

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Metal ion determination

2.1.1 Spectrochemical analysis

It is well known that metal ions are usually determined by instrumentation techniques for accepted concentration defined from various organizations. Inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic absorption spectrometry (AAS) are the most famous techniques.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) or inductively coupled plasma optical emission spectrometry (ICP-OES) is one of the most famous techniques for qualitative and quantitative elemental analysis. Its multi-element capability, high specificity, and low detection limits lead to the use of this technique in many applications. All dissolved samples can be analyzed. A plasma source is used for dissociation of the atoms or ions consisted in sample and excitation all of them to higher energy level. They return to their ground state and emit photons at the same time. The emitted photons show the specific wavelength depending on the element type. This light is recorded by an optical device.

AAS is a spectrometric analytical method for the quantitative determination of chemical elements by measuring the absorption of optical radiation (light) of the free atoms in the gaseous state. The ground state free atom absorbs radiation and move up to excited state. In analytical chemistry, this technique is usually used for determining the concentration of interested element in a sample. The intensity of the absorbed light is proportional to the concentration of the element in the flame.



ICP-OES and AAS can be applied in many fields such as water analysis, food analysis, animal feedstuffs, additives in lubricating oils and greases, soils analysis and clinical analysis.

Colorimeter is any tool used for characterization an objective measured of color characteristics. The colorimeter consists of a device that allows the absorbance of a solution at a particular frequency (color) of visual radiation to be determined. Thus, the concentration of a known solution is proportional to the absorbance unit.

A spectrophotometer is a device for measuring light intensity as a function of the color correlated with the wavelength of radiation. The most important things that should be realized for classification are the wavelengths they work with, the measurement techniques, how to obtain a spectrum including the spectral bandwidth and linear range. The spectrophotometers are usually applied for measuring light absorption correlated with analyte concentration.

White light is consisted of different colors or wavelengths of radiation. Absorption patterns of the visible spectrum depend on different chemical substances. Difference would be measured between initial radiation before passing through the colored sample and that after passing through the colored sample.

2.1.2 Electrochemical analysis

Electrochemistry such as potentiometric method was also reported in several applications [16-18] involving metal ion determination. Potentiometry is a method used in electroanalytical chemistry, usually to determine the concentration of a solute in aqueous samples. For the potentiometric measurements, the difference of potential between two electrodes is measured using a high impedance voltmeter.



Since there is no current observed meant that no net electrochemical reactions or the system is approach equilibrium.

A potentiometer consists of two electrodes. The voltmeter is contacted to both electrodes to measure the difference of potential between them. One of the electrodes is a reference electrode, where the potential is known. The other electrode is the working electrode. The working electrode is usually made from metal immersed in a solution of its own ions or produced from a carbon rod electrode fixing a solution which contains the ions of interest in two different oxidation states.

Derivative stripping potentiometry can be applied for determination of Cd(II), Cu(II), Pb(II), Se(IV) and Zn(II) in cultured sea bass tissues [16], speciation of inorganic arsenic in alimentary and environmental aqueous samples [17]. This technique could also be used to monitor cadmium, lead and copper in powdered milk products [18].

Spectrochemical and electrochemical analysis using instrumental show high sensitivity and selectivity; however, they are still costly, time consuming and have to operate under skillful operator. Determination of metal ions using colorimetric reagent is one of easy method for metal analysis and widely used until now.

2.1.3 Determination of metal ions using colorimetric reagent

Colorimetric analysis is a method for determination of the element or chemical compound concentration in solution with the assistant of color reagents. It is useful in both organic compounds and inorganic compounds.

In other word, the colorimetry meant the measurement of color and a definition of colorimetric method is any technique for evaluation of a color of unknown in reference compared with known colors. The intensity of the color from the reaction product must be proportional to the concentration of the substance.



To determine various metal ions by colorimetric method, the organic molecules are newly synthesized to improve the high selectivity and achieve the detection limit as low as determined by instruments. Thus, most of colorimetric reagents must be synthesized. The response in color change of colorimetric reagent usually present in term of shifting of maximum wavelength [8, 9, 19, 20] or appear the color after interaction [21, 22]. However, decoloration of reagent after interacting with target has been reported [11].

