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Spectrophotometric and Analogue Derivative Spectrophotometric Determination of Chromium(III) with 2-(5-Bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulfopropylamino)phenol

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A sensitive method for the spectrophotometric determination of chromium(III) with 2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulfopropylamino)phenol (5-Br-PAPS) is described. 5-Br-PAPS reacts with chromium(III) to form a 1:2 (metal:ligand) complex in weakly acidic media upon heating at 95 °C. The complex has an absorption maxima at 592 nm and gives a constant absorbance in the pH range of 3.4—6.2. The molar absorptivity and sensitivity for an absorbance of 0.001 are 8.94×10^4 dm^3 mol^{-1} cm^{-1} and 0.58 ng cm^{-2} respectively. The complex, once formed, is not decomposed by the addition of *trans*-1,2-cyclohexanediamine-*N,N,N'N'*-tetraacetic acid (CDTA). Thus, the selectivity of the method can be increased by the use of CDTA as a masking agent. The sensitivity of the method can be increased by employing analogue-derivative spectrophotometry, chromium(III) determination at parts-per-billion levels being feasible.

2-(5-Bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulfopropylamino)phenol (5-Br-PAPS) is a relatively new type of spectrophotometric reagent[1]. It is a water-soluble pyridylazo compound which has been developed by introducing a sulfoalkyl group into the amino group of the mother compound without sacrificing the oridinal spectrophotometric sensitivity. The reagent has the same chelating system as 4-(2-pyridylazo)-resorcinol (PAR), but is more sensitive than PAR for the determination of most metals, having molar absorptivities in the region of 1×10^5 dm^3 mol^{-1} cm^{-1} for several transition-metal complexes. 5-Br-PAPS has been reported to be a spectrophotometric reagent for the determination of zinc(II)[1] and vanadium(V).[2]

In the present work, a sensitive spectrophotometric method for the determination of chromium(III) with 5-Br-PAPS is descrived. The reagent reacts with chromium(III) to form a stable blue complex upon heating at 95 °C. The complex, once formed, is not decomposed by the addition of CDTA, whereas most other metal complexes are readily decomposed by CDTA. The conditions for the color development, the composition of the complex, and the influence of other metal ions are reported. The proposed method is very sensitive and selective for the determination of chromium(III). The sensitivity of the method is comparable to that of the 2-(5-bromo-2-pyridylazo)-5-diethylamino phenol (5-Br-PADAP) method (log $\varepsilon=5.08$)[3],but the former is better in selectivity than the latter because CDTA can be used as the masking agent. The method developed can be made even more sensitive by the use of an analogue derivative spectrophotometric technique.

Experimental

Reagents and Apparatus. The 5-Br-PAPS solution (5×10^{-3} M) was prepared by dissolving 0.120 g of 5-Br-PAPS (Dojindo Co., Ltd., Japan) in 50 cm^3 of water. The solution was stable for one week. The chromium(III) solution (1000 μg cm^{-3}) was prepared by dissolbing 0.500 g of metallic chromium (99.99% pure) in 45 cm^3 of hydrochloric acid by heating on a hotplate, and then by diluting the solution to 500 cm^3 with water. The solution was stable for at least six months. Working solutions were prepared by the dilution of this solution with 0.1 M[†] hydrochloric acid. All reagents were of an analytical-reagent grade, and all solutions were prepared with distilled, deionized water.

A Hitachi 100-10 spectrophotometer and a Hitachi 200-20 recording spectrophotometer were used. To obtain the derivative spectrum, a modified Hitachi 200-0576 derivative unit composed of two analogue-differentiation circuits (each having six different time-constants[4,5] was connected in series between a Hitachi 200-20 recording spectrophotometer's output and a Hitachi 200 recorder's input. Cells with a 10-mm optical-path length were used throughout all the measurements unless stated otherwise.

Procedure. Ordinary spectrophotometry: To an aliquot containing less than 5 μg of chromium(III) in a 10-cm^3 test tube, 1 cm^3 of a 5×10^{-3} M 5-Br-PAPS solution and 1 cm^3 of a 2 M acetate buffer (pH 5) were added. The solution was diluted with water to 7 cm^3, and then heated 95 °C in a water bath for 20 min in order to complete the complexation. After cooling, the solution was transferred into a 10-cm^3 volumetric flask and diluted to the mark with water. The absorbance of the resultant solution was measured at 592 nm against a reagent blank prepared under the same conditions using 1-cm cells. Second-derivative spectrophotometry: When the chromium(III) content of the colored solution obtained by the procedure described above was too low to give a measurable absorbance, the procedure was carried out as follows. The second-derivative spectrum (from 700 to 500 nm) was recorded against a reagent blank by using a combination of both first-and second-order differentiation circuits of No. 6 and a scan speed of 120 nm min^{-1}, and the second-derivative value (the vertical

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[†] 1 M=1mol dm^{-3}.

distance from a peak to a trough) was measured.

