



**OPTICAL MULTI-METAL ION SENSING SYSTEMS
BASED ON IMMOBILISED FLUORESCENT REAGENTS**

A thesis submitted to The University of Manchester for the degree of

Doctor of Philosophy

in the Faculty of Engineering and Physical Sciences

2009

HAFIZA MOHAMED ZUKI

School of Chemical Engineering and Analytical Science

Contents

List of contents.....	2
List of Figures.....	7
List of Tables.....	14
List of Abbreviations and Symbols.....	17
Abstract.....	23
Declaration.....	24
Copyright Statement.....	25
Acknowledgement.....	26
Chapter 1 Introduction.....	26
1.1 Background and thesis outline	26
1.2 Aqueous environment and water pollution	27
1.3 Metals.....	28
1.3.1 Metals of interest	29
1.4 Fluorescence reagent / Fluorophore for the determination of metal ions	33
1.4.1 8-hydroxyquinoline (HQ).....	33
1.4.2 8-hydroxyquinoline-5-sulphonic Acid	36
1.4.3 8-acryloyloxy-quinoline	39
Chapter 2 The Optical Fibre Chemical Sensor.....	42
2.1 Optical fibre	42
2.1.1 Principles of fibre optics	42
2.1.2 Fibre optic technology and application.....	44
2.2 Fibre optics as a chemical sensor.....	45

2.2.1	<i>Introduction</i>	45
2.2.2	<i>Optical fibre chemical sensing system</i>	46
2.2.3	<i>Intrinsic and extrinsic sensors</i>	48
2.3	<i>Fibre optic fluorescence sensors</i>	51
2.4	<i>Optical fluorescence sensors for metal ions</i>	51
2.4.1	<i>Literature on sensors for heavy metal ions</i>	53
2.5	<i>Immobilisation methods for optical chemical sensors</i>	56
2.5.1	<i>Solvent impregnated resins (SIRs)</i>	58
2.5.2	<i>Plasticised polymeric film (PPF)</i>	64
2.5.3	<i>Molecular imprinted polymer (MIP)</i>	69
Chapter 3 Instrumentation and Apparatus		73
3.1	<i>Instrumentation for optical fibre chemical sensors</i>	73
3.1.1	<i>Light sources</i>	73
3.1.2	<i>Fibre optic cable</i>	75
3.1.3	<i>Receiver (Detector)</i>	75
3.2	<i>Principles of the spectroscopic method</i>	76
3.2.1	<i>Optical spectroscopy instrument</i>	76
3.3	<i>Fluorescence spectrometer</i>	79
3.3.1	<i>Fluorescence</i>	79
3.3.2	<i>Fluorescence theory</i>	82
3.3.3	<i>Application of fluorescence methods</i>	84
3.3.4	<i>Fluorescence spectrometer</i>	86
3.4	<i>Flow injection analysis</i>	88
3.5	<i>Flow cell design</i>	89

3.5.1	<i>A flow cell for resin type polymer studies</i>	89
3.5.2	<i>A flow cell for film type polymer studies</i>	90
3.6	<i>Buffer solutions</i>	90
Chapter 4	<i>Solution Studies</i>	92
4.1	<i>Introduction</i>	92
4.1.1	<i>Chemicals and Reagents</i>	92
4.1.2	<i>Synthesis of 8-acryloyl-oxyquinoline (AOQ)</i>	93
4.1.3	<i>AOQ Characterisation</i>	94
4.1.4	<i>Instrumentation and Measurement Procedure</i>	95
4.2	<i>Result and Discussion</i>	95
4.2.1	<i>Complex Formation and Spectral Features</i>	95
4.2.2	<i>Influence of pH</i>	100
4.2.3	<i>Stoichiometry and Formation Constants of the Complexes</i>	104
Chapter 5	<i>Immobilised Sensing Systems</i>	121
5.1	<i>Immobilisation of HQS as solvent impregnated resin (SIR)</i>	121
5.1.1	<i>Introduction</i>	121
5.1.2	<i>Preparation of SIR</i>	122
5.1.3	<i>Instrumentation and measurement procedure</i>	124
5.1.4	<i>Result and discussion</i>	124
5.1.5	<i>Regeneration of the reagent phase</i>	126
5.1.6	<i>SIR stabilisation</i>	132
5.1.7	<i>Reproducibility of response</i>	136
5.1.8	<i>Metal-HQS response in a SIR system</i>	137
5.1.9	<i>Limit of detection (LOD)</i>	139

