CHAPTER II

LITERATURE REVIEWS AND THEORY

2.1. Heavy metal in environment

Heavy metals are defined as metals of a density higher than 5 g cm^{-3} [24]. Heavy metals are natural components of the Earth's crust and used in many industries. They have caused contamination in environment that can be harmful to human or animal due to their toxic effects [25]. Maximum acceptable concentration of heavy metals in drinking water and industrial wastewater are summarized in Table 2.1. Therefore heavy metal analysis has been developed for improvement of sensitivity, accuracy and cost of instrument.

Table 2.1 Maximum acceptable concentration of heavy metals in drinking water and industrial wastewater

Heavy metals	Maximum acceptable concentration (mg L^{-1})	
	Drinking water [26]	Industrial wastewater [27]
Arsenic (As)	0.050	0.250
Cadmium (Cd)	0.005	0.030
Copper (Cu)	1.000	2.000
Iron (Fe)	0.300	10.000
Lead (Pb)	0.050	0.200
Mercury (Hg)	0.002	0.005
Silver (Ag)	0.050	1.000
Zinc (Zn)	5.000	5.000

Silver is one of heavy metal used in industry because of its property. Silver ion has the highest electrical and thermal conductivity; therefore, it is used in several industries such as pharmaceuticals, electric, chemical catalyst, silverware, jewelry,

mirror, coating, etc. It is released into environment affecting to our health and environment. Silver ion inactivates sulfhydryl enzymes and combines with amine, imidazole and carboxyl groups of various metabolites. Silver contamination is toxic to fish and microorganisms. It is toxic to all living cell, deposited deeper skin layers and around nerves and may cause permanent skin damage. It can stick to fish gills and can be a cause of death [1]. Therefore, the silver determination methods have been developed for many years ago.

Since nowadays, consumer products containing silver nanoparticles are used extensively such as cosmetic, fabric, medicine, electronics, and in the computer industry. Property of silver nanoparticles is inhibition of bacteria which causes decay, itching, disease, smell and wound infection. Nanoparticles of silver can pass through cell wall of bacteria to bind with sulfur of sulfhydryl group of protease enzyme and with DNA lead to cell damage and death of bacteria cell [2]. However, researchers have serious concern about the toxicity of silver nanoparticles to aquatic microorganism, plants and animals. Therefore, the determination method of silver nanoparticles has been developed in recent years.

2.2. Determination of silver

The determination of silver ions such as voltammetry [8], spectrophotometry [9], electrothermal atomic absorption spectrometry (ETAAS) [10, 11], ICP-AES [12] and ICP-MS [13, 14] has been reported. Some techniques for determination of silver ions are shown in Table 2.2.

Table 2.2 Some techniques for determination of silver ions

Techniques	Sample preparations	Ref.
Voltammetry	modified glassy carbon electrode	[8]
Spectrophotometry	quantitative extraction of the ion pair	[9]
ETAAS	adsorption on a tungsten wire	[10]
ETAAS	ligand-less cloud point extraction	[11]
ICP-AES	extraction using Cyanex-471X (triisobutylphosphinesulphide) in xylene	[12]
ICP-MS	anion exchange resin	[13]
ICP-MS	sequential injection analysis	[14]

Several techniques for determination of silver nanoparticles have been reported such as ICP-AES, ICP-MS and GFAAS.

In 2008, Benn and Westerhoff [4] determined the amount of silver nanoparticles releasing from nano sock wash water to the environment. The six types of socks were digested by nitric acid and were determined by ICP-AES. They contained up to a maximum of 1,360 μg Ag/g sock. Silver from the sock wash water leached in ionic and nanoparticle forms were characterized via filtration and the ionic forms were analyzed by ISE analysis. It leached as much as 650 μg of silver in 500 mL of distilled water. Because of property of silver nanoparticles that is antibacterial, silver nanoparticles producing washing machine was purchased. In 2011, Farkas *et al.* [5] determined silver nanoparticles released from washing machine by ICP-MS. The washing machine released silver in its effluent at an average concentration of 11 μg L^{-1}. The effluent had negative effects on a natural bacterial community as its abundance was clearly reduced when exposed to the wash water. If washing machines capable of producing silver nanoparticles become a common feature of households in the future, silver nanoparticles will be released into the environment that can be harmful to human or animal due to their toxic effects. In 2010, Kornphimon Kulthong *et al.* [7] determined silver nanoparticles released from washing antibacterial fabrics into artificial sweat. Five laboratory-prepared fabrics and

six commercial fabrics were digested and determined by GFAAS. The quantity of silver released was likely dependent on the amount of silver coating. In 2013, Echegoyen and Nerin [6] studied the nanoparticle release from nano-silver antimicrobial containers. Migration solutions were evaluated by ICP-MS and SEM-EDX analysis. The total silver migration values ranging between 1.66 and 31.46 ng cm^{-2} were found.

