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Two sensitive fluorescence methods for the determination of cobaltous in food and hair samples

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Abstract

Fluorescence reactions among Co(II), with two new 8-sulfonamidoquinoline derivatives, 5-(4-chlorophenylazo)-8-(benzenesulfonamido)quinoline (CPBSQ), and 5-(3-fluo-4-chlorophenylazo)-8-(benzenesulfonamido)quinoline (FCPBSQ), and H_2O_2 were investigated. CPBSQ or FCPBSQ reacted with cobalt(II) in the presence of H_2O_2, and basic medium forming a chelate, which exhibited intensive fluorescence in ultraviolet region. The fluorescence intensities were proportional to the concentration of cobalt(II) over the range of 0.1–100 and 0.5–200 μg/l with the detection limits of 0.05 and 0.10 μg/l for CPBSQ and FCPBSQ systems, respectively. A range of metal ions, including Cu(II) and Ni(II) did not interfere with the determinations for both systems. The methods, which are high sensitive and more selective, have been successfully applied to the determination of trace amount of cobalt in food and hair samples.

Keywords: Cobalt; Food; Hair; Spectrofluorimetry; 8-Sulfonamidoquinoline derivatives

1. Introduction

Cobalt plays an important role in the metabolism of iron and synthesis of hemoglobin, and it is also a main composition of Vitamin B_{12} and other biological compounds. Several investigations showed that chronic cobalt-deficiency in humans is one of the main risk factors for cardiovascular disease and vitiligo (Qiu, 1979; Sun, 1984; Zhang, 1996). This has increased the interests in studying cobalt in environmental and food samples. A large number of spectrophotometric methods have been developed for the determination of cobalt (Jin, Zhu, Jiang, Xie & Cheng, 1997; Khambekar & Sawant, 1997; Zeng & Jewsbury, 1998). However, many of these proposed methods are not sensitive enough to determine cobalt in environmental and biological samples (Jin et al., 1997; Khambekar & Sawant; Zeng & Jewsbury). The sensitivity of fluorophotometirc method is much higher than that of spectrophotometric method, but fluorescence reagents and methods suitable for the determination of cobalt are limited (Burns, Hanprasopwattana & Kheawpintong, 1983; Mori, Fujita, Toyoda, Hamada & Akagi, 1992; Zeng & Jewsbury, 1998). All these methods suffer from serious interference from some metal ions, or require extensive using organic solvents.

The derivatives of 8-aminoquinoline, which donate only nitrogen atoms to the metal ions in the complexing process, are more selective reagents for some metal ions compared with the reagents using nitrogen and oxygen, like 8-hydroxylquinoline derivatives, or nitrogen and sulfur, like 8-mercaptoquinoline reagents. However, the proton of amino ($-NH_2$) in quinoline is difficult to dissociate, and the reaction between 8-aminoquinoline and the metal ion is usually slow (Cao, Zhao & Xu, 1993; Ruan & Zu, 1991; Sou, Xu & Zhao, 1990). The acid strength of the sulfonamido group is about the same as a phenolic hydroxyl group, the derivatives of 8-sulfonamidoquinoline can overcome this disadvantage and provide a high selective and rapid analytical method for some metal ions (Billman & Chernin, 1962; Cao, Wang, Hu & Xu, 1998).

In this paper, we report for the first time the application of two new 8-sulfonamidoquinoline derivatives, 5-(4-chlorophenylazo)-8-(benzenesulfonamido)- quinoline (CPBSQ), and 5-(3-fluo-4-chlorophenylazo)-8-(benzenesulfonamido)- quinoline (FCPBSQ), which were synthesized and characterized by ourselves (Cao et al.,

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1998), as fluorescence reagents for the determination of cobalt in the presence of H_2O_2. It was found that both methods are selective, simple and sensitive and have been satisfactorily used for the determination of trace cobalt in food and hair samples.