5.1.10	<i>Summary and conclusion</i>	140
5.2	<i>Immobilisation of HQ as plasticised polymeric film</i>	142
5.2.1	<i>Film preparation and response measurements</i>	142
5.2.2	<i>Results and discussion</i>	143
5.2.3	<i>Summary and conclusions</i>	153
5.3	<i>Immobilisation of 8-acryloyl-oxy-quinoline (AOQ) as a molecular imprinted polymer (MIP)</i>	155
5.3.1	<i>Polymerisation of metal-MIPs</i>	155
5.3.2	<i>Template removal and rebinding</i>	156
5.3.3	<i>Molecular imprinted polymer (MIP) of metal-AOQ</i>	156
5.3.4	<i>Instrumentation and measurement procedure</i>	157
5.3.5	<i>Result and discussion</i>	157
5.3.6	<i>Summary and conclusion</i>	166
Chapter 6	<i>Multi Metal Ion Analysis</i>	168
6.1	<i>Multivariate Kinetic Analysis</i>	168
6.1.1	<i>Partial Least Square Regression Analysis</i>	169
6.1.2	<i>Microsoft Excel LINEST Function</i>	170
6.1.3	<i>Binary Metal Ions System</i>	173
6.1.4	<i>Quaternary Metal Ions Mixture</i>	201
6.1.5	<i>Artificial Neural Networks (ANN)</i>	205
6.1.6	<i>Simultaneous determination of multi-metal ions based on the ANNs</i>	207
6.2	<i>Summary and Conclusion</i>	216
Chapter 7	<i>Conclusions and Further Work</i>	218
7.1	<i>Works summary and conclusions</i>	218

7.2 *Suggestions for further work* 223

7.2.1 *Modification of the immobilisation process* 223

7.2.2 *Further investigation of the MIPs system*..... 225

7.2.3 *Immobilisation technique and new polymer material and complexation reagent*..... 227

References229

Appendix239

Words count: 40406 words

List of Figures

<i>Figure 1-1 The distribution of the world's water</i>	<i>27</i>
<i>Figure 1-2 Molecular structure of (a) quinoline (b) pyridine and (c) 8-hydroxyquinoline.....</i>	<i>34</i>
<i>Figure 1-3 Three different molecular species of 8-hydroxyquinoline occurring at three different pH conditions: (a) acidic, (b) neutral and (c) basic</i>	<i>35</i>
<i>Figure 1-4 Possible structures for complex formation with a metal.....</i>	<i>35</i>
<i>Figure 1-5 Metal-HQ complex.....</i>	<i>36</i>
<i>Figure 1-6 Molecular structure of 8-hydroxyquinoline-5-sulphonic acid</i>	<i>37</i>
<i>Figure 1-7 Different conjugate acid-base forms of HQS</i>	<i>38</i>
<i>Figure 1-8 A metal-HQS complex.....</i>	<i>38</i>
<i>Figure 1-9 Molecular structure of 8-acryloyloxy-quinoline.....</i>	<i>40</i>
<i>Figure 1-10 Probable structure for the formation of AOQ with metal ions... </i>	<i>41</i>
<i>Figure 2-1 Total internal reflection in an optical fibre (θ_c = critical angle, θ_i = incident angle).....</i>	<i>42</i>
<i>Figure 2-2 Schematic diagram of the optical fibre chemical sensor.....</i>	<i>47</i>
<i>Figure 2-3 Intrinsic fibre optic sensor.....</i>	<i>48</i>
<i>Figure 2-4 Extrinsic fibre optic sensor.....</i>	<i>48</i>
<i>Figure 2-5 The schematic diagram of an intrinsic chemical sensor: (a) with the reagent as the cladding (b) with the reagent as the core.....</i>	<i>49</i>
<i>Figure 2-6 Schematic diagram of the extrinsic sensor: (a) immobilised reagent</i>	