Furthermore, ion-selective-electrode (ISE) technique was used to determine silver nanoparticles [15, 16] and silver ions [17-20]. For example, In 2008, Wittaya Ngeontae *et al.* [16] fabricated silver ion selective membrane electrodes containing CU1 for speciation analysis of silver nanoparticles. The logarithm of potentiometric selectivity coefficients (log $K^{pot}_{Ag,j}$) was -2.8 with a response time less than 5 s. It also provided a calibration over a wide working range of 10^{-6} to 10^{-2} mol L^{-1}.

However, some drawbacks of ion-selective electrode technique are matrix interference [21, 22] and electrical interference [23] because the ISE technique measures the potential generated across a membrane. Therefore, optical sensors technology has been interesting.

2.3. Optical sensor

An optical sensor device consists of the following components:

(a) a recognition component, where specific interaction and identification of the analyte takes place

(b) a transducer composition that converts the recognition process into a measurable optical signal

(c) an optical device which consists of at least a light source

(d) a detector which detects and converts the change of optical properties, after amplification of the primary signal, into a unit readout

The optical properties measured can be absorbance, reflectance, luminescence, light polarization, Raman and other [28]. They have many advantages such as high sensitivity or dynamic range, high selectivity, fast response time, good signal-to-noise ratio and long-term stability [29]. Therefore, optical sensors have been found in various application such as biomedical [30, 31], clinical [32-34], environmental monitoring [35, 36] and process controlling [37].

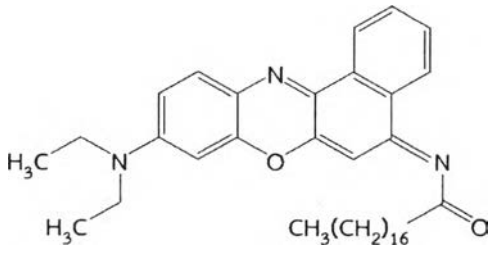
Bulk optode sensors have been widely used in analytical chemistry to determine heavy metal ions. We are interested in the bulk optode technique because of its advantages such as simple preparation, high selectivity, high sensitivity, fast response time, low cost of instrument, reversibility, repeatability and this technique can be detected by naked-eye. In the previous research, the optical sensors as optode membranes have been used for determination of various cations.

2.3.1. Components of optode membrane

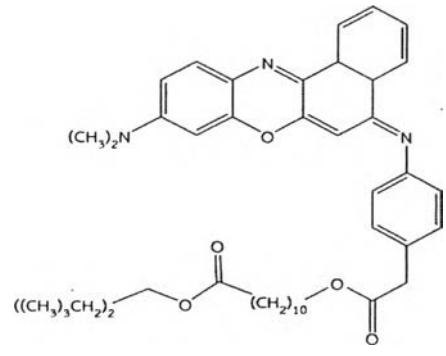
Optode membrane is a sensor for determination of target ion for bulk optode technique. The optode membrane is a polymeric film consisted of ionophore, chromoionophore, ion-exchanger, plasticizer and polymer.

Ionophore is the most important component of the optode membrane. The selectivity of ionophore with target ion has to be higher than with the interfering ions. The target ion in solution is extracted into the membrane to bind with ionophore.

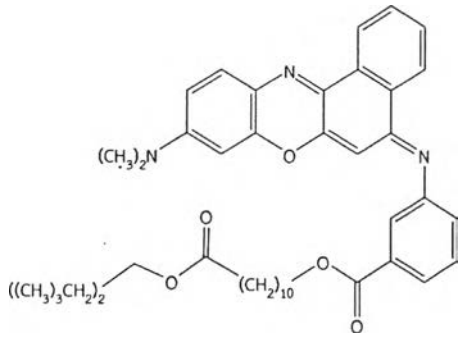
Chromoionophore is a pH indicator. The protonated and deprotonated forms of chromoionophore provide absorption maxima at different wavelengths. Its color change is observed when the target ion is extracted into the membrane because chromoionophore is deprotonated. Therefore, we can determine the amount of target ion by observing the change in absorbance of chromoionophore. Figure 2.1 shows some examples of chromoionophore structures used by various researches.



