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PRECONCENTRATION OF 1-(2-PYRIDYLAZO)-2-NAPHTHOL–IRON(III)–CAPRIQUAT ON A MEMBRANE FILTER, AND THIRD-DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF IRON(III)

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Summary—Iron(III) was preconcentrated by collection on an organic solvent–soluble membrane filter (nitrocellulose (NC)) of the iron(III)–1-(2-pyridylazo)-2-naphthol (PAN) complex in the presence of capriquat as an oily quaternary ammonium salt. Third-derivative spectrophotometry was used for measurement of the third-derivative distance ($d^3A/d\lambda^3$) between $\lambda_1 = 520$ nm and $\lambda_2 = 590$ nm or $\lambda_3 = 660$ nm and $\lambda_4 = 724$ nm of the iron(III)–PAN–capriquat complex or PAN–capriquat in dimethylsulfoxide (DMSO) following preconcentration. The calibration curve was linear in the range of 1–10 μg iron(III)/5.0 ml DMSO solution. The proposed method was about five-fold more sensitive and more selective than using zero-order spectrophotometry.

Recently, preconcentration of complex species using a membrane filter has been used as an alternative to organic solvent extraction; the method is based on the collection on a membrane filter of associated complexes such as Malachite green–phosphate, tetrachlorofluorescein–palladium(II)–papaverine, *etc.*[1–5] Also, second- and third-derivative spectrophotometry in certain cases, has been noted to be sensitive, and selective in comparison with classical zero-order spectrophotometry.[6–9] Although numerous zero-order or second-derivative spectrophotometric methods for various metal ions such as nickel(II), zinc(II), indium(III), copper(II), palladium(II), cobalt(II), iron(III)[10–16] have been reported with 1-2-(pyridylazo)-2-naphthol (PAN) as reagent, the filter preconcentration technique for the collection of the PAN–iron(III) complex and the third-derivative spectrophotometry of this complex have not been investigated. In this paper, with a view to obtaining more selective and sensitive spectrophotometric measurement of iron(III), we have systematically investigated this methodology.

EXPERIMENTAL

Apparatus and reagents

The zero-order and third-derivative absorption spectra were recorded on a Shimadzu UV 160 spectrophotometer ($N = 9$) with 1.0-cm cells. A Toyo TM 3 membrane filter (nitrocellulose (NC), 25 mm in diameter, 0.3 μm pore size) and Toyo KGS-25 filter holder were used for preconcentration.

All materials and reagents were of analytical grade and were used without further purification. Solutions of $1.0 \times 10^{-3}M$ PAN and $1.0 \times 10^{-2}M$ capriquat were prepared by dissolving PAN and capriquat (trioctylmethyl ammonium chloride, Dojindo Chemical Co., Ltd.) in methanol. Standard $5.0 \times 10^{-4}M$ iron(III) and copper(II) solutions were prepared according to previous reports.[17,18]

Standard procedure

To a sample solution containing 1.0–10.0 μg iron(III) in a 10-ml calibrated flask 3.0 ml each of $1.0 \times 10^{-3}M$ PAN and pH 5.5 buffer solutions (Walpole acetic acid–sodium acetate buffer), and 2.0 ml of $1.0 \times 10^{-2}M$ capriquat solution were added. The mixture was diluted to the mark with water (A-aqueous solution), kept at 60°C for 10 min together with a reference solution (B-aqueous solution, without iron(III)), and cooled to room temperature (10–30°C) for 5 min. The A- and B-aqueous solutions were filtered through the NC membrane filter, and washed with 20 ml water, respectively. After drying with a hot air dryer, these membrane filters were dissolved in 5.0 ml

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of dimethylsulfoxide (DMSO) (A- and B-DMSO solutions). The third-derivative distance ($d^3A/d\lambda^3$) for the A-DMSO solution was measured (1) between λ_1 520 nm and λ_2 590 nm in the absence of copper(II) or (2) between λ_3 660 nm and λ_4 724 nm in the presence of copper(II) against the B-DMSO solution.