2. Experimental

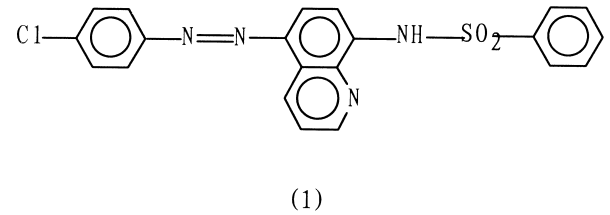
2.1. Apparatus

Fluorescence measurements were performed on a Hitachi M-850 fluorescence spectrometer (Tokyo, Japan) with a 150W Xenon lamp and an 1 cm quartz cell. All of the fluorescence data were given with correction. The pH measurements were made with a model pHs-2 pH meter (Shanghai Analytical Instrument Factory, Shanghai, China).

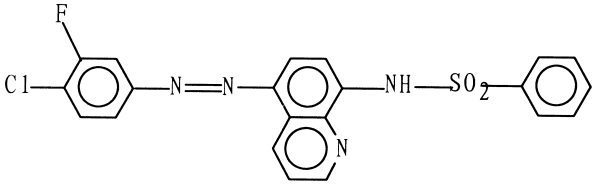
The AAS measurements carried out using a Hitachi 180-80 polarized Zeeman-effect background corrected atomic absorption spectrometer equipped with a Hitachi Model 056 recorder (Tokyo, Japan). The instrumental settings of the spectrometer were: absorption line: 240.7 nm, lamp current: 12.5 mA, slit: 0.2 mm, air pressure: 1.60 kg/cm$_2$, acetylene pressure: 0.35 kg/cm^2, burner height: 5 mm.

2.2. Reagents and chemicals

All chemicals were of analytical reagent grade and obtained from Beijing Chemical Plant (Beijing, China); Double-distilled water was used throughout. CPBSQ and FCPBSQ solutions were 2.0×10^{-4} mol/l in 95% ethanol. Their structures are shown in Fig. 1. Cobalt(II) standard solution, 1.000 mg/ml, was prepared by dissolving 0.10 g of pure cobalt in 10 ml of 1:1 (v/v) nitric acid. The solution was then heated to 60–70°C to remove nitrogen oxide. After cooling, it was transferred to a 100-ml volumetric flask and diluted to volume with water. A working solution of 1.0 mg/l was prepared by diluting the standard solution with water daily. A buffer solution was prepared with 0.1 mol/l $Na_2B_4O_7$ solution and 0.1 mol/l HCl or NaOH solution. Tween-80 and CTAB (Cetyltrimethyl ammmonium bromide) aqueous solution 2.0% (v/v) and H_2O_2 aqueous solution 0.6% (v/v) were used in this work.



(1)



(2)

Fig. 1. The structure of CPBSQ (1) and FCPBSQ (2).

2.3. Procedure for CPBSQ Method

An appropriate amount [contained 0.001–1.0 g Co(II)] of sample solution or standard cobalt(II) solution was transferred to a 10-ml volumetric flask, and the following were added: 2.0 ml CPBSQ solution, 2.0 ml buffer solution (pH = 11.0), 1.0 ml Tween-80 solution and 1.0 ml H_2O_2. The solution was diluted to volume with water and mixed well. The mixture was heated for 6 min on a boiling-water bath, after cooling to room temperature, the fluorescence intensity was measured at 332 nm [excitation (ex)] and 370 nm [emission (em)].

2.4. Procedures for FCPBSQ Method

The procedure for FCPBSQ method is similar as that for CPBSQ method, except that 1.0 ml FCPBSQ solution, 2.0 ml buffer solution (pH 11.0), 2.0 ml CTAB, 1.0 ml H_2O_2 were added and then heated for 5 min in a boiling-water bath. The fluorescence intensity was measured at 326/365 nm (ex/em).

2.5. Determination of cobalt in flour, tea, vegetable, vitamin B_{12} and human hair samples

After 50 g hair sample (obtained from two healthy men living in Lanzhou, China) was washed with water, it was immersed in acetone for 5 min, then washed with water and dried under an infrared lamp.

