratory are used to control some commercial devices through the serial or USB port such as peristaltic pump (ISMATEC), multi-position (Valco instrument), UV-Vis spectrophotometer (Jenway 6305) for fabrication of FIA analyzer. The proposed simple FIA system was evaluated by determination of Ni(II) in water samples with spectrophotometric detection. This method is based on the reaction of nitroso-R salt and Ni(II) in ammonium acetate buffer pH 8.5 solution resulting in orange complex. A small volume of a sample/standard solution was injected into a nitroso-R salt carrier steam. Then they were mixed well in the mixing coil and then pass through the detection cell followed by spectrophotometric detection at 490 nm. The optimized conditions were performed by univariate method. It was found that, the suitable conditions were; wavelength 490 nm, ammonium acetate buffer pH 8.5, Nitroso-R salt concentration

1.04×10^{-2} mol l^{-1}, mixing coil length 30 cm, flow rate 2.5 ml min^{-1} and sample injection volume 80 μl. Under the optimum conditions**,** the calibration curve was established and it was linear over the range of 0.25 – 3.5 mg L^{-1}, with a correlation coefficient 0.9998. The limit of detection (LOD) and the limit of quantification (LOQ) were 0.081 mg L^{-1} and 0.272 mg L^{-1} respectively. The recoveries for the standard addition method were found to be 99.20 – 101.60 % indicating that the proposed method was accurate. The relative standard deviation for 11-replicate injections was found to be 1.76% for 1.0 mg L^{-1} of Ni(II). Moreover, the percentage recoveries were studied by spiking 0.5 mg L^{-1} of Ni(II) standard solution into water samples for checked accuracy of this method. It was shown that the range of percentage recovery was calculated to be 98.3-101.8 % (n=3) and rapid with a sample throughput of 80 h^{-1}. This method has been successfully applied to the determination of Ni in water sample from electroplating and electronic industry and comparing to the FAAS. The results obtained by the proposed FIA are not significantly different from those obtained by FAAS method at a confidence interval of 95% (verified by student's t-test).

4.2 Mini-CNC machine modified with diode laser for fabrication of PMMA chip

The mini-CNC machine was successfully modified with diode laser for fabrication of a PMMA chip. The power of laser diode is controlled by the pulse width modulator. The maximum power of diode laser is 5 W at wavelength 808 nm. The scanning speed is 1.0-10.0 mm s^{-1} by the combine moving of X-Y stages. The movement of combined X-Y stage is achieved commands by KCAM program. various patterns of T-junction microchannel designed using the drawing software.Each designed pattern of PMMA (4×6 cm^2) microchannel are sent onto

KCAM program to control the fabrication of microchannel on a PMMA sheet. PMMA chip are easily to produce by direct writing with diode laser mini-CNC machine with different the length of microchannel. The depth and the width of microchannel can be controlled by the laser power and the movement speed of X-Y stages. The depth and the width of microchannel were measured using the SEM by cross-sections of microchannel. The effect of laser power and the movement speed of X-Y stage were investigated. When the laser power was fixed at 5 W, whereas the speed of X-Y movement was varied from 1.0 to 10.0 mm s^{-1}. It was shown that the microchannels widths decreased with the speed of X-Y movement from 300 µm to 147 µm. In the case of microchannel depth, it dropped from 424 µm to 74 µm. In addition, when the speed of X-Y movement was kept at a constant value of 4.0 mm s^{-1}, whereas the diode laser power was varied from 2.5 W to 5.0 W. It was found that the width of the grooves went up from 193 µm to 393 µm with the increase in diode laser power, whereas the depth of microchannels increased significantly from 114 µm to 554 µm when the power laser is climbed. Moreover, the smoothness of PMMA microchannel were investigated with SEM. The results displayed that the higher the speed of X-Y stages leading to the more rough surface. Therefore, lower speed gives rise to the smoother of tiny channel surface, but the smoothness of channel can be improved by exposure to CH_2Cl_2 vapor. The suitable dimensions of PMMA microchannel using diode laser mini-CNC machine is 226 µm width and 202 µm depth. The diode laser power used was at 5 W and the scanning of X-Y movement of 3 mm s^{-1}. Due to these sizes are close to geometric configuration that allows the best form of dispersion zone in flow system is obtained. The selected PMMA microchannel (20 cm of length) is bonded with the PMMA cover plate for sealed open channel with thermal at 140ºC for 15 min and then the PMMA chip is applied to fabricate microflow analyzer integrated with fiber optic sensor for optical detection with spectrometer. The proposed microflow analyzer system was displayed to be appropriate for measurements of Fe(III) using CTC as chromogenic reagent with a detection limit of 0.17 mg L^{-1}. The proposed method was acceptably applied to the determination of total iron in water samples from Chiang Mai Province. The results obtained by the proposed μrFA are not significantly different from those obtained by FAAS method at a confidence interval of 95% (verified by student's t-test).