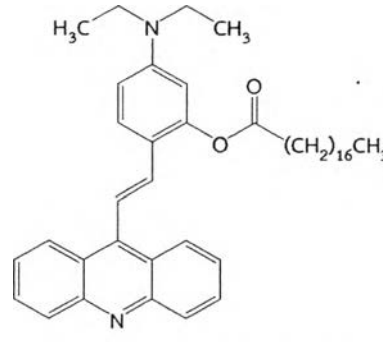
Chromoionophore I, ETH 5294



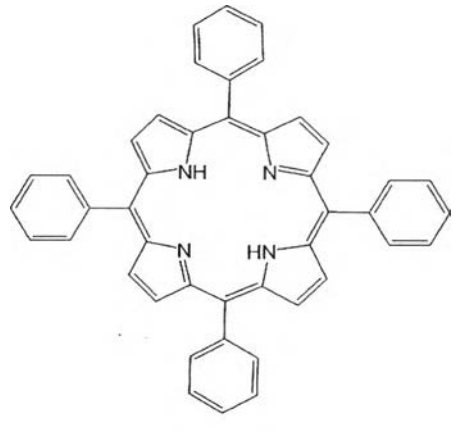
Chromoionophore II, ETH 2439



Chromoionophore VII, ETH 5418



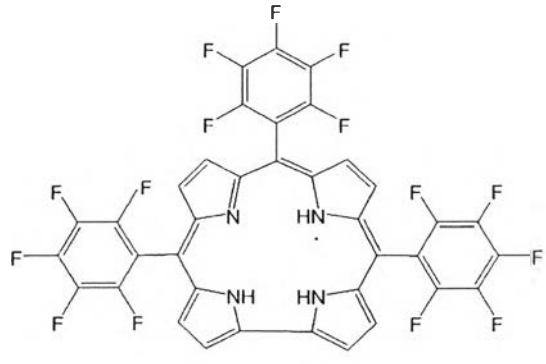
Chromoionophore XIV



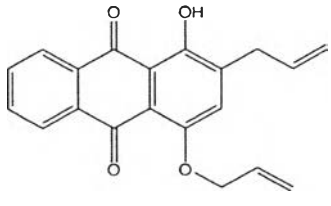
TPP

Figure 2.1 Some chromoionophore structures

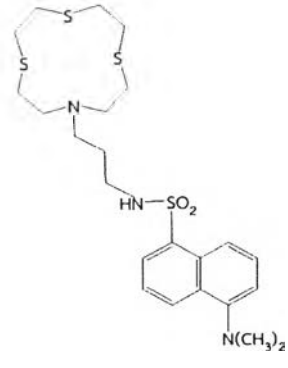
Fluoroionophore is the molecule that has ability to emit fluorescence and selectivity to bind with the target ion. Fluorescence is observed when the target ion is exracted into the membrane. Therefore, we can determine the amount of target ion by observing the change in intensity of fluorescence. Figure 2.2 shows some examples of fluoroionophore structures used by various researches.



H_3(tpfc)



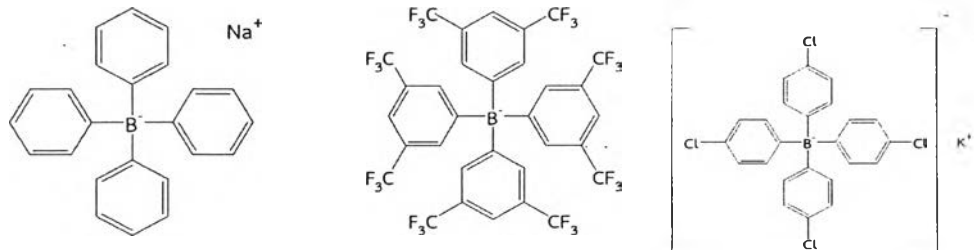
AQ



[12]aneNS$_3$

Figure 2.2 Some fluoroionophore structures

Ion-exchanger is a lipophilic salt. Anionic site (R^-) and cationic site (R^+) maintain the electroneutrality in the membrane phase for cationic and anionic analytes, respectively. Figure 2.3 shows some examples of ion-exchanger structures used by various researches.



NaTPB NaTm$(CF_3)_2$PB KT*p*ClPB

Figure 2.3 Some ion-exchanger structures

Plasticizer is a composition of membrane to improve elasticity and plasticity of membrane. Figure 2.4 shows some examples of plasticizer structures that were used by various researches.