Results and Discussion

Absorption Spectra. The absorption spectra of the chromium(III)-5-Br-PAPS complex at pH 5 is shown in Fig. 1, together with its second-derivative spectrum. The absorption spectra have an absorption peak at 592 nm and a shoulder on the shorter-wavelength side of the main absorption band. The absorption spectra of the complex was little affected by the addition of such cationic or anionic surfactants as tetradecyldimethylbenzylammonium chloride or dodecylbenzenesulfonic acid.

Effect of Experimental Variables. The pH dependence of the chromium(III) complex formation with 5-Br-PAPS by heating at 95 °C for 20 min is illustrated in Fig. 2. It was found that a constant absorbance at 592 nm was obtained in the pH range of 3.4—6.2. The absorbance of 5-Br-PAPS increases abruptly below pH 4 by increasing the protonated form of the amino group.

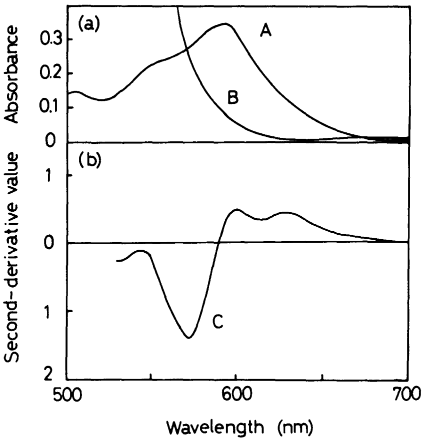

Fig. 1. (a) Absorption spectra of chromium (III)-5-Br-PAPS complex. (b) Second-derivative spectra of chromium-5-Br-PAPS complex. chromium (III), 0.2 μg ml^{-1}; 5-Br-PAPS, 5×10^{-4} M; pH, 5.
A: chrromium(III)-5-Br-PAPS complex, B: reagent blank, C: chromium(III)-5-Br-PAPS complex.

The reaction between chromium(III) with 5-Br-PAPS at room temperature is very slow. Therefore, the formation of the complex should be accelerated by heating. The effect of the heating time at 95 °C on the formation of the complex was examined. It was found that a constant absorbance was obtained by heating for more than 15 min at 95 °C. The complex, once formed at pH 5, was stable and gave a constant absorbance after 2 h.

The effect of the 5-Br-PAPS concentration on the absorbance of the complex was also examined. A concentration of more than 4×10^{-4} M was required to obtain a constant absorbance.

Composition of the Complex. The molar composition of the complex formed under the conditions described in the foregoing procedure was examined by Job's method of continuous variation. The results are shown in Fig. 3. The method indicated that the metal/ligand ratio of the complex was 1:2.

Calibration Graph. A straight-line calibration graph passing through the point of origin was obtained for chromium(III) concentrations of 0.04—0.6 μg cm^{-3} using the foregoing procedure. The equation for the graph was Cr (μg cm^{-3})=0.58 A (1), where A is the absorbance. The sensitivity for an absorbance of 0.001 and the molar absorptivity calculated from Equation (1) were 0.58 ng cm^{-2} and 8.94×10^4 dm^3 mol^{-1} cm^{-1} respectively.

Effect of Diverse Ions. The use of masking agents is required for the determination of chromium(III) with 5-Br-PAPS because many metal ions interfere with the formation of the colored complex. As masking agents, 0.2 cm^3 of 0.1 M tartaric acid was added before the addition of 5-Br-PAPS and 0.2 cm^3

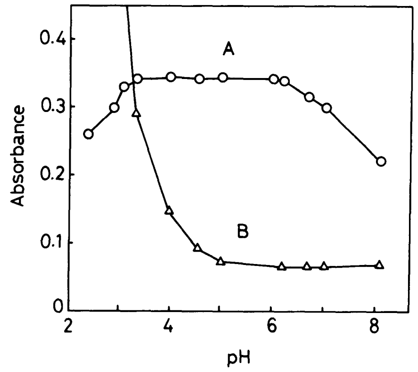

Fig. 2. Effect of pH.
chromium(III), 0.2 μg ml^{-1}; 5-Br-PAPS, 5×10^{-4} M; A: chromium(III)-5-Br-PAPS complex; B: reagent blank.

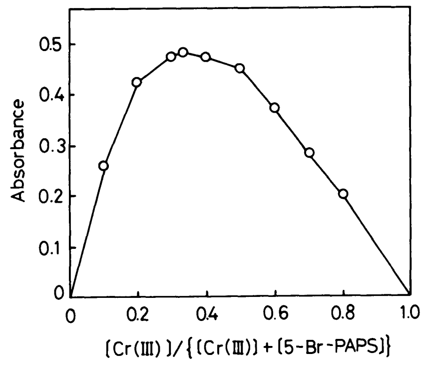

Fig. 3. Continuous variation plots of chromium(III)-5-Br-PAPS complex.
[chromium(III)] + [5-Br-PAPS] = 2×10^{-4} M; cell length, 2 mm; pH, 5.