<i>at the fibre tip (b) immobilised reagent in the flow cell</i>	50
<i>Figure 2-7 Illustration of the three methods of fluorescence detection</i>	52
<i>Figure 2-8 Two types of resin structure</i>	61
<i>Figure 2-9 Styrene-divinylbenzene copolymer</i>	62
<i>Figure 2-10 Functional group on the active site of styrene-divinylbenzene polymer</i>	63
<i>Figure 2-11 The structure of the poly vinyl chloride polymer</i>	65
<i>Figure 2-12 Phthalate plasticiser</i>	67
<i>Figure 2-13 PVC film structure;</i>	68
<i>Figure 2-14 The schematic representation of the MIP</i>	71
<i>Figure 3-1 A basic fibre optic sensor system</i>	73
<i>Figure 3-2 Basic components of various types of instruments for optical spectroscopy (hv = photon, I = information data)</i>	78
<i>Figure 3-3 (a) Sources and (b) Detectors for optical spectroscopic instruments</i>	79
<i>Figure 3-4 Jablonski energy diagram: ABS = Absorption, EX = Excitation, IsC = Intersystem crossing, FL = Fluorescence, IC = Internal conversion, and PH = Phosphorescence</i>	80
<i>Figure 3-5 Components of various types of instruments for optical fluorescence spectroscopy (hv = photon, I = information data)</i>	86
<i>Figure 3-6 Components of a fluorometer and spectrofluorometer</i>	87
<i>Figure 3-7 Flow injection analysis system</i>	88

Figure 3-8 Schematic of a basic flow cell design for SIRs and MIPs	89
Figure 3-9 Schematic of a basic flow cell design for films.....	90
Figure 4-1 Reaction scheme of the AOQ monomer synthesis	93
Figure 4-2 IR spectra of AOQ	94
Figure 4-3 Fluorescence of reagents and reagent complexes	96
Figure 4-4 Metal-HQ complexes spectra (excitation spectra measured at emission wavelength and emission spectra measured at excitation wavelength)	97
Figure 4-5 Metal-HQS complexes spectra (excitation spectra measured at emission wavelength and emission spectra measured at excitation wavelength)	98
Figure 4-6 Metal-AOQ complexes spectra (excitation spectra measured at emission wavelength and emission spectra measured at excitation wavelength)	99
Figure 4-7 Plots of fluorescence of Metal-HQ complexes as a function of pH	101
Figure 4-8 Plots of fluorescence of Metal-HQS complexes as a function of pH	102
Figure 4-9 Plots of fluorescence of Metal-AOQ complexes as a function of pH	103
Figure 4-10 Typical Job plot:.....	107
Figure 4-11 Job plot for Al-HQ complexes at pH 7	112
Figure 4-12 Job plot for Cd-HQ complexes at pH 6.....	112

Figure 4-13	Job plot for Mg-HQ complexes at pH 6.....	113
Figure 4-14	Job plot for Zn-HQ complexes at pH 6	113
Figure 4-15	Proposed structures of the (a) Al-HQ complex, (b) Cd-HQ complex, (c) Mg-HQ complex and (d) Zn-HQ complex.....	114
Figure 4-16	Proposed structures of the (a) Al-HQS complex, (b) Cd-HQS complex, (c) Mg-HQS complex and (d) Zn-HQS complex	115
Figure 4-17	Proposed structures of the (a) Al-AOQ complex, (b) Cd-AOQ complex, (c) Mg-AOQ complex and (d) Zn-AOQ complex.....	117
Figure 5-1	HQS impregnated onto a strongly basic polystyrene-divinylbenzene anion-exchange resin (Dowex 1x2 200).	122
Figure 5-2	Excitation and emission spectra of the metals-HQS complexes (excitation spectra measured at emission wavelength and emission spectra measured at excitation wavelength)	125
Figure 5-3	Effect of pH on metal-HQS complexation on SIRs	126
Figure 5-4	The time function reaction of the HQS-SIR system with metal ions	129
Figure 5-5	Regeneration cycle of Al-HQS complexes with NaF.....	130
Figure 5-6	Regeneration cycle of Cd-HQS complexes with EDTA.....	130
Figure 5-7	Regeneration cycle of Mg-HQS complexes with EDTA	131
Figure 5-8	Regeneration cycle of Zn-HQS complexes with EDTA.....	131
Figure 5-9	Regeneration of stabilised SIRs (modified wet drying method)	135
Figure 5-10	Reproducibility of the metal-HQS complexes responses in SIRs system	137