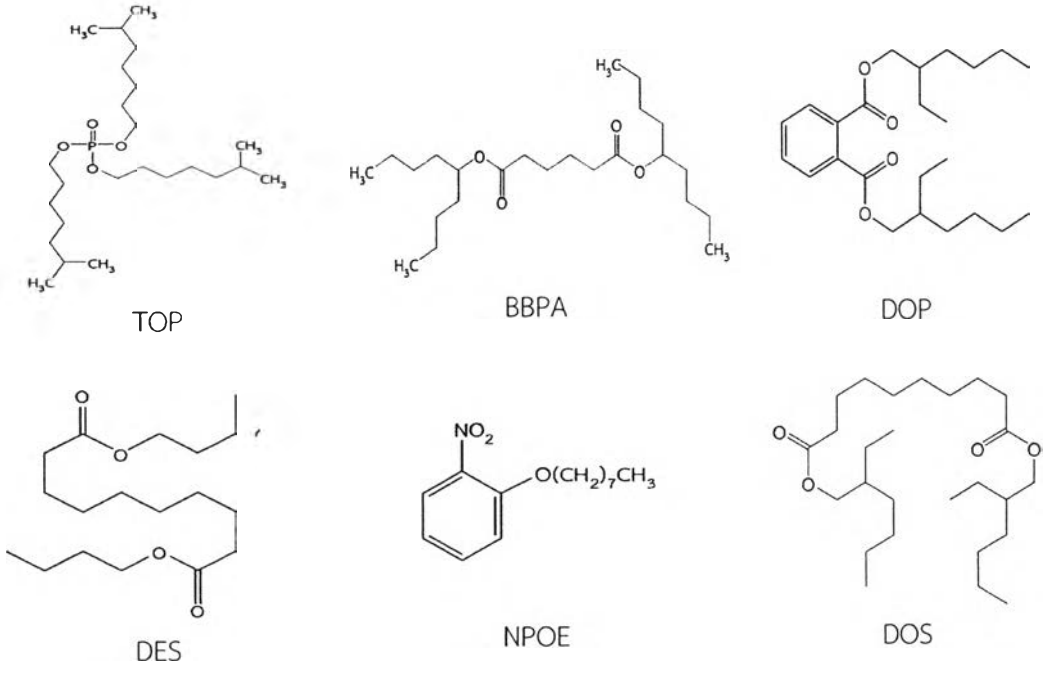


Figure 2.4 Some structures of plasticizer

All of compositions are incorporated and traped into PVC. PVC is polymer which is the most commonly used in bulk optode membrane because it can easily trap all of compositions in membrane.

2.3.2. Principle of operation and theory [38]

The bulk optode sensor is usually made from a polymer containing an ion-exchanger (R), an ion-selective ionophore (L) and a chromoionophore (C), the following ion-exchange reaction is shown in Equation (2.1):

$$M^{n+}_{(aq)} + zL_{(org)} + nCH^{+}_{(org)} + R^{-}_{(org)} \overset{K_{Exch}}{\rightleftharpoons} ML_z^{n+}{}_{(org)} + nC_{(org)} + nH^{+}_{(aq)} + R^{-}_{(org)} \quad (2.1)$$

where z is the ion-ionophore complex ratio and K_{Exch} is the exchange constant expressed by Equation (2.2) as follows:

$$K_{Exch} = \frac{[ML_z^{n+}][H^+]^n[C]^n}{[M^{n+}][CH^+]^n[L]^z} \quad (2.2)$$

According to this equation, a target ion M^{n+} is extracted from the aqueous solution into the organic membrane phase, CH^+ is protonated and its color changes. The absorbance of CH^+ increases and the absorbance of C decreases.

The degree of deprotonation of chromoionophore (α) is obtained as Equation (2.3):

$$\alpha = \frac{[C]}{[C]+[CH^+]} = \frac{[C]}{[C_{tot}]} \quad (2.3)$$

The bulk optode response depends on the exchange of M^{n+} and H^+ between the membrane and the solution, resulting in a change of the optical properties. The response of optode membrane represents in the degree of deprotonation of chromoionophore (α) as expressed by Equation (2.4):

$$\alpha = \frac{A_{prot} - A}{A_{pro} - A_{deprot}} \tag{2.4}$$

where A_{prot} and A_{deprot} are the absorbances of fully protonated chromoionophore (α=0) and fully deprotonated chromoionophore (α=1), respectively and A is the absorbance of chromoionophore at equilibrium. The optode membranes used for measuring A_{prot} and A_{deprot} are immersed in 1 mol L^{-1} HNO_3 and 1 mol L^{-1} M NaOH, respectively whereas the optode membranes used for measuring A are immersed in the solution containing the target ion (M^{n+}).