2.2 Plant pigments

Pigment is the colored material that insoluble in aqueous solution and performable color by itself. It is different from dye which is the color substance soluble in aqueous solution. Natural plant pigments are normally found in fruit skin, flower, roots and even in seed. The natural pigments are usually extracted in organic solvent such as methanol, ethanol and acetone etc.

Most of pigment colors and its color change result from the production, interaction, and breakdown of three classes of substances such as porphyrins, carotenoids and flavonoids. In Table 2.1, the types of compounds included in each of these three classes are given together with the colors they produce in plants. The colors depend on some instances upon factors such as pH or upon chemical interactions [23-25].



Table 2.1 Natural plant pigments

Class	Compound type	Color
Flavonoid	Flavone	yellow
	Flavonol	yellow
	Anthocyanin	red, blue, purple, magenta
Porphyrin	Chlorophyll	green
Carotenoid	Carotene (α , β , γ and lycopene)	yellow, orange, red
	Xanthophyll (Lutein)	yellow
Betalain	Betanin	red or yellow

Several research works reported about plant pigments interacting with some metal ions resulting in color change for example anthocyanin can coordinate with Cu(II), Pb(II) and Cd(II). Betanin extracted from red beetroot, its structure can be degraded after interacting with some metal ions. It is widely known that Mg(II) is the major element consisted in chlorophyll a structure. Mg(II) replaces 2 H atoms at N atoms in the center of molecule. Chlorophyll a also has an additional ring and various groups are attached to the fundamental porphin ring as shown in Figure 2.1 and Table 2.2 shows some of interaction of pigments and metal ions.



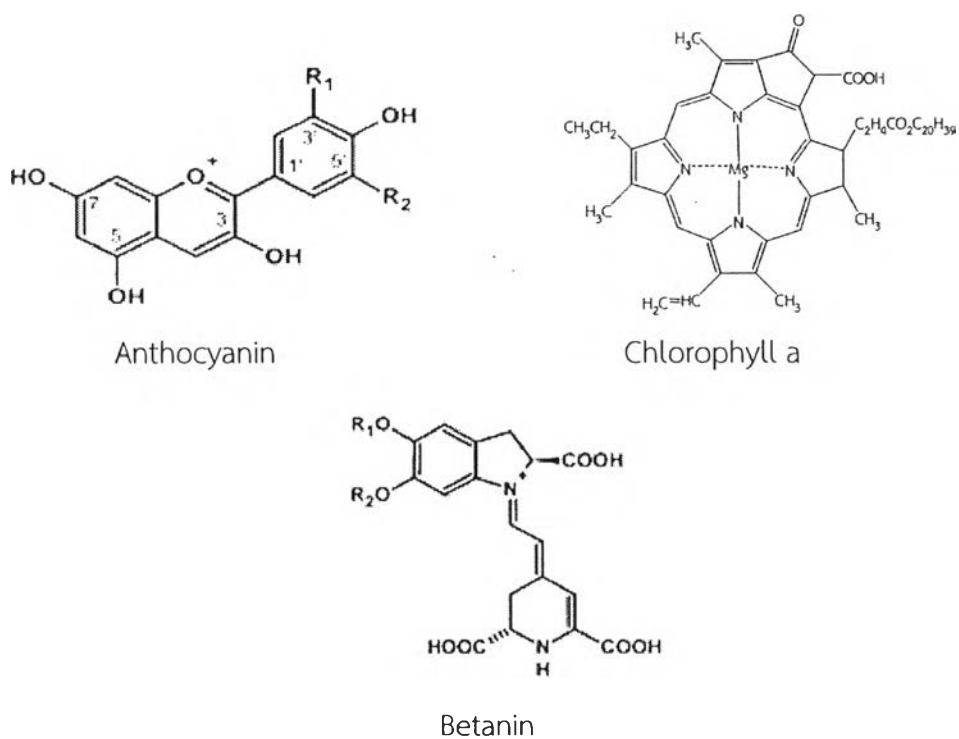


Figure 2.1 Plant pigment structures

Table 2.2 Plant pigment interacting with metal ions

Plant pigment	Interaction with metal ions
Anthocyanin [15]	Complexation with Al(III)
3, 3 ¹ , 4 ¹ , 5, 7-pentahydroxy-flavylium [26]	Complexation with Pb(II), Cr(III) and Cd(II)
Betanin [23]	Degradation by metal ions
Chlorophyll a [24]	Complexation with Mg(II)

2.3 Anthocyanin

Anthocyanin is one of the well-known pigment found in tissue of many higher plants and it shows several colors for example, red, violet, blue or yellow.