In summary, The PMMA chips are designed and fabricated using a relatively inexpensive diode laser technique, the mini-CNC machine modified with diode laser has a powerful for fabrication of a PMMA chip. This machine is very cheaper than a commercial machine and need small area for operation. Moreover, the proposed μFA analyzer with PMMA chip has proven to be promising as a forceful analytical device for metal ion determinations in real samples.

Suggestion for further work

To improve mini-CNC machine modified with diode laser system about the transfer of heat from diode laser, it was found that heat sink is too small. Therefore, while machine is operated, diode is collected a lot of heat that make the short life time of diode. Consequently, CPU water cooling sink of desktop computer is interesting device for transferring heat in this system.

4.3 Fabrication of a PMMA chip using CO_2 laser for determination of Zn(II)

The CO_2 laser machine discharges radiation beam continuously with a relatively long specific wavelength of 1060 nm with maximum power of 80 W. A focused laser beam (2 cm) can scan over a two-dimensional region by moving laser beam. The maximum velocity of the CO_2 laser is 400 mm s^{-1} in the cut mode. It is the instrument available with a wide range of scanning speed with suitable price. In the present work, Y-junction with U-turns microchannels are designed using drawing software with various lengths of tiny channels. Each pattern is applied to laser cutting software coupled with the CO_2 laser machine for direct writing of laser beam on the 1 mm thickness PMMA sheet with the size of 4.0 x 4.0 cm^2. The parameters (changing laser power and beam speed) that affected on the depth, width and smoothness of the PMMA microchannels were examined using SEM. It was shown that, when laser power was fixed at 8 W, whereas the beam speed of CO_2 laser was varied from 1 to 20 mm s^{-1}. It was demonstrated that the microchannels widths decreased from 249 μm to 112 μm with increasing the scanning of laser beam. In the case of microchannel depth, it dropped from 528 μm to 26 μm. Moreover, when the speed of laser beam was kept at a constant value of 5.0 mm s^{-1}, whereas the CO_2 laser power was varied from 8 W to 16 W. It was displayed that the width of the grooves increased from 195 μm to 418 μm with the increase of diode laser power, whereas the depth of microchannels increased significantly from 194 μm to 890 μm when the laser power was climbed. The results indicated that the depths and the widths of microchannels were opposite proportionation to the scanning beam speed. The geometric dimensions of the PMMA microchannel produced by the CO_2 laser machine is 193 μm width and 194 μm depth that use the CO_2 laser power at 8 W and the scanning beam of 3 mm s^{-1}. In addition, the smoothness of microchannel walls can be improved by exposure to CH_2Cl_2 vapor.

The open microchannel on the PMMA chip produced by the CO_2 laser is sealed with a PMMA cover plate using thermal method resulting in a micro reactor, the micro reactor was then fixed with a fiber optic probe as an optical sensor and applied to microflow analyzer for determination of Zinc(II). It is based on the measurement of absorbancearising from Zn(II)-$(XO)_2$ complexes as red-violet color in an acetate buffer solution in the presence of quinine hydrochloride as photosensitizer. The univariate optimization was investigated both chemical and physical factors. The optimum conditions were 590 nm detection wavelength, 1.0 x 10^{-4} mol L^{-1} XO concentration, 1.0 x 10^{-3} mol L^{-1} quinine hydrochloride concentration, pH 5.5, injection volume 5 µl and flow rate 40 µl min^{-1}. The calibration graph was linear in the range 0.1– 1.5 mg L^{-1} of Zn(II) with correlation coefficient 0.9996. It was shown that, the relative standard deviation (RSD) was less than 2 % (n=11) with the percentage recoveries over the range of 98.25-102.8. The limit of detection (LOD) and the limit of quantification (LOQ) were 0.06 mg L^{-1} and 0.19 mg L^{1} respectively with a sample throughput of 40 h^{-1}. The results obtained by the proposed µFA using the PMMA chip are not significantly different from those obtained by FAAS method at a confidence interval of 95% (verified by student t-test).

The proposed microflow analysis method also consumes very small amount of reagent and sample with minimum waste production (less than 3.0 mL h^{-1}) comparison to the conventional analytical method, it is also simple with inexpensive instrumentation. Therefore, it is regarded to be a green analytical and environmental friendly method.

Suggestion for further work

The increase application to a variety of chip is challenging, owing to the advantages of the μFA techniques such as fully automation, portability, cost effectiveness, minimum sample/standard consumption and waste released. Unfortunately, chips produced in Chiang Mai are mostly made of PMMA which possess limitation of the material itself, due to a PMMA chip is not suitable for some systems such as organic solvents, strong acid. Therefore, the other chip materials should be considered. Glass is another material used for making chips, though it is more expensive than PMMA, but it has excellent optical properties and resistance to solvents, strong acid and strong base. However, fabrication of microchannel on glass is difficult to control the size of tiny channel. Therefore, the fabrication of tiny channel on glass with laser technique is interesting, if this method can avoid the crack on glass area.