The activity of M^{n+} in the mix solution is calculated by Equation (2.5) as follows:

$$a_M = \left(K_{Exch}^{M}\right)^{-1} \left(\frac{\alpha}{1-\alpha} a_H\right)^n \times \frac{R_{tot} - (1-\alpha)C_{tot}}{n \left\{L_{tot} - (R_{tot}(1-\alpha)C_{tot})\left(\frac{z}{n}\right)\right\}^z} \tag{2.5}$$

where R_{tot}, L_{tot} and C_{tot} are the total concentration of anionic sites, the total concentration of ionophore and the total concentration of chromoionophore in the membrane, respectively. In practice, a calibration curve is plotted between 1- α versus the logarithm of the activity of a given ion (a_M) as shown in Figure 2.5.

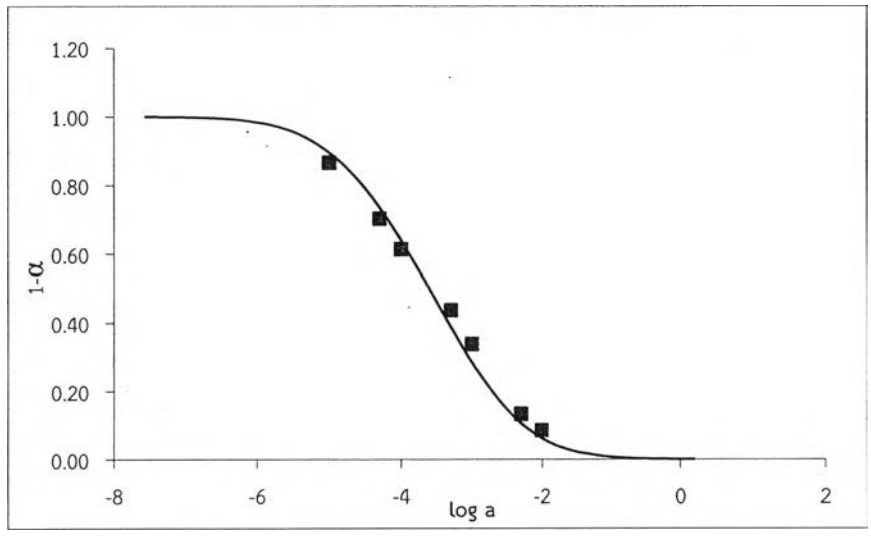
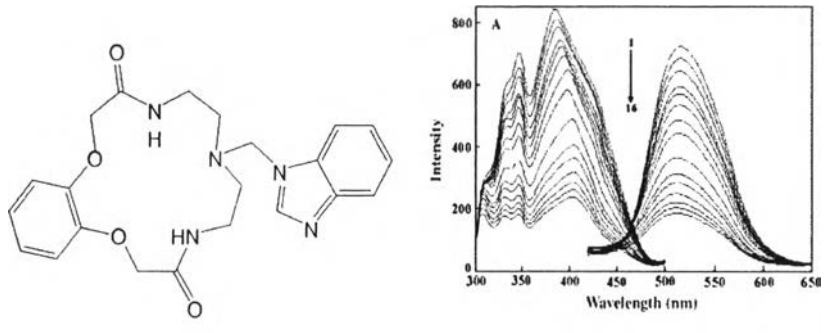


Figure 2.5 A calibration curve plotted between 1−α versus the logarithm of the activity of a given ion (a_M)

2.3.3. Bulk optode for determination of metal ions

In the previous research, the optical sensors as optode membranes have been used for determination of various cations using fluorescence and absorbance detection.

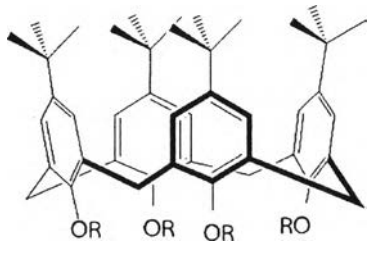
In 2008, Shamsipur *et al.* [39] prepared a fluorescence chemical sensor for determination of cobalt ions. The optode membrane contained 7-[(5-chloro-8-hydroxy-7-quinolinyl)methyl]-5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxa-triazacyclopentadecine-3,11(4H,12H)-dione (L) (Figure 2.6 A) as a cobalt-selective fluoroionophore. The response of proposed membrane based on quenching of L (Figure 2.6 B). The optode displayed a wide working range of 5.0×10^{-7}-2.0×10^{-2} mol L^{-1} with a fast respose time of less than 5 min. It was successfully applied for the determination of cobalt in vitamin B12 ampoule, cobalt alloy and tap water samples.