Anthocyanin is the common name of a flavonoid pigment based on the flavylium as core structure. It normally bonds to hydroxyl groups, sugars and organic acids. The aglycone flavylium cation is referred to an anthocyanidin. There are more than 600 different species which have been reported. The structure of an acylated anthocyanin proposed by Arapitsas *et al.* (2008) is shown in Figure 2.2 [25].

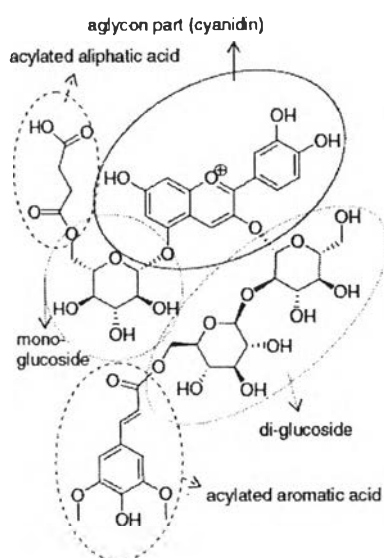
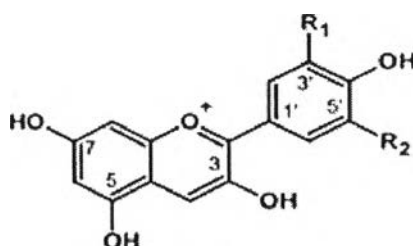


Figure 2.2 Structure of an acylated anthocyanin

There are 6 common anthocyanin types as shown in Table 2.3. They are different from each other at R_1 and R_2 positions resulting in different color [27, 28]. The distributions of these 6 common anthocyanidins in fruits and vegetables are 50% for cyanidin, 12% for pelargonidin, 12% for peonidin, 7% for petunidin and 7% for malvidin [29].

Table 2.3 Common anthocyanin types

Pigment	R ₁	R ₂	Spectral max in MeOH/HCl	Aluminum chloride shift	Visible color
Pelargonidin (Pg)	H	H	520 nm	-	Orange
Cyanidin (Cy)	OH	H	535 nm	18 nm	Magenta
Peonidin (Pn)	OCH ₃	H	532 nm	-	Magenta
Delphinidin (Dp)	OH	OH	546 nm	23 nm	Mauve
Petunidin (Pt)	OCH ₃	OH	543 nm	14 nm	Mauve
Malvidin (Mv)	OCH ₃	OCH ₃	542 nm	0	Mauve



Anthocyanin structures

2.3.1 Influent of pH

Anthocyanin can be performed several colors depended on solution pH change as shown in Figure 2.3. In acidic solution (pH < 3) the flavylium cation is predominated species and contributed to purple and blue color in neutral and basic solution, respectively. Decoloration of anthocyanin can be occurred in an aqueous solution due to hydration effect at 2 or 4 positions of hydroxyl groups. In addition, in

the solution pH in the range of 4-6, the four species; flavylium cation, anhydrous quinoidal base, colorless carbinol base and the pale yellow chalcone are found.

