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

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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
hv	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 constan
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
ø	efficiency
λ	wavelength
$Ø_F$	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 $Al^{3+} > Zn^{2+} > Cd^{2+} > Mg^{2+}$. 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).