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Effectively simultaneous naked-eye detection of Cu(II), Pb(II), Al(III) and Fe(III) using cyanidin extracted from red cabbage as chelating agent

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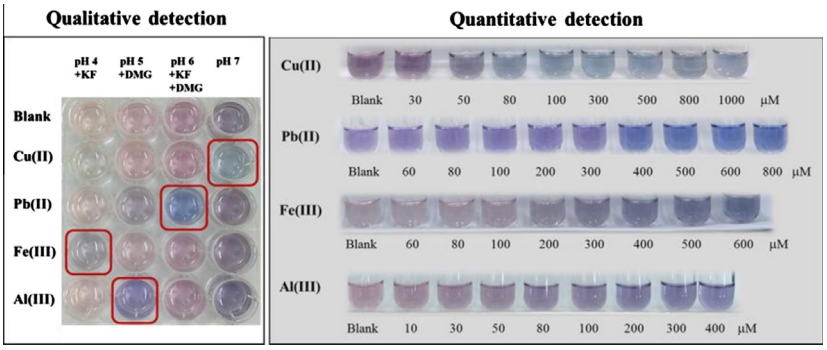
HIGHLIGHTS

- Cyanidin shows simultaneous detection of Cu(II), Pb(II), Al(III) and Fe(III).
- LOD by naked-eye detection was in the range of micromolar level.
- Qualitative and quantitative determinations can be performed.
- Enhance the selectivity by slightly varying pH of solution and using masking agents.
- Validating the method by comparing naked-eye results with the ICP technique.

GRAPHICAL ABSTRACT



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ABSTRACT

Simultaneous determination of Cu(II), Pb(II), Al(III) and Fe(III) using cyanidin as a chelating agent was investigated in terms of both quantitative and qualitative detections. Cyanidin was extracted and purified from red cabbage which is a local plant in Thailand. The selectivity of this method was examined by regulating the pH of cyanidin solution operated together with masking agents. It was found that Cu(II), Pb(II), Al(III) and Fe(III) simultaneously responded with the color change at pH 7, pH 6, pH 5 and pH 4, respectively. KF, DMG and the mixture of KF and DMG were used as masking agents for the determination of Fe(III), Al(III) and Pb(II), respectively. Results from naked-eye detection were evaluated by comparing with those of inductively coupled plasma (ICP), and there was no significant difference noticed. Cyanidin using as a multianalyte reagent could be employed for simultaneous determination of Cu(II), Pb(II), Al(III) and Fe(III) at the lowest concentration at 50, 80, 50 and 200 μM, respectively, by slightly varying pHs. Moreover, the proposed method could be potentially applied for real water samples with simplicity, rapidity, low cost and environmental safety.

Introduction

Heavy metal ions are harmful for environmental and life processes. Copper, for example, can be toxic to biological systems when they exceed the levels of cellular needs and it is also able to displace other metal ions which act as cofactors in enzyme-catalyzed reactions [1]. Lead is well known as a heavy metal which is harmful to human health and environments even at a low level [2,3]. Aluminum is the third common element existing in rock and soil. Nowadays, aluminum is released in several forms from many manufacturing processes. Aluminum can also contribute to several neurodegenerative disorders such as Alzheimer's disease [4,5]. Moreover, iron plays an important role at a cellular level. Both deficiency and excess of iron can induce a variety of diseases [6,7]. There are various methods to determine metal ions such as

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photometric methods and electrometric methods. In addition, most of these methods need expensive equipments, time consuming and trained operators. Determination of metal ions in environmental water samples by using inexpensive measurements is widely interesting. Color developing is one of the popular methods which have been investigated. Various reagents used as chelating agents for determination of metal ions must be synthesized and it is usually not environmental friendly. Moreover, the synthesized compounds would be costly.

Cyanidin (Cy) is one kind of anthocyanin which can be isolated from plants in its red colored flavylium form. Cyanidin can present in reddish color in an acidic medium. In addition, its color is changed to purple and dark blue color corresponding to its quinoidal and anhydrobase ion, respectively upon pH increasing the solution pH [8]. Anthocyanin can react with some metal ions like Cu(II), Fe(III), Al(III), Cr(III), Pb(II), Mg(II) through different reactions such as redox, complexation or even catalytic reactions [9–11]. The *ortho*-dihydroxyl group of the cyanidin molecule can coordinate with another atomic ion and give bathochromic shift in the UV–vis spectra [12]. Several research groups reported that cyanidin is the major type of anthocyanin in many plants such as Hibiscus [13], purple wheat [14], berry [15,16] including red cabbage [17–19]. Cyanidin is not widely used as a color reagent due to its stability and extraction yield. Nevertheless, cyanidin is still challenging because it can react with various toxic metal ions and also be simply extracted from plants. Although previous works have improved the design of new chemicals in terms of the selectivity or detection limit of metal ion determination [20–24], simultaneous detection by naked-eye method was not widely reported, especially of both qualitative and quantitative determinations. There are many advantages of simultaneous detection by naked-eye such as rapid, sensitive, inexpensive and realtime on-sight analysis. Besides that, the intricate mathematical system is not required. Cyanidin was proposed to use as a primary screen for identifying the quality of various aqueous samples. Some chemical sensors have no need to be highly selective, but should be semiselective and could discriminate many analytes [25]. To date, few metal ions could be simultaneously identified by naked-eye detection [23,26–28]. However, such ions must be determined individually [23,26] or with complicated methods such as using first-derivative method to eliminate interfering effect [27], resulting in complicate experiments.