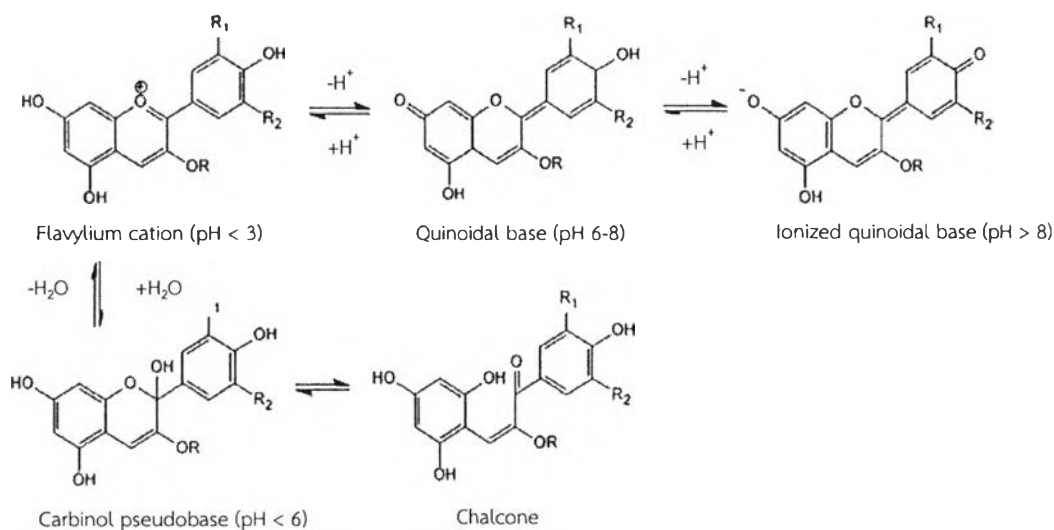


Figure 2.3 Anthocyanin structures and its color depended on pH of solution [30-32]

2.3.2 Co-pigmentation effect

Co-pigmentation effect is the association between the pigments and other colorless organic compounds or metal ions to form new molecule or complex, generating a change or an increasing in the color intensity [33]. Some investigations reported that co-pigmentation between anthocyanins and other compounds such as flavonoids, alkaloids, organic acids, amino acids, nucleotides, sugar molecules, metals or another anthocyanin that if the co-pigment is other anthocyanin, an intramolecular co-pigmentation is formed. When the interaction is with a metal ion, a complexation is undergone whereas in the case of co-pigments with free electron pairs, an intermolecular co-pigmentation takes place. When the co-pigment is another phenolic compound, the π - π interactions or charge-transfer complex formation is performed [34].

2.3.3 Cyanidin

Cyanidin belongs to the kind of anthocyanins and contains the typical C6-C3-C6 skeleton. Cyanidin is a pigment soluble in water. The color of cyanidin depends on the pH of the solution. Cyanidin is red when pH is below 3, blue at pH higher than 11 and violet at neutral pH. In natural plants, cyanidin is normally bound to a sugar molecule to be cyanidin 3-O-beta-glucoside.

Cyanidin is widely found in nature. Its simple structure contains a catechol terminal group which responses as the active chromophore in optoelectronic systems. Moreover, the -OHs linked to the chromophore provide useful active sites on inorganic surfaces or large biomolecules such as nucleic acids and proteins [35].

Cyanidin structure responses magenta or reddish color in HCl/MeOH solution. The maximum absorption wavelength in visible region can be shifted to the longer wavelength after adding $AlCl_3$. It is indicated that there is *ortho*-dihydroxyl group in the molecular structure [28].

Cyanidin is an polyphenolic antioxidant compound with assisted cell protectant effects. Cyanidin shows protection against UV-light lipid peroxidation and performs a capacity for radical species scavenging such as NO and oxygen radical resulting in cells protection against various mechanisms of oxidative damage.

Red cabbage contains several anthocyanins having different substituents and functional groups. Jin-Yuarn Lin and co-workers (2008) have been characterized the pigment components in red cabbage juice and its heated products. The most anthocyanin found was malvidin glycosides [36]. Red cabbage was also analyzed and tentatively identified anthocyanin species by using HPLC/DAD-ESI/Qtrap MS. Twenty four types of anthocyanins were potentially separated and identified, all consisted of cyanidin as aglycon with mono- and/or di-glycoside, and acylated, processing aromatic and aliphatic acid structure [25]



2.3.4 How to identify anthocyanin

(1) UV-Visible spectrophotometric method

UV-Visible spectrophotometry is the classical method for determination and characterization of anthocyanin. Figure 2.4 shows the spectrum pattern of anthocyanin molecule.

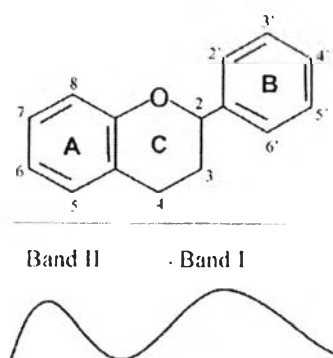


Figure 2.4 Spectrum pattern of anthocyanin molecule

Phenols absorb the ultraviolet (UV) light, while flavonoids structure are characterized with a maximum absorption band in the 240–285 nm region due to the A-ring and with another maximum absorption band in the range 300–550 nm due to the B-ring of anthocyanin.