Twenty-five g of tea (retail casually from Yunnan, China), flour, fresh vegetable (retail casually from Lanzhou, China) and dried hair samples were first carbonized at 250°C, then burned in the muffle furnace at 700°C for 3 h. After the residue was cooled to room temperature, it was extracted by heating in 1.0 ml of 6 mol/l HCl. Then, to precipitate iron and some other metal ions as hydroxide, an excessive amount of $NH_3{\cdot}H_2O$ was added under agitation till the final pH of the solution was 10. The mixture was filtered and the filtrate was heated at 95°C to remove NH_3. The solution was allowed to cool, then diluted to 50 ml with water and analyzed directly.

One g Vitamin B_{12} standard was placed in a flask, 10 ml concentrated nitric acid added, and the mixture was heated gently, and evaporated to nearly dry. The residue was dissolved in water and then transferred to a 50-ml volumetric flask and diluted to volume with water, 1.0 ml of this solution were taken for analysis.

3. Results and discussion

3.1. Fluorescence spectra

The fluorescence intensities of the reagent blanks and the complex systems in the absence of H_2O_2 were all very low, but the fluorescence intensities of the Co(II)–CPBSQ and Co(II)-FCPBSQ complex systems could be enhanced remarkably by H_2O_2. The presence of H_2O_2 did not affect the fluorescence intensity of the reagent blanks. The fluorescence spectra of the reagent blanks and the corresponding complex systems in the presence of H_2O_2 are shown in Fig. 2. The maximum excitation and emission wavelengths of the reagent blanks and the corresponding complexes in the presence of H_2O_2 were as follows: 330/375 nm (ex/em) and 326/365 nm (ex/em) for FCPBSQ and its complex, and 330/390 nm (ex/em) and 332/370 nm (ex/em) for CPBSQ and its complex, respectively.

3.2. Effect of acidity

Intensive fluorescence of the two systems could be obtained only in the basic medium. In the acid medium, the fluorescence intensities of them were very low. The optimum pH ranges for the CPBSQ and FCPBSQ systems were found over 10.0–11.5 and 9.0–12.0, respectively. Thus, further work was carried out at pH 11.0, obtained with a $Na_2B_4O_7$–NaOH buffer solution, for both systems.

3.3. Effects of reagent concentration

Fig. 3 showed the effects of reagent concentration on the fluorescence intensity of the two systems. It could be seen that the optimum concentration ranges of reagents were as follows: $(3.0–8.0)\times10^{-5}$ mol/l CPBSQ and $(2.5–7.0)\times10^{-5}$ mol/l FCPBSQ. Therefore, 4.0×10^{-5} mol/l CPBSQ and 5.0×10^{-5} mol/l FCPBSQ were selected.

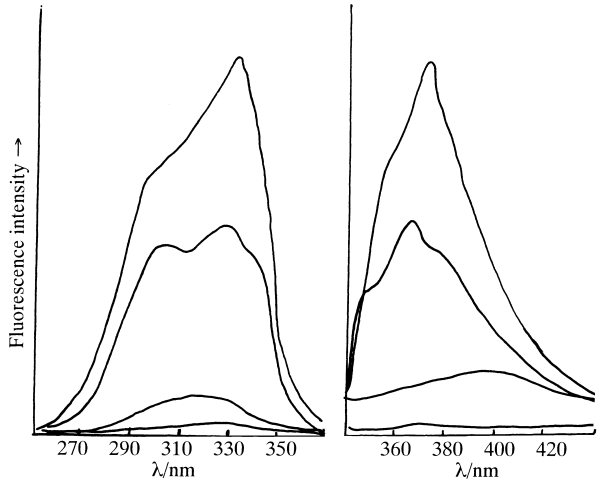


Fig. 2. The excitation (left) and emission (right) spectra of the complexes and reagent blanks in the presence of H_2O_2. From bottom to top: FCPBSQ, CPBSQ, FCPBSQ–H_2O_2–Co(II), FCPBSQ–H_2O_2–Co(II) [the concentration of Co(II) in both the systems were 50 μg/l].

