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Determination of Manganese (II) in Foodstuffs by β-Cyclodextrin Polymer Phase Spectrophotometry with 1-(2-Pyridylazo)-2-naphthol

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The chromogenic agent, 1-(2-pyridylazo)-2-naphthol (PAN) was included in β-Cyclodextrin polymer (β-CDP) and the modified polymer of inclusion of PAN (β-CDP-PAN) was obtained. Based on the fact that β-CDP-PAN can adsorb Mn (II) in solution to form Mn (II)-PAN complex, a sensitive and selective solid phase spectrophotometric method for the determination of trace amounts of Mn (II) has been developed. The maximum absorbance of Mn (II)-PAN complex in β-CDP was at 514 nm. The working range of the calibration graph was 2–12 μg of Mn (II). The interference of molybdenum, lead, cobalt, chromium, iron, nickel, zinc, tin, cadmium, and copper that form colored species with PAN in the polymer phase was investigated. The method was applied to the determination of Mn (II) in black rice and tea samples.

A new method for the determination of trace amounts of manganese by polymer phase spectrophotometry is described. Manganese reacted with 1-(2-pyridylazo)-2-naphthol (PAN) that was included in a β-cyclodextrin polymer. The absorbance of the colored polymer, packed into a 5 mm quartz cell, was determined directly at 514 nm. The proposed method was applied to the determination of manganese in black rice and tea samples.

Keywords: β-Cyclodextrin polymer; Polymer phase spectrophotometry; Manganese; PAN

INTRODUCTION

β-Cyclodextrin (β-CD) is a very stable oligosaccharide that is composed of seven glucose units. It can form the supramolecular complexes with several organic compounds by incorporating them into the hydrophobic cavities of β-CD. β-Cyclodextrin polymer (β-CDP) that was synthesized using epoxy chloropropane as a cross-linking reagent [1], still retains the inclusion property of β-CD. β-CDP used in present investigation is a transparent, colorless solid and is insoluble in aqueous solutions. Its cavities are fairly hydrophobic and can be applied to include organic compounds that contain the hydrophobic aromatic group to form the supramolecular complexes. A few applications of β-CDP have been reported in the previous studies [2–7].

Manganese is a component of several enzyme systems and is essential for normal bone structure. Intake varies greatly, depending mainly on the consumption of rich sources, such as unrefined cereals, green leafy vegetables, and tea. The usual intake of this mineral is 2–5 mg day^{-1}, and absorption is 5–10%. Different techniques have been proposed for the determination of manganese. Mn (II) has been determined by atomic absorption spectrometry (AAS) [8–12], electrothermal AAS [13,14], and graphite furnace AAS [15,16]. Extraction-spectrophotometry procedures have also been reported [17–20]. Moreover, flow injection spectrophotometric catalytic determination of manganese has been described [21,22]. In addition, others such as the electrochemical method [23], the radiochemical method [24], the catalytic kinetic method, [25,26] and the ion chromatography [27] have been recently developed. Conventionally, AAS has more sensitivity, selectivity, and lower detective limitation, but a more expensive instrument is needed in the

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method. Some of the above-mentioned, especially extraction-spectrophotometry, have often shown low sensitivity and selectivity [28,29], low stability of the complex obtained and a troublesome procedure of pre-concentration [28,30].

In present work, the azoic chromogenic agent, 1-(2-pyridylazo)-2-naphthol (PAN), which may form complexes of very high absorptivity with many kinds of metal ions and has been used for spectrophotometric analysis [31–33], is irreversibly included or adsorbed in β-CDP to form the modified polymer of inclusion of PAN (β-CDP-PAN) and develops a colored complex with a trace amount of manganese in the polymer phase. A new kind of solid phase spectrophotometry that used β-CDP as a support has been developed. This method has shown several important advantages such as the sensitivity and selectivity are much higher than those of the conventional spectrophotometry, low interference level, the use of conventional instrumentation and the concentration and color development for the metal ion took place simultaneously. Solid phase spectrophotometry used β-CDP seems to be an excellent and useful technique for determination of trace amounts of constituents. This paper describes a procedure for β-CDP polymer phase spectrophotometry and the trace amounts of manganese in black rice and tea samples are determined with PAN and a 5 mm quartz cell.