(2) Shinoda's test

Shinoda's test is a magnesium hydrochloride reduction test to confirm flavonoid property. The extract is added with ethanol and a few drops of concentrated HCl. To this solution, some magnesium ribbons are added. Pink or red coloration indicates the presence of flavonoids. The color is due to the reductive conversion of the flavone into the corresponding anthocyanidin pigment [37].

(3) Mass spectrometry (MS)

Up to date, hyphenated techniques such as HPLC coupled to MS APCI-MS, ESI-MS and FAB-MS have become powerful for the anthocyanins identification. Among these desorption sources FAB, ESI and MALDI are considered smooth ionization sources, because they produce very low fragmentation and allow determine exact molecular weight. It can be also observed that by using these kindly ionization techniques, it is possible to analyze molecules sensitive to suffer major fragmentations such as anthocyanins and their acylated derivatives.

(4) Nuclear magnetic resonance spectrophotometry (NMR)

NMR has also been very useful to identify the anthocyanin structure, anthocyanin derivatives [38] including the reaction products of anthocyanins with other compounds such as cinnamic acid derivatives [39].

2.4 Chemically modified solid sorbent

Nowadays, the solid material is widely used and developed as sorbent products depended on various proposes. The properties such as stable chemical structures, high porosity and surface areas, and good sorption capacities should be improved. Chemically modified solid sorbent is one of important process for developing its properties to achieve those interested applications. Their advantages include good selectivity, preconcentration factor, binding energy and mechanical stability, easy to regenerate for sorption-desorption process and good reproducibility in the sorption characteristics [40].



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2.4.1 Modification method

Chemical modification on solid sorbent has been reported for a long time with different applications such as extraction, removal, separation, preconcentration or even sensor. The modification is also different, however, based on its applications. The different methods are depended on the characteristics of the surface, such as polarity, charge, surface energy, biocompatibility and reactivity.

(1) Coating or impregnation

Impregnating, coating, or loading a solid support is the physical reaction. This method offers a benefit preparation of a sorbent for metal ion separation. The impregnation method is also easy encountered in chemically linking a chelating reagent to a support sorbent hence there is a famous choice selected the reagents for desired selectivity.

(2) Functionalization

Functionalization is the chemical reaction of chelating agent and a functional group of solid structure. This produced method can generate new functional group which higher specific for interested analyte.

2.4.2 Modified solid sorbent and its application

There are many applications using solid sorbent for sorption of target molecules depended on modification processes or even its traditional structure. Solid material such as Amberlite, silica gel, alumina and activated carbon are widely selected upon they stability, high porous surface and low cost.

Modification of solid phase for extraction, preconcentration called solid phase extraction (SPE) is famous nowadays. For example alumina immobilized with 1,10-phenanthroline was used for on-line extraction of copper and cadmium couple with the flame atomic absorption spectrometry [41]. The chloromethylated polystyrene functionalized with N,N-bis(naphthylideneimino)diethylenetriamine was applied for on-line preconcentration of cadmium determined by FAAS [42]. Multi-elements (Cd, Co, Zn, Cu, Pb, Fe and Ni) was also extracted by using modified silica gel coated with 8-hydroxyquinoline [43].

For removal any metal ion from the aqueous samples, using Amberlite XAD-7 impregnated with di-(2-ethylhexyl)-phosphoric acid (DEHPA) for Cr(III) [44] Cr(VI) sorption into toluidine blue impregnated XAD-7 [45] were reported. In addition, activated carbon, low cost material, was also used for adsorption of the 3d transition metals: Cu(II), Co(III), Ni(II), Fe(III), and Cr(III) in water samples [46]. Moreover, the polymeric resin, Amberlite XAD-2 and XAD-7, they can adsorb the organic molecule such as di-2-pyridyl ketone salicyloylhydrazone from liquid samples without any modification [47]. Table 2.4 shows the modified solid sorbents and its applications as described above.