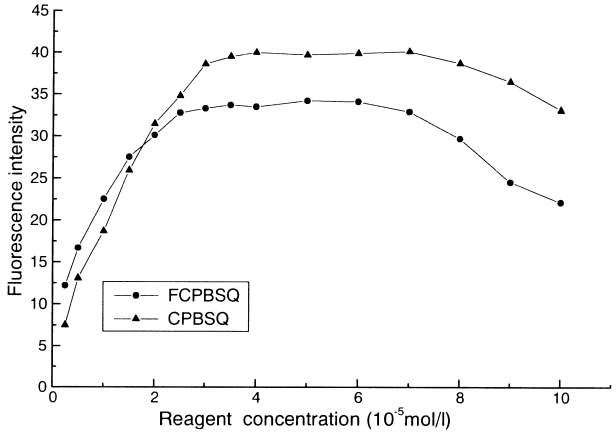


Fig. 3. The effect of the reagent concentration on the fluorescence intensity [the concentration of Co(II) was 100 μg/l for FCPBSQ and 50 μg/ml for CPBSQ, respectively].

3.4. Effect of surfactant

The water solubility of the complexes of the two systems was poor. They precipitated out of aqueous solution in the absence of a surfactant, the presence of a nonionic or a cationic surfactant, such as emulsifying agent OP, poly(vinyl alcohol) (PVA), Triton X-100, Tween-80, Tween-60, Tween-20, arabic gum or cetyltrimethyl ammmonium bromide (CTAB), could improve the solubility and increase the fluorescence intensities of both the systems remarkably. The suitable additive for CPBSQ system was found to be Tween-80 and for FCPBSQ system was CTAB. The concentration of Tween-80 between 0.10 and 0.60% and CTAB between 0.3 and 1.2% gave optimum results for CPBSQ and FCPBSQ systems. Thus 0.20% of Tween-80 and 0.40% of CTAB were selected for the two systems, respectively.

3.5. Effect of H_2O_2

The fluorescence intensities of both complex systems were very low in the absence of H_2O_2, and could be enhanced remarkably by H_2O_2 while the addition of H_2O_2 did not affect the fluorescence intensity of the two blank systems. The fluorescence intensity of the complex systems increased proportionally with the concentration of H_2O_2 in the concentration range of 0.0–0.06%. The maximum and constant fluorescence intensities for the two systems were obtained above 0.06% H_2O_2, and 0.09% H_2O_2 was used for two systems, respectively.

3.6. Effect of heating time

The complexes of cobalt with two reagents were difficult to form at room temperature. The fluorescence

intensities reached maximum by heating on a boiling-water bath for at least 5 min for CPBSQ system and 3 min for FCPBSQ system. Hence 6 and 5 min were selected for both the systems, respectively. When the maximum fluorescence intensity of the systems were reached, its intensities remained constant at least 12 h at room temperature.

3.7. Effect of foreign ions

The effects of foreign ions on the determination of 0.5 μg Co(II) in CPBSQ system and 1.0 μg of Co(II) in FCPBSQ system are shown in Table 1. The tolerance limit was taken as the maximum concentration of the foreign ions causing a ±5% error in the determination. For both the systems, several foreign ions did not interfere at 10–1000-fold concentration of Co(II). Main interference for the two systems were found from Fe(III), which could be removed by adding excessive amount of $NH_3{\cdot}H_2O$ followed precipitation as hydroxide.

Table 1
Tolerance limits of the foreign ions (μg) in the determination of 0.5 μg Co(II) (for CPBSQ system) and 1.0 μg Co(II) (for FCPBSQ system)

Ions added	CPBSQ	FCPBSQ
Ca^{II}, Mg^{II}, Li^{I}, F^-, Br^-, NO_3^-, NH_4^+, ClO_4^-	1000	1000
NO_2^-, IO_4^-, WO_4^-, Cd^{II}	150	200
Al^{III}, VO_3^-, MoO_4^-, $Cr_2O_7^-$, SiO_3^{2-}	100	100
$C_2O_4^{2-}$, SCN^-, Zn^{II}	100	50
Mn^{II}, Sn^{II}	40	25
Th^{III}, Hg^{II}, Ir^{III}, Tl^{III}, Pb^{II}	20	20
Sb^{III}, Bi^{III}	10	20
Cu^{II}, Ni^{II}, Pd^{II}, Ag^+, Pt^{II}, Au^{III}	10	10
Fe^{III}	5 (200[a])	8 (200[a])

[a] After removal as described in the text.