RESULTS AND DISCUSSION

Effect of PH-values on Preparation of β-CDP-PAN

The results are shown in Fig. 1. Thus, it can be seen that the *Q* was essentially constant between pH of 4.0 and 9.0. Therefore, pH-value in the range of 4.0–9.0 was selected for preparation of β-CDP-PAN procedure.

Molar Ratio of Manganese to PAN in the Polymer Phase

β-CDP-PAN used for analysis contains 5.5 μmol of PAN per gram. In the polymer phase, the molar ratio of manganese to PAN in the supramolecular complex was found to be 1:2 that is identical with that observed in solution. From this result, we may suppose that the whole molecule of PAN is not resided in the cavity of β-CD, only one group of the molecule, such as a pyridine ring.

Conditions for Measurement of Manganese (II)

Absorption Spectra

The absorption spectra of PAN and its manganese complex in the polymer phase are shown in Fig. 2.

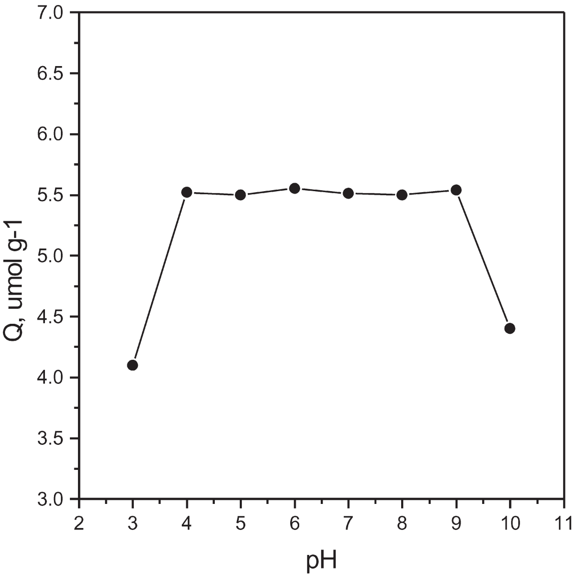

FIGURE 1 Effect of pH on preparation of β-CDP-PAN. The ionic strength, 0.1 mol l^{-1}; PAN, 1.0 × 10^{-4} mol l^{-1}; solution volume, 25 ml; shaking time,120 min; β-CDP, 0.5 g.

Maximum absorbance of manganese-PAN complex was at 514 nm in the polymer phase and at 535 nm in solution phase. Maximum absorbance in the polymer phase moved 21 nm toward the shorter wavelength region than that in solution phase. Moreover, maximum absorbance of PAN was at 472 nm in the polymer phase and at 468 nm in solution phase. Maximum absorbance in the polymer phase moved 4 nm toward the longer wavelength region than that in solution phase. Each

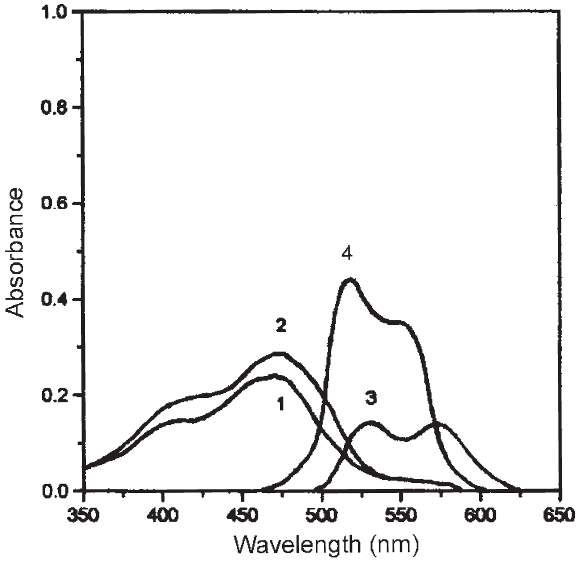

FIGURE 2 Absorption spectra of PAN and its manganese complex in β-CDP. Solution volume: 25 ml; PAN, 1.0 × 10^{-4} mol l^{-1}; pH, 9.0; Mn(II), 8 μg; β-CDP, 0.5 g; (1) PAN in solution; (2) PAN, in the polymer; (3) Mn(II)-PAN, in solution; (4) Mn(II)-PAN in β-CDP.