Table 2.4 Modified solid sorbents and its applications

Solid sorbent	Reagent	Modifying method	Application
Alumina [41]	1,10-phenanthroline	Impregnation	Cu(II), Cd(II) extraction
Polystyrene [42]	N,N-bis (naphthylideneimino) diethylenetriamine	functionalization	Cd(II) extraction
Silica ge l[43]	8-hydroxyquinoline	Impregnation	Cd(II), Co(II), Zn(II), Cu(II), Pb(II), Fe(III) and Ni(II) extraction
Amberlite XAD-7 [44]	di-(2-ethylhexyl)- phosphoric acid (DEHPA)	Impregnation	Cr(III) removal
Amberlite XAD-7 [45]	toluidine blue o	Impregnation	Cr(VI) removal
Activated carbons [46]	-	-	Cu(II), Co(III), Ni(II), Fe(III), Cr(III) extraction
Amberlite XAD-2 and XAD-7 resins [47]	-	-	Di-2-pyridyl ketone salicyloylhydrazone

In comparison to silica gel, alumina and activated carbon have been extensively used to remove organic compounds from aqueous solutions, polymeric adsorbents, namely synthetic resins, possess many striking features such as stable chemical structures, high porosity and surface areas, and great adsorption capacities. XAD resins exhibit good physical properties such as porosity, uniform pore size distribution, high surface area, and chemically homogeneous non-ionic structure [47].

Amberlite XAD-7, which is an inert polymeric substance based on acrylic ester is hydrophobic, continuous pore phase with a weak dipole moment. The structure of Amberlite XAD-7 is shown in Figure 2.5. It is usually used for removal of organic molecules from aqueous media and vapor streams [48]. It is also used in impregnation processes for preparing the various impregnated resin applied for selective separation of target metal ions. An acrylic polymer bearing ester functions, Amberlite XAD-7 can be hydrolyzed in highly acidic conditions to form carboxylic functions. Navarro *et al.* commented that a resin bearing weak ester groups may be hydrolyzed by contacting with highly acidic solutions to form $R-COOH^+$ groups [49]. They summarized the physical properties of Amberlite XAD-7 as shown in Table 2.5.

Table 2.5 Physical properties of Amberlite XAD-7

Properties	Item
Particle size	20/60 mesh-250/850 μm
Superficial area	450 m^2/g
Resin porosity	0.55
Pore size (mean value)	85-90 \AA
Pore volume	0.97-1.14 cm^3/g
Skeleton density	1.24 g/cm

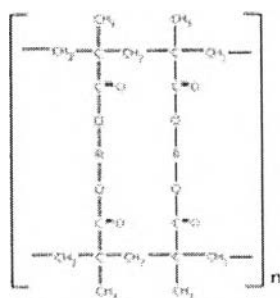


Figure 2.5 Amberlite XAD-7 structure

2.5 Literature review

Up to date, metal ion determination is usually determined by instrumentations. However, these techniques still have limitation as mentioned in section 2.1. Using chelating agent to form metal complex is widely used for a long time, the detection limit is still higher than measuring by instrumentation.

2.5.1 Determination of metal ions using synthetic colorimetric reagent

It is well known that the producing processes of all reagents are usually complexity and also harmful for human health and environment. Moreover, its high price should be considered. However, it is still popular used in several proposes because of its selectivity. The new synthetic colorimetric reagents for determination of metal ions in water samples have been reported. For example, a heavy metal chelating agent namely N^1, N^2, N^4, N^5 -tetrakis(2-mercaptoethyl) benzene-1,2,4,5-tetracarboxamide (TMBTCA) was designed with four chelating groups. This heavy metal chelating agent having more bonding sites and showed more affinity for cadmium and copper than some traditional commercial precipitants [50]. Kaur and Kumar (2010) synthesized 1-aminoanthracene-9,10-dione derivatives as a colorimetric reagent for metal ion detection. They studied the effect of nature and number of nitrogen atoms on metal ion sensing properties of four different types of nitrogen atom based on 1-aminoanthracene-9,10-dione as chromogenic moiety. All the four chemosensors showed the response toward Cu(II), Ni(II) and Co(II) and also increased the usability and the dynamic range of estimation [19]. In addition, chemosensor based-on naphthol for detection of Al(III) and Cu(II) was reported. This sensor provided both visual and fluorescent detections. The color changed from yellow to orange and fluorescence enhancement with a bathochromic shift upon binding to Al(III) in aqueous acetonitrile. It can also selective for Cu(II) ions detection through ion-promoted oxidation reaction



in acetonitrile media, resulting in a selective color change from yellow to dark blue and a fluorescence quenching effect. The detection limit was quite low (1×10^{-5} M) [51].