Figure 5-11	Calibration plots for metal-HQS response in the SIR system	138
Figure 5-12	The fluorescence spectra for the metal-HQ complexes in the PVC films (excitation spectra measured at emission wavelength and emission spectra measured at excitation wavelength)	143
Figure 5-13	Metal-HQ complexation within the PVC film at different pHs	145
Figure 5-14	Regeneration cycle of Al-HQ complex with NaF	147
Figure 5-15	Regeneration cycle of Cd-HQ complex with EDTA	147
Figure 5-16	Regeneration cycle of Mg-HQ complex with EDTA	148
Figure 5-17	Regeneration cycle of Zn-HQ complex with EDTA	148
Figure 5-18	Reproducibility of the metal-HQ complex responses in a plasticised polymeric PVC film system	150
Figure 5-19	Calibration plots for metal-HQ response in the plasticised PVC films	151
Figure 5-20	The removing and rebinding of metal templates from the MIP	156
Figure 5-21	Suggested molecular structure of (a) Al-IP (b) Cd-IP (c) Mg-IP and (d) Zn-IP	157
Figure 5-22	The fluorescence spectra of the MIPs (excitation spectra measured at emission wavelength and emission spectra measured at excitation wavelength)	158
Figure 5-23	Change in intensities observed during the metal-templates removal	159

Figure 5-24	The response signals of the Al-IP in different pH conditions .	161
Figure 5-25	Regenerability and reproducibility of the Al-IP system.....	162
Figure 5-26	Regenerability and reproducibility of the Cd-IP system.....	163
Figure 5-27	Regenerability and reproducibility of the Mg-IP system.....	163
Figure 5-28	Regenerability and reproducibility of the Zn-IP system.....	164
Figure 5-29	Calibration plots for the MIP responses.....	165
Figure 6-1	Calibration plots for Al^{3+} with fixed concentrations of Mg^{2+} (excitation wavelength =398 nm)	175
Figure 6-2	Calibration plots for Mg^{2+} with fixed concentrations of Al^{3+} (excitation wavelength = 398 nm)	176
Figure 6-3	Experimental versus model intensity values for Al^{3+} / Mg^{2+} mixtures	178
Figure 6-4	Effect of total metal ion concentration ($[Al^{3+}] + [Mg^{2+}]$) on the intensity response of the HQS-SIRs system.....	180
Figure 6-5	Calibration plots for Al^{3+} with fixed concentrations of Zn^{2+} (excitation wavelength = 398 nm)	181
Figure 6-6	Calibration plots for Zn^{2+} with fixed concentrations of Al^{3+} (excitation wavelength = 398 nm)	182
Figure 6-7	Experimental versus model intensity values for Al^{3+} / Zn^{2+} mixtures	184
Figure 6-8	Calibration plots for Cd^{2+} with fixed concentrations of Al^{3+} (excitation wavelength = 398 nm)	186
Figure 6-9	Calibration plots for Al^{3+} with fixed concentrations of Cd^{2+} (excitation	

wavelength = 398 nm).....	186
Figure 6-10 Experimental versus model intensity values for Cd ²⁺ / Al ³⁺ mixtures	188
Figure 6-11 Calibration plots for Cd ²⁺ with fixed concentrations of Mg ²⁺ (excitation wavelength = 398 nm).....	189
Figure 6-12 Calibration plots for Mg ²⁺ with fixed concentrations of Cd ²⁺ (excitation wavelength = 398 nm).....	190
Figure 6-13 Experimental versus model intensity values for Cd ²⁺ / Mg ²⁺ mixtures	192
Figure 6-14 Calibration plots for Cd ²⁺ with fixed concentrations of Zn ²⁺ (excitation wavelength = 398 nm).....	193
Figure 6-15 Calibration plots for Zn ²⁺ with fixed concentrations of Cd ²⁺ (excitation wavelength = 398 nm).....	194
Figure 6-16 Experimental versus model intensity values for Cd ²⁺ / Zn ²⁺ mixtures	196
Figure 6-17 Calibration plots for Mg ²⁺ with fixed concentrations of Zn ²⁺ (excited at 398 nm).....	197
Figure 6-18 Calibration plots for Zn ²⁺ with fixed concentrations of Mg ²⁺ (excited at 398 nm).....	198
Figure 6-19 Experimental versus model intensity values for Mg ²⁺ / Zn ²⁺ mixture	200
Figure 6-20 Experimental versus model intensity values for Al ³⁺ /Cd ²⁺ /Mg ²⁺ /Zn ²⁺ mixtures.....	204
Figure 6-21 General model of an ANNs.....	205