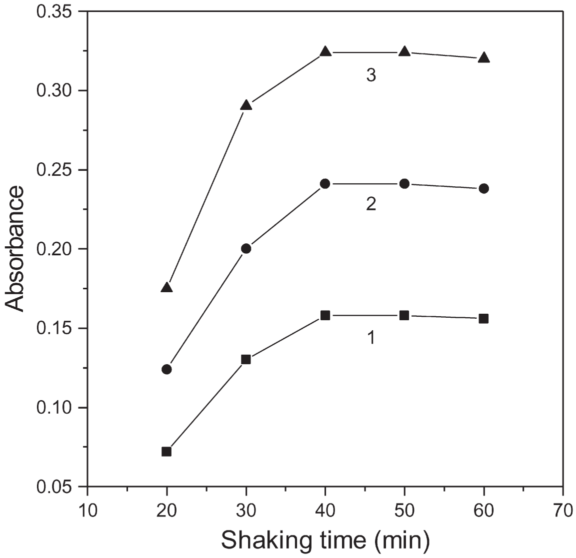

FIGURE 3 Effect of shaking time on β-CDP-PAN adsorbing manganese(II). Solution volume, 25 ml; pH, 9.0; β-CDP-PAN (60–80 mesh), 0.5 g; Mn (II): (1) 4 μg; (2) 6 μg; (3) 8 μg.

spectrum in the polymer phase is similar to that observed in solution.

Effect of Shaking Time on β-CDP-PAN Adsorbing Manganese (II)

In general solid-phase extractions, in order to adsorb the analytes on the solid adsorbent, the solution sample was often stirred with the adsorbent for a fixed time. In this work, shaking was adopted instead of stirring. In such conditions, no destruction of the polymer particles occurred, but often observed when stirred rapidly. The shaking time that required for attaining the adsorption equilibrium depended on the volume of the sample solution. Almost all the manganese (II) in a 25 ml sample solution was adsorbed on β-CDP-PAN within 40 min as shown in Fig. 3 and a 250 ml within 60 min by shaking.

Effect of PH-value on β-CDP-PAN Adsorbing Manganese (II)

The color of the manganese complex had a maximum intensity for pH-values in the range of 8.0–10.0. The results are the same as in solution. Furthermore, the β-CDP-PAN had a maximum stability for pH-values in the range of 4.0–9.0. For the reasons given the pH-value of 9.0 was selected for analysis.

Calibration

The calibration curve was reasonably linear and might be expressed by the equation:

$$A_{(\lambda,514\,\mathrm{nm})} = 0.0417X(\mu\mathrm{g}) - 0.0097, R = 0.9987,$$

$$N = 6$$

where X is the weight of manganese in the sample solutions of 25 or 250 ml, A is the absorbance of the sample solutions, R is the correlation coefficient and N is the number of the dependent variable data point used to derive regression.

Sensitivity

The sensitivity for the system had been compared with that of the conventional spectrophotometric method [33,35]. The sensitivity was 50 times as high as that of the previous method [33,35] with a 25 ml sample solution, and 498 times with a 250 ml sample solution which contain 8 μg of manganese (II).

The results of Chiswell *et al.* [18] indicated that the precision and accuracy of PAN method in the solution phase were poor over the manganese concentration range of $0-100\,\mu\mathrm{g\,l}^{-1}$ with an average error of 11% for a set of 10 samples containing a known manganese concentration. Their results suggest that the method is useless for low manganese concentration. For the $100-1000\,\mu\,\mathrm{l}^{-1}$ ranges, better linearity was obtained and the average

TABLE I Effect of foreign ions on determination of 8 μg manganese (solution volume, 25 ml)

Foreign ions	Weight-ratio of Mn to foreign ion	Mn found (μg)	Relative error (%)
Cu^{2+}	1:125	8.22	2.75
Pb^{2+}	1:15	8.16	2.00
Cr^{3+}	1:125	8.10	1.25
Co^{2+}	1:50	7.83	−2.13
Fe^{3+}	1:20	8.03	0.38
	1:100	8.38	4.75
Ni^{2+}	1:125	8.27	3.38
Cd^{2+}	1:125	8.41	5.13
Sn^{4+}	1:125	7.66	−4.25
Zn^{2+}	1:10	8.15	1.88
	1:100	8.45	5.63
Mo^{2+}	1:20	8.04	0.50