(A) (B)

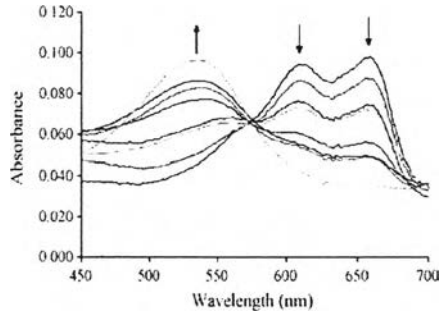
Figure 2.6 Structure of (A) L, (B) excitation and emission spectra of L in the presence of cobalt ion at various concentrations

In 2010, Chantana Bualom *et al.* [21] prepared an optode membrane containing *tert*-butyl calix[4]arene-tetrakis (*N,N*-dimetylthioacetamide) or Lead IV (Figure 2.7 A) as a lead-selective ionophore, chromoionophore I as a proton-selective chromoionopore. Absorption spectra of the optode membranes after equilibrium in Tris buffer solutions containing different concentrations of Pb^{2+} at pH 7.0 was shown in Figure 2.7 B. The optode provided the response range of 3.16×10^{-8}–5.00×10^{-5} mol L^{-1} lead within the response time of 30 min. It was successfully applied to determine lead in real water sample. The other works were summarized in Table 2.3.



$R=CH_2C(S)N(CH_3)_2$

(A)



(B)

Figure 2.7 Structure of (A) Lead IV, (B) absorption spectra of the optode membranes after equilibrium in Tris buffer solutions containing different concentrations of lead at pH 7.0

Table 2.3 Determination of metal ions by bulk optode technique

Metal ion	Composition		Measurement	Response time	Working range (M)	Ref.
	Ionophore	Chromoionophore or fluorophore				
Cu^{2+}	-	AQ	fluorescence	<40 s	1.0×10^{-6}-1.0×10^{-2}	[40]
Hg^{2+}	-	H_3(tpfc)	fluorescence	5 min	1.2×10^{-7}-1.0×10^{-4}	[41]
Hg^{2+}	L1	ETH 5418	absorbance	10 min	5.0×10^{-7}-5.0×10^{-4}	[42]
Hg^{2+}	L2	ETH 5294	absorbance	<40 s	2.0×10^{-10}-5×10^{-5}	[43]
Hg^{2+}	L3	ETH 5294	absorbance	100 s	3.3×10^{-9}-2.5×10^{-5}	[36]
Na^{+}	L4	ETH 2439	absorbance	30 s	1.0×10^{-6}-1.0×10^{-4}	[44]
Na^{+}	L5	TPP	fluorescence	20 min	5.0×10^{-5}-1	[45]
Zn^{2+}	L6	-	absorbance	2-3 min	2.5×10^{-6}-5×10^{-5}	[46]