Table 1. Tolerance Limits for Various Metal Ions in the Determination of 2 μg of Chromium(III). Tolerable Error: ±3%

Ions	Tolerance limit
Bi(III), La(III), Sc(III)	200 μg
Th(IV)	120 μg
Pb(II), Zr(IV)	40 μg
Fe(III), In(III), Mn(II), Mo(VI), Zn(II)	20 μg
V(V)[a]	4 μg
U(VI)[a]	2 μg
Ni(II)	400 ng
Co(II)	40 ng

a) Two hundred μl of 10% hydroxylamine hydrochloride was added after the formation of the chromium(III) complex.

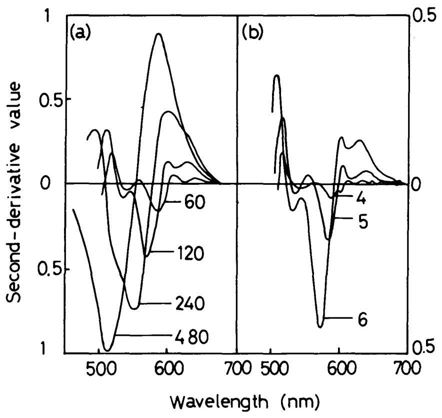

Fig. 4. Influence of (a) scan speed (with circuits all No.6) and (b) circuit number (with scan speed 120 nm min^{-1}) on second-derivative spectra of chromium–5-Br-PAPS complex. chromium(III), 60 ng ml^{-1}; 5-Br-PAPS, 5×10^{-4} M; pH, 5.

of 0.05 M CDTA after the formation of the chromium(III)-5-Br-PAPS complex in the foregoing procedure, then the mixture was heated at 95 °C for 5 min. Many metal complexes of 5-Br-PAPS decomposed upon the addition of CDTA. The absorbance of the chromium(III) complex, however, decreased only 5% compared with that in the absence of masking agents, because ligand exchange between CDTA with 5-Br-PAPS of the chromium(III) complex is very slow. The effects of foreign ions on the determination of chromium(III) when masking agents are used as has been described above are summarised in Table 1. The amounts of bismuth(III), lanthanum(III), scandium(III), thorium(IV), lead(II), zirconium(IV), iron(III), indium(III), manganese(II), molybdenum(VI), and zinc(II) tolerated are 200—20 μg. The masking of vanadium(V) and uranium(VI) with hydroxylamine hydrochloride are incomplete. Cobalt(II) and nickel(II) interfere seriously because these complexes with 5-Br-PAPS, once formed, are very stable and are little decomposed by the addition of CDTA.

Selection of Conditions for Measurement of the Second-Derivative Spectrum. Ishii and his coworkers have previously reported that derivative spectrophotometry using an analogue differentiation circuit is extremely effective in the sensitisation of ordinary spectrophotometry.[4,5] In this work, a derivative unit which is analogous to their apparatus was used. The second-derivative spectrum of the analyte is recorded, and the vertical distance from a peak to a trough, or from the base line to a trough of the spectrum, is measured. Since this distance(D) depends on both the time constant of the analogue differentiation circuits and the scanning speeds used, these need to be selected so as to give a large, well-resolved peak. The second-derivative spectra of the chromium(III)-5-Br-PAPS complex measured with varying circuit numbers and scan speeds are shown in Fig. 4. The largest peaks, but a poor linearity of the calibration graph, were obtained in the conditions of circuit No. 6 and a scan speed of 480 nm min^{-1}. The conditions of circuit No. 6 and a scan speed of 120 nm min^{-1} are found to be preferred for the determination of chromium(III) because reproducible data and a linear relationship for the chromium(III) concentration are obtained under these conditions.

Calibration Graph. The calibration graph, prepared by plotting the second-derivative value versus the chromium(III) concentration, was a straight line passing through the point of origin when either the peak-to-trough values or the base line-to-trough values were plotted. The equations for each graph, measured by employing a combination of circuit No.6 and a scan speed of 120 nm min^{-1}, are as follows; $\mathrm{Cr(ng\,cm^{-3})}=106$ D (2) for the peak-to-trough measurements and $\mathrm{Cr(ng\,cm^{-3})}=134$ D (3) for the base line-to-trough measurements, where D is the second-derivative value represented by the conversion of the value into the absorbance. From Eqs. 2 or 3, it can be seen that chromium(III) down to the 5 ng cm^{-3} level can be easily determined by the proposed method.

Comparison with Other Methods. Sensitive chromogenic reagents for the determination of chromium(III) include 5-Br-PADAP,[3] 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol,[6] chromazurol S–hexadecyltrimethylammonium bromide,[7] phenylarsenazo,[8] PAR,[9] and diphenylcarbazide.[10] The first three are sensitive enough ($\log\varepsilon\fallingdotseq5$), but have a poor selectivity. The last three have a higher selectivity, but are they less sensitivity than the first two. In comparison with the methods using these reagents, the proposed method is sensitive ($\log\varepsilon=4.95$), selective, and stable. Further, the method can be applied to more dilute samples by employing analogue-derivative spectrophotometry.

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