RESULTS AND DISCUSSION

Zero-order and third-derivative absorption spectra

Figure 1 shows the third-derivative and zero-order absorption spectra of the PAN–iron(III) DMSO solution against the PAN DMSO solution following preconcentration on the membrane filter of PAN–iron(III)–capriquat complex. As shown in the figure, the third-derivative spectrum of the PAN–iron(III) DMSO solution gave a high, apparent and characteristic signal; three peaks, $\lambda_1 = 520$ nm, $\lambda_3 = 660$ nm, $\lambda_4 = 724$ nm, one trough, $\lambda_2 = 590$ nm. And the $d^3A/d\lambda^3$ distance between λ_1 and λ_2 was distinguished and remarkable in comparison with the zero-order absorbance, but its $d^3A/d\lambda^3$ value was affected by coexisting foreign ions such as copper(II). Conversely, the $d^3A/d\lambda^3$ distance between $\lambda_3 = 660$ nm and $\lambda_4 = 720$ nm was relatively small, but was scarcely affected by coexisting metal ions such as copper(II).

Accordingly, further investigation was made using the $d^3A/d\lambda^3$ distance between λ_1 and λ_2 in the absence of copper(II), or $d^3A/d\lambda^3$ distance between λ_3 and λ_4 in the presence of copper(II), respectively.

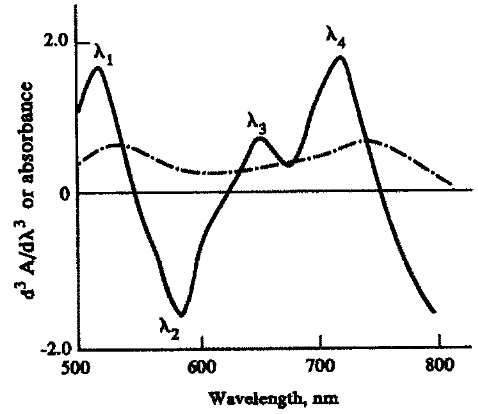

Fig. 1. Zero-order and third-derivative spectra of PAN–iron(III)–capriquat DMSO solution following collection on the NC membrane filter: PAN, $2.0 \times 10^{-4}M$; iron(III), capriquat, $2.0 \times 10^{-3}M$; pH, 5.5; Reference, reagent blank (B-DMSO solution); ——, third-derivative spectrum; —·—·, zero-order spectrum.

Effects of quaternary ammonium salt and pH

In the preconcentration technique following collection on the NC membrane filter, the filtration of the PAN–iron(III) binary complex was incomplete, but that of the PAN–iron(III) ternary complex in the presence of an oil quaternary ammonium salt such as capriquat was quantitative. From this result, the effect of the coexistence of various surfactants (cationic-, anionic-, nonionic-surfactants) were systematically examined, and the coexistence of 1.5–$4.0 \times 10^{-3}M$ capriquat was found most effective as oily quaternary ammonium salt.

The optimum pH for the preconcentration technique was pH 5.3–5.8 for the aqueous phase A- and B-solutions by using Walpole acetate buffer (sodium acetate–acetic acid) solution. Further investigation into the presence of $2.0 \times 10^{-3}M$ capriquat gave an optimum pH of about 5.5 for the aqueous phase solution.

Effects of membrane filter and organic solvent

Membrane filters of different types, diameter, and pore size were investigated: NC, acetylcellulose, pore size (0.20–0.80 μm). The NC membrane filter with 0.3 μm pore size (diameter 25 mm) was most optimum. Also, the dissolving solvent for the membrane filter (following collection of the PAN–iron(III)–capriquat ternary complex) was optimum using 5.0 ml DMSO; tested solvents included DMSO, acetone, methyl–cellulose, and *N,N*-dimethylformamide.

Effect of PAN concentration, temperature, and stability

A stable and constant $d^3A/d\lambda^3$ value between λ_1 and λ_2 was obtained using 2.0–$4.0 \times 10^{-4}M$ PAN. From studies of reaction temperature and reaction time, heating at 60°C for 10 min of the PAN–iron(III)–capriquat aqueous solution before filtration was sufficient. Under these conditions, the $d^3A/d\lambda^3$ value was stable and reproducible. Therefore, the selected colour-forming conditions were $3.0 \times 10^{-4}M$ PAN, heating time for 10 min, and heating temperature 60°C.