<i>Figure 6-22</i>	<i>The arrangements of the data set for the modelling ANN (binary metal system)</i>	<i>.....208</i>
<i>Figure 6-23</i>	<i>The continuous arrangements of the data set for the modelling ANN (quaternary metal system)</i>	<i>..... 208</i>
<i>Figure 6-24</i>	<i>Training data fitting and predictions by the network where o – Mg, x – Al, + - Zn, and ■ - Cd</i>	<i>..... 213</i>
<i>Figure 6-25</i>	<i>Error obtained from the training model fitting</i>	<i>..... 213</i>
<i>Figure 6-26</i>	<i>Validation data fitting and predictions by the network where o - Mg, x - Al, + - Zn, and ■ - Cd</i>	<i>..... 214</i>
<i>Figure 6-27</i>	<i>Error obtained from the validation model fitting</i>	<i>..... 214</i>
<i>Figure 7-1</i>	<i>Representation of the preparation and testing of an MIP sensor array</i>	<i>.....227</i>

List of Table

<i>Table 2-1 Sensor Review</i>	<i>53</i>
<i>Table 2-2 Glass transition temperature for certain polymer</i>	<i>65</i>
<i>Table 4-1 Fluorescence spectra of the metal-reagents complexes.....</i>	<i>99</i>
<i>Table 4-2 Fluorescence spectra of the metal-reagents complexes.....</i>	<i>103</i>
<i>Table 4-3 Formation constants for the Metal-HQ complexes.....</i>	<i>114</i>
<i>Table 4-4 Formation constant values for the Metal-HQS complexes.....</i>	<i>116</i>
<i>Table 4-5 Formation constant values for the Metal-AOQ complexes.....</i>	<i>117</i>
<i>Table 4-6 The stoichiometry and formation constant of the metal-reagent complexes.....</i>	<i>119</i>
<i>Table 5-1 Specification and description of the resin used (data obtained from SUPELCO - Sigma Aldrich).....</i>	<i>122</i>
<i>Table 5-2 Formation constants for metal-HQS complexes and metal-EDTA complexes [155]</i>	<i>127</i>
<i>Table 5-3 Summary of parameters used in regeneration studies</i>	<i>128</i>
<i>Table 5-4 Calculated value of the LOD in metal-SIR system.....</i>	<i>139</i>
<i>Table 5-5 Summary of metal-HQS complexes properties in SIR system.....</i>	<i>140</i>
<i>Table 5-6 Summary of parameters used in the regeneration experimentation</i>	<i>146</i>
<i>Table 5-7 Calculated value of the LOD in a metal-PVC film system.....</i>	<i>152</i>
<i>Table 5-8 Summary of metal-HQ complex properties in a PVC film system</i>	

.....	153
Table 5-9 Summary of metal-AOQ complexes properties in the MIP systems	166
Table 6-1 Layout of regression results and statistics returned by LINEST ...	171
Table 6-2 List of metal 1 (M1) and metal 2 (M2) ions pairs investigated.....	173
Table 6-3 Factorial design of the calibration and test sets for the M1/M2 mixture ions system (X = calibration set sample, O = test set sample).....	174
Table 6-4 Input array for Al^{3+} / Mg^{2+} calibration set.....	177
Table 6-5 Output regression array return by LINEST (data with references to Table 6.1)	177
Table 6-6 input array for Al^{3+} / Mg^{2+} calibration set	183
Table 6-7 Output regression array return by LINEST (data with references to Table 6.1)	183
Table 6-8 Input array for Cd^{2+} / Al^{3+} calibration set.....	187
Table 6-9 Output regression array return by LINEST (data with reference to Table 6.1)	187
Table 6-10 Input array for Cd^{2+} / Mg^{2+} calibration set	191
Table 6-11 Output regression array return by LINEST (data with references to Table 6.1)	191
Table 6-12 Input array for Cd^{2+} / Zn^{2+} calibration set	195
Table 6-13 Output regression array return by LINEST (data with references to Table 6.1).....	195

<i>Table 6-14 Input array for Mg²⁺/ Zn²⁺ calibration set.....</i>	<i>199</i>
<i>Table 6-15 Output regression array return by LINEST (data with reference to Table 6.1).....</i>	<i>199</i>
<i>Table 6-16 Factorial design of the calibration and test sets for the Al³⁺/Cd²⁺/Mg²⁺/Zn²⁺ system (X = calibration set sample, O = test set sample)</i>	<i>201</i>
<i>Table 6-17 Input array for Al³⁺/Cd²⁺/Mg²⁺/Zn²⁺ calibration set.....</i>	<i>202</i>
<i>Table 6-18 Output regression array return by LINEST</i>	<i>203</i>
<i>Table 6-19 Feed forward ANN optimisation parameters (tansig function) ...</i>	<i>211</i>
<i>Table 6-20 Prediction of the network for the test set.....</i>	<i>215</i>