2.5.2 Naked-eye determination of metal ions using colorimetric reagent

Colorimetric method using naked-eye detection is the basic and very simple method by the aid of color reagent. Nowadays, it is widely useful due to no requirement of any convoluted instruments or expert operators. There are many reports using synthetic reagents for naked-eye determination of metal ions in aqueous medium.

Suresh and co-workers (2010) synthesized colorimetric sensor based on per-6-amino- β -cyclodextrin/*p*-nitrophenol and investigated the ratiometric response (A_0/A) of this sensor for determination of transition metal cations as Fe^{3+} and Ru^{3+} in water samples. This naked-eye sensing provided the color change from intense yellow to colorless. The selective complexation of trivalent cations (Fe^{3+} and Ru^{3+}) rationalized in principle by several factors such as ionic radii, electronegativity as well as described in HSAB theory [11].

Kaur and Sareen (2011) reported the synthesis of a colorimetric sensor for simultaneous dual analysis of Hg^{2+} and Fe^{3+} . Naked-eye detection of color changes for both Hg^{2+} (yellow to purple) and Fe^{3+} (yellow to red) were quantified. Furthermore, they coated this dye on paper strip for determination of Hg^{2+} in water sample [52].

For Cu(II) detection by naked-eye, 2 research groups reported newly designed color reagents. Wang *et al.* (2008) reported that 3-nitro-4-ethylenediamido-nitrobenzene showed high selectivity and sensitivity for Cu^{2+} and a new peak at 525 nm appeared after interaction. Detection by naked-eye was obtained in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ at pH 7.6 under the color change from yellow to red [1]. While, Kumar *et al.* (2013) used the synthetic ninhydrin-quinoxaline derivative for determination of Cu^{2+} in aqueous

medium (ethanol: H₂O, 1:9, v/v). It performed high sensitivity and selectivity with the detection limit of 3.43×10^{-7} M which was probably the lowest concentration determined by naked-eye never reported until year 2013 [53].

However, these reagents must be synthesized which the production might not be safe and lead to high price due to the difficult masking process.

2.5.3 Determination of metal ions using natural colorimetric reagent

Till now, only a few reports using natural product as colorimetric reagents for quantitative determination of metal ions.

Anthocyanin was studied in various research. For long time ago, Jurd (1966) reported that the formation of co-pigment-aluminum anthocyanin complexes depended not only on pH but also on the type of organic acids which constituted the buffering system [13]. Some reports showed that anthocyanin and anthocyanidin with *o*-dihydroxyl group (Cy, Dp, Pt) could be formed metal-anthocyanin complexes. In addition, it was found that the presented blue color in plant due to complexation of anthocyanin and Al, Fe, Cu, Sn, Mg and Mo [54, 55]. The results agreed with the research of Moncada *et al.* (2003). They studied the interaction of Al(III) and the existence of catechol unit in synthetic flavylum salts and natural anthocyanin. It was found that trivalent aluminium had a strong affinity to the catechol unit (Figure 2.6) and could stabilize the blue color in form of complex of ionized quinoidol base (one of anthocyanin structure) [15].

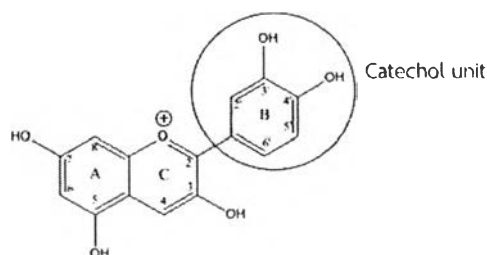


Figure 2.6 Catechol unit of anthocyanin structure



Smyk *et al.* (2008) investigated the interaction between cyanidin 3-glucoside and Cu(II) in a methanol–water solvent and in a phosphate buffer. The reduction of Cu(II)–Cu(I) was first occurred and oxidation of Cy 3-glc then took place and the longer wavelength was occurred. In addition, they also studied the kinetic of this complex. The interaction of Cy 3-glc and Cu(II) ions had two stages; “fast” at the shot beginning period and “slow” to the end of reaction [14].