TABLE II Trace amounts of manganese in black rice and tea samples

Samples	Mn found* (μg g^{-1})		Mn added† (μg)	Recovery (%)
	Present method	AAS		
Black rice 1	14.8	15.3	3.0	93.12
Black rice 2	17.6	17.4	3.0	92.11
Black rice 3	15.1	14.9	3.0	97.45
Tea 1	251.7	249.5	3.0	103.73
Tea 2	270.5	273.1	3.0	97.89
Tea 3	312.0	310.6	3.0	96.68

* Average of three determinations. †In 25 ml of sample solutions.

error for known manganese concentration being 7.2%, but even at these concentrations such a large error makes the PAN method unacceptable in solution.

Effect of Foreign Ions

The effect of foreign ions was examined and the results obtained are shown in Table I. Metals did not interfere except for molybdenum, lead, cobalt, chromium, iron, nickel, zinc, tin, cadmium, and copper. The results of experiments showed that molybdenum (at the 6.6708×10^{-6} mol l^{-1} level), lead (at the 9.2664×10^{-7} mol l^{-1} level), cobalt (at the 2.7151×10^{-4} mol l^{-1} level) and chromium (at the 3.8461×10^{-3} mol l^{-1} level) could be masked with 2.4×10^{-2} mol l^{-1} sodium fluoride solution. Nickel (at the 6.8156×10^{-5} mol l^{-1} level) could be masked with 4.0×10^{-2} mol l^{-1} sodium mercaptoacetate solution. Zinc (at the 4.8937×10^{-5} mol l^{-1} level), tin (at the 3.3698×10^{-4} mol l^{-1} level), cadmium (at the 3.5588×10^{-4} mol l^{-1} level) and copper (at the 6.2944×10^{-4} mol l^{-1} level) could be masked with 3.2×10^{-3} mol l^{-1} potassium cyanide solution. The interference of iron (at the 5.7296×10^{-4} mol l^{-1} level) could be eliminated by 1.6×10^{-2} mol l^{-1} pyrogallic acid solution.

Determination of Manganese in Black Rice and Tea Samples

The proposed method was applied to the determination of manganese in some black rice and tea samples. The results are given in Table II. The manganese content in three different black rice samples obtained from different regions was in the range of 14.8–17.6 μg g^{-1} and in three different tea samples purchased from the local market was in the range of 251.7–312.0 μg g^{-1}. The recovery of manganese added is in the range of 92.1–103.7%. As can be seen, the developed method is very sensitive and selective.

EXPERIMENTAL

Apparatus

A spectrophotometer fitted with matched 5 and 10 mm quartz cell, model Shimadzu UV-240 (Shimadzu, Japan), was used to measure the absorbance and spectra. In order to release the solution in the developed color polymer that was packed into a sample cell, a small hole was made at the bottom of 5 mm quartz cell by an emery wheel before use. A pH-meter, model Tianjin pHs-2C (Tianjin No. 2 Analytical Instruments, China), was used to measure pH. A thermostatic shaker, model Peking SHZ-2 (Peking Medical Apparatus and Instruments, China) was used to perform all inclusion procedures.

Reagents

All chemicals used were of analytical reagent grade. Prior to use, deionized water was distilled and used throughout.

Manganese (II) standard solution was prepared by dissolving 0.1 g of manganese in 10 ml of sulfuric acid (~50%) and making upto 1 l to give a 100 μg ml^{-1} standard stock solution. Working standard solutions containing 5 and 10 μg ml^{-1} manganese (II) were prepared from the stock solution by appropriate dilutions.

PAN solution in ethanol was prepared by dissolving an appropriate amount of PAN in 95% ethanol to give a 1.0×10^{-4} mol l^{-1} solution.

β-CDP was synthesized as described earlier [1]. Before use, the polymer was first ground and sieved into 40–60, 60–80, 80–100 and over 100 mesh fractions. Each of these was immersed in redistilled water to remove the remaining metal ions. Then they were dried under vacuum and kept in a desiccator. The 60–80 mesh fraction was used in our experiment.