where L1= trityl-picolinamide
L2= 2-mercapto-2-thiazoline

L3= tetrathia-12-crown-4

L4= 3,4-bis[(dicyclohexylcarbamoyl)methoxy]phenyl}methyl octadeca noate

L5= 4-*tert*-butylcalix[4]arene tetraacetic acid tetraethyl ester

L6= 1-(2-pyridylazo)-2-naphthol

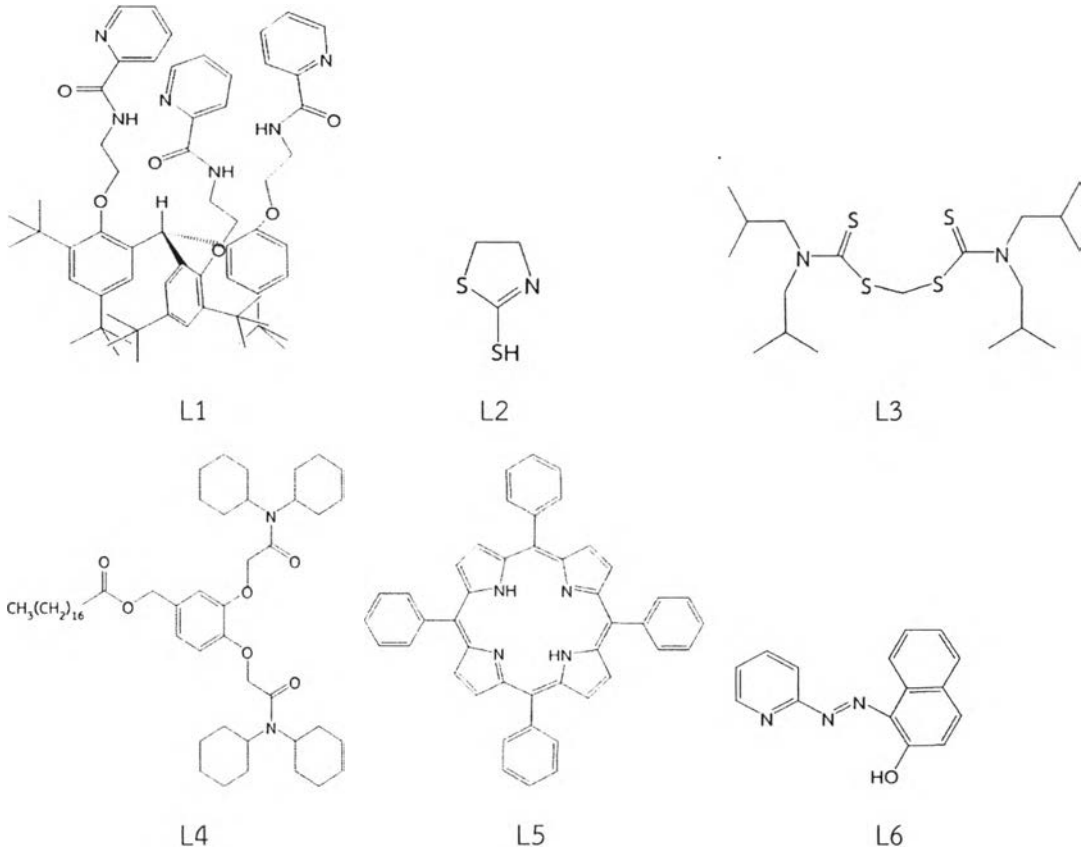
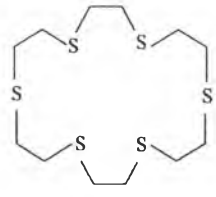


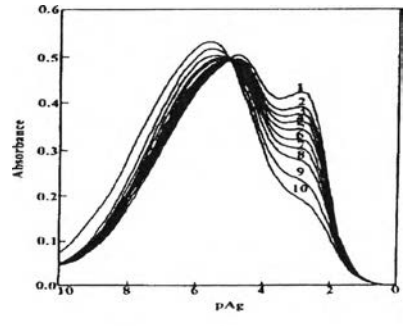
Figure 2.8 Structures of ionophore for determination some metal ions

Bulk optodes have been developed for silver ion determination by varying the components of optode membrane including silver-selective ionophore. In 2003, Shamsipur *et al.* [47] prepared a silver-selective optode membrane. In this work, the ionophore was hexathia-18-crown-6 or HT18T6 (Figure 2.8 A) and chromoionophore was chromoionophore I. Visible spectra of the optode membrane

after equilibration with pH-buffered solutions (citrate, pH5) containing different concentrations of silver ion were shown in Figure 2.8 B. The response range of this optode was 5.0×10^{-9}-5.0×10^{-5} mol L^{-1}. This silver-selective optode was applied to the determination for silver ion from a drinking water sample.



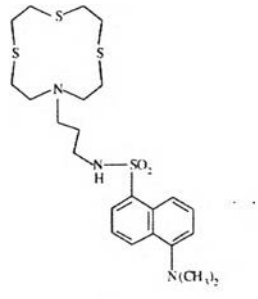
(A)



(B)

Figure 2.9 Structure of (A) HT18C6, (B) visible spectra of the optode membrane after equilibration with pH-buffered solutions (citrate, pH5) containing different concentrations of silver ion

In 2006, Shamsipur *et al.* [48] designed selective flourimetric optode membrane for silver ion determination. The membrane incorporated 1-(dansylamidopropyl)-1-aza-4,7,10-trithiacyclododecane ([12]aneNS$_3$) (Figure 2.9 A) as fluoroionophore. The response of the proposed membrane based on quenching of [12]aneNS$_3$ was shown in Figure 2.9 B. It displayed a wide working range of 5.0×10^{-7} to 1.7×10^{-2} mol L^{-1} of silver ion with the response time of less than 40 s. It was successfully applied to determine silver ion in real sample. The other works were summarized in Table 2.4.