Ukwueze *et al.* (2009) reported the potentials of 3, 3¹, 4¹, 5, 7 pentahydroxyflavylum of *Hibiscus rosa-sinensis* L. flowers as a ligand for quantitative determination of Pb(II), Cd(II) and Cr(VI) by UV-Visible spectrophotometry. This method could simultaneous those 3 metal ions by varying pH of the solution. Pb(II) complex was formed at pH 4.2 (λ_{\max} = 555 nm, in methanol). Cr(III) complex was formed at pH 1.0 (λ_{\max} = 682 nm, methanol and ethanol) while a Cd(II) complex was formed at pH 3.0 (λ_{\max} = 706 nm in methanol and 679 nm in ethanol) [26].

Interestingly, the relative research of Fuleki and Francis (1967) showed that lead acetate could be proposed as a colorimetric reagent for detection of anthocyanin which consisted of catechol unit in its structure. The reaction was faster and the color change was more definite than those reacted with AlCl₃ [56].

Moreover, Borsari *et al.* (2002) reported that curcuminiod (curcumin and diacetylcurcumin) was used as a ligand for Fe(III). The coordination of curcuminiod and Fe(III) was occurred through β -diketone structure to form the stable complex [57].



2.5.4 Modified solid sorbent for coloring sensor

Applications of modified solid sorbent as coloring sensors have been reported. All of designs based on colorimetric reagents properties cooperated together with the high quality of solid sorbents such as high surface area, stability, low cost, etc. The advantages of using these solid sensors were easy to detect, high sorption capacity, high stability [58, 59], convenient for keeping, easy to deposit and even reusable [60].

Polyacrylonitrile fiber was first aminating with ethylenediamine and then covalently immobilizing with 4-(2-pyridylazo)-1,3-benzenediol (PAR). The modified sorbent was applied for Hg^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Cu^{2+} with a color change from red-orange to dark-brown in neutral solution. Decreasing in pH such as at pH 3.0, it showed a color change only for Hg^{2+} and Cu^{2+} [58]. In addition, polyacrylonitrile fiber was also used as acid–base indicator by functionalizing and immobilizing with tetraethylenepentamine and the mixture of ethyl orange and phenolphthalein, respectively. The color changed from deep pink ($\text{pH} < 1.1$) to yellow ($1.1 < \text{pH} < 13.0$) and then to dark violet ($\text{pH} > 13.0$) [59].

Hydrogel was also newly developed and applied for Fe(III) detection. The naked-eye colorimetric hydrogels were synthesized using 2-hydroxyethylmethacrylate (HEMA) and acrylamide (AAm) as the primary monomer and N-(rhodamine-6G)lactam-N'-acryloyl-ethylenediamine as co-monomer by free radical polymerization. This sensor was applied for water sample analysis and also reusable [60].

Matsunaga *et al.* (2005) designed the chelating resin having β -hydroxypropyl-di (β -hydroxyethyl) amino moiety for determination of As(V) in liquid medium by coating with molybdenum as a colorimetric reagent. The resin beads showed greenish blue in the presence of a reducing agent under acidic conditions and



the intense color was depended on As(V) concentration. Detection limit was found to be 1×10^{-6} M and probably be 1×10^{-7} M for long time reaction [61].

The summary of some modified solid sorbent as coloring sensor described above are shown in Table 2.6.

Table 2.6 Modified solid sorbents as coloring sensor and its applications

Solid sorbent	Reagent	Analyte
Polyacrylonitrile fiber with ethylenediamine [58]	4-(2-pyridylazo)-1,3-benzenediol	- Hg ²⁺ , Pb ²⁺ , Cd ²⁺ , Zn ²⁺ , Ni ²⁺ and Cu ²⁺ (neutral solution) - Hg ²⁺ and Cu ²⁺ (pH 3.0)
Polyacrylonitrile fiber with tetraethylenepentamine [59]	Ethyl orange and phenolphthalein	Acid-base indicators
Hydrogel [60]	Rhodamine	Colorimetric naked-eye sensors for Fe ³⁺
Chelating resin having β -hydroxypropyl-di (β -hydroxyethyl) amine (HDEA) [61]	Molybdenum	Trace As(V) in aqueous media