Buffer solutions used for pH-values in the range of 1.0–12.0 were prepared by mixing sodium citrate and hydrochloric acid solutions for pH-values in the range of 1.0–4.0, by mixing acetic acid and sodium acetate solutions for pH-values in the range of 4.0–6.5 and by mixing sodium hydroxide and potassium dihydrogen phosphate solutions for pH-values in the range of 6.5–12.0.

The masking solutions used for molybdenum, lead, cobalt, chromium, iron, nickel, zinc, tin, cadmium, and copper were 0.6 mol l^{-1} sodium fluoride solution [34], 0.1 mol l^{-1} sodium mercaptoacetate solution, 0.08 mol l^{-1} potassium cyanide solution [18,33,35], and 0.4 mol l^{-1} pyrogallic acid solution [36], respectively.

Procedure

Preparation of β-CDP-PAN

β-CDP (60–80 mesh) with a pH 8.0 of PAN solution was shaken mechanically for 120 min at room temperature (25°C). The polymer was filtered off, washed with redistilled water, dried under vacuum, and kept out of light in a desiccator. In order to determine the amount of PAN in β-CDP-PAN, the amount of PAN in supernatant solution was determined by the measurement of its absorbance with 10 mm cell at 468 nm (the absorption maximum of PAN in the solution) against a reference blank solution that did not contain PAN. The inclusive quantity (Q) was calculated as following:

$$Q = \{[G]_0 - [G]_{eq}\}V/m$$

where $[G]_0$ is the initial concentration of PAN, $[G]_{eq}$ is the equilibrium concentration of PAN, m is the weight of β-CDP used and V is the volume of solution.

Determination of the Molar Ratio of Manganese to PAN in the Polymer Phase

To a 50 ml stoppered conical flask, 0.1 g of β-CDP-PAN and 10.0 ml of buffer solution (pH 9.0) were added. The mixture was allowed to stand for approximately 15 min and then 5.0 ml of manganese (II) solution (10 μg ml^{-1}) was added and made upto 25 ml with redistilled water. After the mixture was shaken mechanically for 40 min, 5.0 ml of the colorless supernatant solution was transferred into a 10 ml volumetric flask, then 1.0 ml of buffer solution and 3.0 ml of PAN solution were added and made upto the mark with redistilled water and mixed well. The absorbance was measured with a 10 mm cell at 540 nm (the absorption maximum of manganese-PAN complex in the solution) against a reference blank solution that did not contain manganese. The molar ratio of manganese to PAN in the polymer phase was calculated.

Determination of Manganese

To a 50 ml volumetric flask, 0.5 g of β-CDP-PAN and 10.0 ml of buffer solution (pH 9.0) were added. The mixture was allowed to stand for approximately 15 min and then 2.0 ml of manganese (II) solution (5 μg ml^{-1}) was added and diluted to 25 ml with redistilled water. After the mixture was shaken mechanically for 40 min, the colored polymer was transferred into a 5 mm quartz cell. The absorbance was measured at 514 nm (the absorption maximum of manganese-PAN complex species in the polymer phase) against a β-CDP-PAN blank as a reference.

Determination of Manganese in Black Rice and Tea Samples

Black rice (5.0 g), or tea (1.5 g) was reduced to ashes using a general method [37]. The ash samples were dissolved by dilute nitric acid and filtered into a 25 ml or a 100 ml volumetric flask, respectively, and made upto the mark with redistilled water. A 2 ml aliquot of the sample was transferred into a 50 ml stoppered conical flask, and pH-value of the solution was adjusted to 9.0 with dilute sodium hydroxide. Then 0.5 g of β-CDP-PAN, 10.0 ml of buffer solution (pH 9.0), 1.0 ml of 0.6 mol l^{-1} sodium fluoride, 1.0 ml of 0.1 mol l^{-1} sodium mercaptoacetate, 1.0 ml of 0.08 mol l^{-1} potassium cyanide and 1.0 ml of 0.4 mol l^{-1} pyrogallic acid solutions were added, respectively. After 15 min, the mixture was diluted to 25 ml with redistilled water and shaken mechanically for 40 min. The absorbance was determined as described above.

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