Calibration

The calibration graph was prepared according to the standard procedure, and was linear in the range of 1.0–10.0 μg iron(III) in final volume of 5.0 ml DMSO. The precision for 5.0 μg iron(III) per 5 ml DMSO was 1.8% rsd ($N = 5$). The apparent molar absorption coefficient of

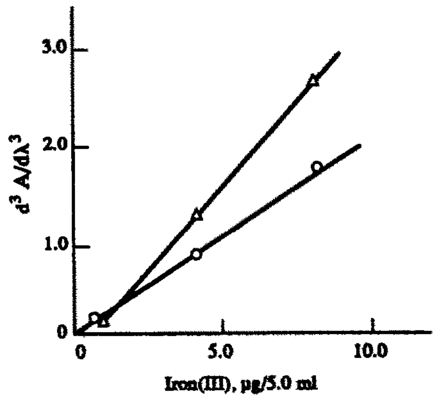

Fig. 2. Calibration curve for iron(III) by third-derivative spectrophotometry: PAN, $3.0 \times 10^{-4} M$; capriquat, $2.0 \times 10^{-3} M$; pH, 5.5; Reference, B-DMSO solution; —△—, $\lambda_1 + \lambda_2$; —○—, $\lambda_3 + \lambda_4$.

iron(III) was 1.7×10^5 l./mol/cm for the third-derivative measurement between λ_1 and λ_2. The proposed method for iron(III) following the preconcentration technique was five times more sensitive than zero-order spectrophotometry.

Interference of foreign ions, alternative assay, and recovery test

The influence of foreign ions on the third-derivative spectrum of the iron(III) complex, using the preconcentration technique, was reduced by about half, in comparison with zero-order spectrophotometry. Results are summarized in Table 1 for the third-derivative measurements. Equal amounts of copper(II) and nickel(II), and 20-fold excess aluminium(III) over iron(III) could be tolerated. As mentioned in the standard procedure, the coexistence of large amounts of copper(II) gave a positive error on the $d^3A/d\lambda^3$ distance between λ_1 and λ_2, but the $d^3A/d\lambda^3$ distance between λ_3 and λ_4 permitted the presence of copper(II) 20-fold excess over iron(III). In addition, the coexistence of aluminium(III) or copper(II) could be masked by addition of $10^{-3} M$ sodium fluoride or sodium citrate in the $d^3A/d\lambda^3$ distance between λ_1 and λ_2, respectively.

Thus, by selection of the analytical wavelengths ($d^3A/d\lambda^3$ distance between λ_3 and λ_4 in the presence of copper(II)) or by addition of masking agent (sodium fluoride or sodium citrate), the alternative and simultaneous assay of iron(III) and copper(II) was feasible.

Recovery tests of 5.0 μg iron(III) in waste artificial water containing iron(III), copper(II), aluminium(III), and calcium(II) (1 (iron(III), 5 μg): 2:20:20 mole ratio) were satisfactory (95.4–106%) by addition of masking agent and measuring the $d^3A/d\lambda^3$ distance between λ_1 and λ_2 or by selection of the distance between λ_3 and λ_4.

Table 1. Effect of foreign ions on third-derivative and zero-order spectra*

Foreign ions	as	Added mole ratio Iron:metal ion	Recovery (%) $d^3A/d\lambda^3$	zero-order
—	—	—	100.0	100.0
Co(II)	Nitrate	1:1	100.0	110.0
Ni(II)	Nitrate	1:1	99.9	112.3
Cu(II)	Sulphate	1:2	110.0	120.4
			100.0†	
			99.5§	
		1:20	102.1†	
Zn(II)	Chloride	1:2	102.2	125.9
Al(III)	Nitrate	1:20	102.3	135.8
		30	99.4‡	
Ca(II)	Chloride	10	100.0	99.8
F^-	Sodium	100	99.6	96.4
Citrate	Sodium	10	100.0	94.2

*Iron(III) taken, 5.0 μg/5.0 ml DMSO; PAN, $3.0 \times 10^{-4} M$; capriquat, $2.0 \times 10^{-3} M$; pH, 5.5; Reference, B-DMSO solution.

†$d^3A/d\lambda^3$ distance between λ_3 and λ_4 instead of λ_1 and λ_2.

‡Addition of sodium fluoride as masking agent, $d^3A/d\lambda^3$ distance between λ_1 and λ_2.

§Addition of sodium citrate as masking agent, $d^3A/d\lambda^3$ distance between λ_1 and λ_2.

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