

CHAPTER 7

CONCLUSION

In conclusion, the TCAA-imprinted polymers were created as a thin film onto the surface of a cyclic voltammetric (CV), inter-digitated conductometric (IDC) transduction unit, and a piezoelectric quartz crystal microbalance (QCM) transduction unit. They were also embedded in the RC micro-filtration membrane. The recognition and sensing property of the TCAA-imprinted polymers integrated in these transducer systems and the membrane have been assessed for the application of these sensors and the modified membrane in the determination and separation of haloacetic acid in drinking water.

The QCM, IDC and voltammetric sensor incorporated with the same TCAA-imprinted polymer showed different sensitivity and specificity. It has been shown that mass-sensitive QCM transducer integrated with imprinted cross-link poly(EDMA-co-VPD) or non-cross-link conducting polypyrrole can specifically measure concentration of the HAAs group in drinking water. The selectivity of the QCM to HAA analogs was exceptional. The analytical working range for six structurally related HAAs (trichloro-, dichloro-, monochloro-, tribromo-, dibromo-, and monobromo-acetic acids) was also broad (0.1-200 ppm) with a good correlation coefficient (0.955-0.998). While the imprinted poly(EDMA-co-VPD) (0.1-100 ppm) showed narrower working range than that of imprinted polypyrrole (1-200 ppm). These two sensors manifested comparable limits of detection (22-59 ppb). Their values were higher than those commonly found in actual drinking water samples, but still were well below the maximum permissible levels of HAAs ($60 \mu\text{g l}^{-1}$) in water sample recommended by USEPA. Various concentrations of TCAA and HAA spiking in drinking water samples can be recovered by two sensors in the range of 97-100%. The signal response of these sensors was considerably interfered by the ionic contaminants in the sample. The measurement was therefore recommended to perform in aqueous medium. When compared between two different recognition materials studied, the sensor coated with imprinted poly(EDMA-co-VPD) expressed well the HAA group specificity. On the contrary, the sensor modified by imprinted polypyrrole demonstrated greater specificity to template than that of analogs. The stable sensor system after much usage was the sensor coated with imprinted poly(EDMA-co-VPD). However, its drawback still concerned the complexity in the electrode and

sensor construction. In contrast, imprinted polypyrrole modified sensor offered easier preparation, unfortunately, its toughness was not up to standard. From the overall results, perhaps it can be used as a screening material for drinking waters contaminated with HAAs. The proposed method offered a fast, convenient and inexpensive cheap measure.

Development of an inter-digitated conductometric sensor selective to haloacetic acid based on TCAA-imprinted cross-linked poly(ethyleneglycoldimethacrylate-co-4-vinylpyridinium) and non-cross-link polypyrrole on screen-printed inter-digitated electrode has been proposed for real time detection of haloacetic acid concentrations. The sensors incorporated with imprinted poly(EDMA-co-VPD) sensing element showed good sensitivity towards the trichloacetic acid template and structurally related analogs with a promising correlation coefficient (0.972-0.993). Meanwhile the sensors incorporated with imprinted polypyrrole showed specific sensitivity to the analysis of TCAA with correlation coefficient of 0.997. The sensor made with former material has possibility for use in detecting and measuring HAAs, the usual contaminants in water. The sensitivity and detection limit of the sensors were found in the range of 0-500 $\mu\text{g l}^{-1}$ and 0.5-5.3 $\mu\text{g l}^{-1}$, respectively. The broader range was detected when used imprinted poly(EDMA-co-VPD) (0-500 $\mu\text{g l}^{-1}$), compared with the imprinted polypyrrole (10-120 $\mu\text{g l}^{-1}$) for TCAA.

The TCAA-imprinted polypyrrole integrated with the voltammetric sensing system was specifically sensitive towards both the TCAA template and other HAA analogs with a very good correlation coefficient (> 0.993). This made the TCAA-pyrrole polymer useful as a detection tool for TCAA (the most commonly occurring HAA found in drinking waters) and a group of HAAs. The recognition ability of the TCAA-imprinted polypyrrole thin-film incorporated into the voltammetric transduction system for various TCAA and HAA concentrations was in the range of 76-95%, lower than that of QCM and IDC sensors. This sensor showed specificity and limits of detection in the range of 0.1-817 mg l^{-1} and 34-46 $\mu\text{g l}^{-1}$, respectively. The detection limits of TCAA for the assay with voltammetric transducer incorporated with the MIP were at present higher than concentrations commonly found in actual drinking water samples. However, they are well below the maximum permissible levels of HAAs in water samples as set either by WHO ($\sim 200 \mu\text{g l}^{-1}$) or USEPA ($\sim 60 \mu\text{g l}^{-1}$). The analytical application of the prepared TCAA-imprinted pyrrole thin film for the direct detection of HAA in real-life samples or water samples spiking

with HAAs and voltammetric system showed good agreement with those of HAA analyzed by the QCM and IDC method.

A TCAA-imprinted polypyrrole membrane was developed by using electrochemical polymerization using ammonium persulfate as initiator. The influences of several parameters on the properties of the membranes were investigated, especially physical robustness and selective adsorption. Polymer deposition, swelling of membrane and permeate flux increased when ammonium persulfate concentration increased. The amount of polymer deposited decreased, but the swelling of membrane increased, with an increase in pH of synthesis, and permeate flux was not significantly changed with the altered pH of synthesis. Among three different membrane modification conditions (0.5 M APS + pH 0.7 of synthesis + pH 7 of filtration, 1.0 M APS + pH 1 of synthesis + pH 7 of filtration and 1.0 M APS + pH 4 of synthesis and filtration), the membrane prepared using the first condition showed more template specific than the other conditions, whereas the third condition gave the membrane with HAA specificity. The stability of modified membrane kept over 3 months was also studied. The results showed that the properties of the aged membrane was not significantly changed after 3 months. The membrane modified with 0.5 M ammonium persulfate at pH 0.7 revealed no change in the properties. It can be concluded that the TCAA imprinted RC membrane with a good recognition ability and stability can be achieved using of 0.5 M ammonium persulfate at pH 0.7 while the filtration should be performed at pH 7 to gain optimum selectivity.