List of Abbreviations and Symbols

a	pre-exponential factor
A	absorbance
ABS	absorption
Al-IP	Aluminium imprinted polymer
ANN	Artificial neural network
C	concentration
CA	cellulose acetate
Cd-IP	cadmium imprinted polymer
CLS	classical least squares
d	distance
dof	degree of freedom
E	energy
e	exponential
Epochs	number of training loops
Ex	Excitation
F	F-statistic
FL	Fluorescence
f	fraction of concentration
FANN	feed-forward artificial neural network
f (net)	input net function
GAS	genetic algorithm
h	Planck's constant
$h\nu$	photon

HSAB	hard soft acid base
I	intensity
I_0	incident light
IC	internal conversion
ILS	inverse least squares
IR	infrared
IsC	intersystem crossing
IUPAC	international Union of Pure and Applied Chemistry
K	number of regression coefficients
K_a	association constant
K_f	formation constant
K_Q	quenching constant
l	light path length
L	ligand
LD	laser diode
LED	light emitting diode
LOD	limit of detection
Logsig	logarithmic sigmoid
M	metal
m	regression coefficient
MIP	molecular imprinted polymer
MSE	mean squared error
N	number of data points
n	refractive index

n	number of sample
NA	numerical aperture
PCR	principle component regression
PH	phosphorescence
pK _a	Acid dissociation constant
PLS	partial least squares
PPF	Plastises polymeric film
PMT	photo multiplier tube
PIN	positive intrinsic negative
R ²	R squared
RMSD	root mean square deviation
RSD	relative standard deviation
S	singlet electronic site
s _e	standard error
SE _y	standard error of the y estimate
SIR	solvent impregnated resin
SPE	solid phase extraction
SS _{reg}	regression sum of squares
SS _{resid}	residual sum of squares
T	triplet electronic state
T _g	glass transition temperature
Tansig	tangent sigmoid
TIR	total internal reflection
TSA	transition state analogue

UV	Ultra Violet
V	vibrational state
Vis	visible
Vs	versus
Var_{err}	variance of the error
Var_{obs}	variance observed
W_i	weight factor
x	input data
Xe	xenon
X_i	input signal
y_{mean}	y- mean
y_{obs}	y- observed
y_{calc}	y- calculated
σ	standard deviation
θ	angle
θ_c	critical angle
ϵ	molar absorptivity
π	phi
\emptyset	efficiency
λ	wavelength
\emptyset_F	quantum yield

Abstract

This thesis describes the studies of various stages in the development of a fibre optic sensor capable of detecting and measuring Al^{3+} , Cd^{2+} , Mg^{2+} and Zn^{2+} ions in aqueous solutions. A well known non-selective reagents 8-hydroxyquinoline (HQ) and its derivatives such as 8-hydroxyquinoline-5-sulphonic acid (HQS) and 8-acryloyl-oxy-quinoline (AOQ) reagents were considered to be suitable candidates for incorporation into the sensor. From the solution studies, the stoichiometry evaluated for metal-reagent complexes are 1:3 for Al-R and 1:2 for Cd-R, Mg-R and Zn-R (where R = reagent). The formation constants obtained shown that the Al-reagent are the most stable complexes compared to others which shown similar complexes stability. Three different immobilisation mechanisms incorporated with fluorescence-optical instrumentation along with the flow injection system were investigated: impregnated ion exchange mechanism; cast films incorporating the fluorophore as an independent species; and metal imprinted polymerisation in which the fluorophore is incorporated into the polymer structure. All immobilised systems showed good sensitivity towards metal ions with the LODs obtained in a range of 10^{-9} to 10^{-8} M for SIR, a range of 10^{-8} to 10^{-7} M for PVC and a range of 10^{-8} to 10^{-7} M for MIP. The systems also showed good reproducibility of response with low RSD values (RSD between 1 to 7% for SIR, between 1 to 4% for PVC and $< 1\%$ for MIP). However, only MIP shows excellent stability and regenerability of the system meanwhile SIR and PVC show poor stability and regenerability due to the heavy leaching of the reagents from the system. It was also observed that the sensitivity order of the reagent phase is $\text{Al}^{3+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Mg}^{2+}$. Due to the higher sensitivity and shorter response times, SIR system was applied in the simultaneous analysis of metal ions mixture with the aid of a multiple linear regression and ANN algorithms. Both algorithms showed excellent model fitting. However, only the ANN network successfully computed the individual metal ion concentration in the mixture solutions (with very small error obtained, range from 0 to 10^{-4} M).