3.8. Calibration graph

The calibration graphs for the two systems were investigated under the optimum conditions described above. The results were shown in Table 2. It could be seen from the results that the two methods were of high sensitivity and precision.

3.9. Composition of the complexes

To study the molar ratio of cobalt to H_2O_2 in the presence of surfactant in the two systems, H_2O_2 was firstly added to the Co(II) solution to oxidize Co(II) to Co(III). After excessive H_2O_2 was removed by heating the solution to dryness, the Logarithm method (Hu, 1981) was then used to determine the molar ratio of $Co:R:H_2O_2$. The results showed that the molar ratio of $Co:R:H_2O_2$ was 1:2:1 for the two systems, which agreed well with the result obtained from the IR spectra of the Co(II)–R–H_2O_2. The vibration bands of $\nu_{O\text{–}O}$ at about 1130 cm^{-1} in the IR spectra of them also suggested the

Table 2
Analytical characteristics for the two systems

Method	Linear regression equation[a]	r	Linear range (μg/l)	LOD[b] (μg/l)	RSD[c] (%)
FCPBSQ	$F = 2.946 + 29.826C$	0.9989	0.5–200	0.10	1.67
CPBSQ	$F = 0.882 + 75.518C$	0.9992	0.1–100	0.05	2.01

[a] F is relative fluorescence intensity and C is concentration of Co(II) expressed as μg/10 ml.
[b] Limit of detection, calculated from 3×9 blank determinations.
[c] Relative standard deviation for the determination of 1.0 μg/10 ml and 0.5 μg/10 ml of Co(II) by the FCPBSQ and CPBSQ systems, respectively.

Table 3
Determination of cobalt in the real samples

Samples[a]	AAS method	CPBSQ method			FCPBSQ method		
	(μg/g)	Found (μg/g)	RSD (%) ($n = 5$)	Recovery (%)	Found (μg/g)	RSD (%) ($n = 5$)	Recovery (%)
Vitamin B_{12} (990203)	42.8	42.4	1.80	98	41.9	2.10	101
Vitamin B_{12} (960801)	42.1	41.2	1.19	96	41.6	1.41	98
Spinach	3.10	3.01	2.53	104	3.05	2.56	102
Swamp cabbage	2.35	2.41	2.74	106	2.43	2.05	93
Human-hairI	1.75	1.72	2.96	104	1.69	1.96	102
Human-hairII	2.90	2.93	3.01	105	3.00	1.83	97
Flour	1.85	1.75	1.79	93	1.83	2.01	96
Tea	2.17	2.10	2.54	107	2.02	2.34	104

[a] The vitamin B_{12} standard were purchased from Lanzhou Medicinal Plant, the standard value provided by the plant is 43.0 μg/g.

1:1 coordination ratio of cobalt to H_2O_2 (Nakamoto, 1978). The same result was obtained from Job's method of continuous variation and the molar ratio method (Hu & Zhao, 1981).

3.10. Applications

The two methods were applied for the determination of cobalt in Vitamin B_{12} standard, hair and food samples. The results are given in Table 3, The result from the two methods agreed well with the AAS data.

4. Conclusion

The comparison of the CPBSQ and FCPBSQ methods with some other fluorescence methods for the determination of Co(II) indicated that the new reagents and methods have advantages over existing reagents and methods for the fluorescence determination of Co(II). The main advantage of both methods is that they are free of interfere of Cr(III), Cu(II) and Ni(II) while most of the existing methods for Co(II) suffer from interference from metal ions (Burns, 1983; Mori et al., 1992; Zeng & Jewsbury, 1998). Both methods can be directly used for the determination of cobalt in biological and environmental samples without a complex preseparation process, indicating a wide applicability of the new methods compared to existing procedures.

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