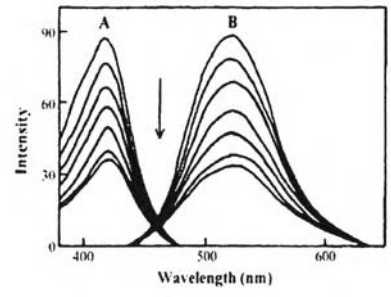


Figure 2.10 Structure of (A) [12]aneNS$_3$, (B) excitation and emission spectra of the ligand [12]aneNS$_3$ in acetonitrile in the presence of varying concentrations of silver ion

Table 2.4 Determination of silver ions by bulk optode technique

Composition		Measurement	Response time	Working range (mol L^{-1})	Ref.
Ionophore	Chromoionophore or fluorophore				
L7	ETH 5418	fluorescence	8 hr	1.0×10^{-12} – 1.0×10^{-8}	[49]
L8	ETH 5418	absorbance	500 min	1.0×10^{-9} – 1.0×10^{-4}	[50]
L9	ETH 5418	absorbance	10 min	1.0×10^{-8}-1.0×10^{-6}	[51]
L10	-	absorbance	2 min	1.0×10^{-4}-1.0×10^{-2}	[52]
L11	ETH 5294	absorbance	150 s	1.02×10^{-11} - 8.94×10^{-5}	[53]
L12	ETH 5294	Absorbance	3.5 min	2.3×10^{-11} - 1.1×10^{-3}	[54]

where L7 = *o*-xylylenebis(N,N-diisobutyldithiocarbamate
L8 = methylene bis(diisobuty1dithiocarbamate) (MBDiBDTC)
L9 = MBTBT
L10 = 9-(4-diethylaminostyryl)acridine

L11 = 7-(1H-benzimidazol-1-ylmethyl)-5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxatriaza cyclopentadecine-3,11(4H,12H)-di-one

L12 = 7-(1H-indol-3-ylmethyl)-5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxatriazacyclopentadecine 3,11(4H,12H)-dione

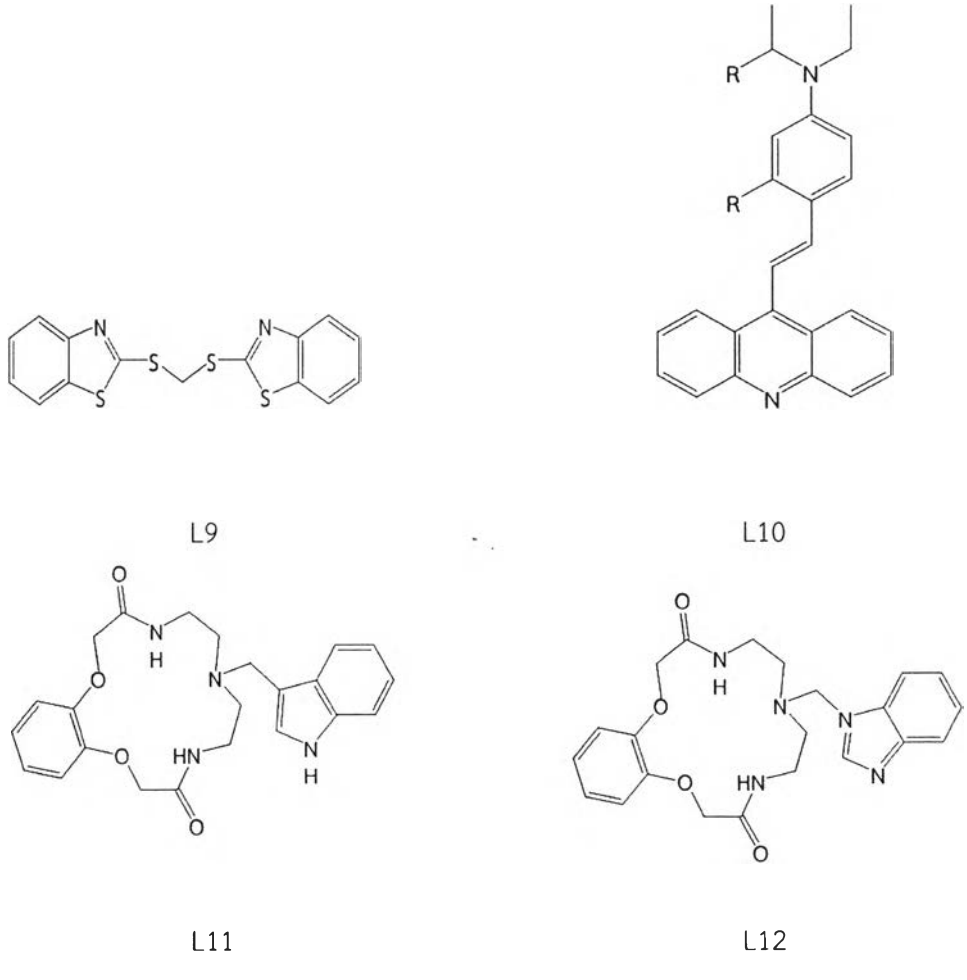


Figure 2.11 Structures of ionophore for determination of silver ions