This research focused on developing the simple method for simultaneous detection of 4 metal ions (Cu(II), Pb(II), Al(III) and Fe(III)) in terms of qualitative and quantitative determinations using cyanidin extracted from red cabbage as a selective chelating agent. Red cabbage is the best choice because it is a Thai local plant growing all year long. Naked-eye detection was the proposed method carried out along with the instrumentation in this research. Advantages of this development were simplicity, rapidity, low cost, no requirement of sample preparation, and environmental friendly detection.

Experimental

Instrumentation

The UV–Visible spectrophotometer of HP 8453 Hewlett Packard was used for all spectrophotometric measurements. For evaluation of this method, metal ion concentration was compared with inductively coupled plasma (iCAP 600 SERIES). Mass spectrometer (Micromass platform II) in MALDI-TOF mode was used for collecting mass spectra of the extract. ^{1}H NMR spectrometer (Bruker with 400 MHz) was used to confirm the structure of cyanidin.

Chemicals and solutions

All chemicals used in this research were analytical reagent grade. Methanol and 2 M of hydrochloric acid were used for extracting cyanidin from red cabbage. Stock solutions of Cu(II), Pb(II), Cr(III), Cd(II), Ni(II), Zn(II), Co(II) and Mn(II) were prepared by dissolving an appropriate amount of analytical reagent grade metal nitrate-salt in milli-Q water. For Fe(III) and Al(III) stock standard solution were prepared from $FeCl_3$ and $AlCl_3$, respectively. The working solutions of metal ions were obtained by diluting the stock solution with milli-Q water. Buffer solutions (0.01 M) pH in the range of 3–6 and 7 were prepared from acetate and phosphate buffer, respectively. Potassium fluoride (KF, 0.1 M) and dimethylglyoxime (DMG, 1% w/v) were used as masking agents for Al(III) and Cu(II), respectively.

Extraction and characterization

Cyanidin was extracted by a slightly modified process of anthocyanin extraction reported by Ukwueze et al. [13]. Red cabbage bought from a local market was cleaned in deionized-water and sliced to small pieces. Then, it was weighed to 270 g before soaking in 600 mL of the mixed solution of MeOH and 2 M HCl (85:15 v/v). Extraction was carried out in a refrigerator for 72 h. The reddish extract was filtered and removed other non-polar molecule using chloroform. The solvent was then evaporated (temp < 38 °C). Concentrated HCl was added into the concentrated anthocyanin solution then refluxed until the deep-red violet solution appeared. The extract was immediately poured and placed in the refrigerator until dark brown powder of cyanidin chloride precipitated. The powder was filtered and dried in a desiccator. Then it was purified through Sephadex LH-20 using methanol as eluent. Anthocyanins were characterized by UV–vis spectrophotometry, NMR and mass spectrometry. Shinoda's method [29] was used to check the flavonoid property by adding a piece of magnesium ribbon and 1 mL of concentrated HCl into 2–3 mL of methanolic extract (pink red or red coloration appeared after a few minutes).

Preparation of standard cyanidin solution

Extracted cyanidin (1.6 mg) was dissolved in 5 mL of methanol. The solution was left to equilibrium for 1 h in a refrigerator. The solution should be freshly prepared before use. The pH of cyanidin solutions was adjusted in a buffer solution.

Optimum conditions for determination of metal ions

Since the pH of the solution effected the cyanidin formation, cyanidin standard solution was prepared in methanol and adjusted to pH 2–7 with the buffer solution. Each metal ion in the concentration of 1000 μM was prepared in milli-Q water before adding to cyanidin solutions. To find out the optimum conditions for determination of metal ions, both concentration and ratio volume of cyanidin, buffer and metal ion were investigated. Masking agents were also studied to ensure that the interferences do not effect in any metal ion determination steps.

Quantitative determination of metal ions

The calibrated quantitative solutions were prepared by adding 1.0 mL of the buffer solution and 0.1 mL of a masking agent into a 0.1 mL of sample solution (10–1000 μM) followed by 0.1 mL of cyanidin solution. In case of Cu(II), Pb(II), Fe(III) and Al(III) detection, buffer pH 7, pH 6, pH 4 and pH 5, respectively were used. Masking agents, KF, DMG and the mixture of KF and DMG was used for Fe(III), Al(III) and Pb(II) detection, respectively.