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A KINETIC DETERMINATION OF ULTRATRACE AMOUNTS OF CHROMIUM(III) BY ITS CATALYTIC EFFECT

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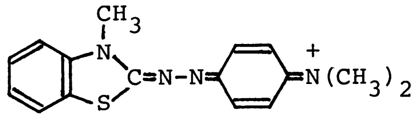
A new sensitive kinetic method is proposed for the determination of chromium(III). The method is based on its catalytic effect on the reaction of 3-methyl-2-benzothiazolone hydrazone with N,N-dimethylaniline to form a violet compound (λ_{max}= 590 nm) in the presence of hydrogen peroxide and ethylenediamine-N,N,N',N'-tetraacetic acid as an activator. The method is selective and sensitive.

Several indicator reactions for the kinetic determination of chromium(III) have been reported. These reactions are based on the hydrogen peroxide oxidation of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione)1) and o-dianisidine,2) and on the periodate - arsenite reaction.3),4) In the latter,3),4) the role of chromium(III) is considered as that of a promoter rather than a catalyst. It is known that 3-methyl-2-benzothiazolone hydrazone (MBTH) is oxidized by an oxidant like iron(III) chloride to form a diazonium ion, which then couples with aromatic amines to form intensely colored dyes, and the reactions are used to detect minute amounts of amines.5)-7) The present authors found that chromium(III) catalyzed the coloration of MBTH with N,N-dimethylaniline (DMA) in the presence of hydrogen peroxide and ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA) as an activator. This paper describes a new catalytic determination of nanogram levels of chromium(III) based on this reaction. Chromium(VI) can be also determined after its reduction to chromium(III) with ethanol. As low as 10^{-8} mol dm^{-3} of chromium can easily be determined.

The recommended procedure is as follows: To 20 - 25 cm^3 of a sample solution (< 500 ng Cr(III)) in a beaker, 4 cm^3 of EDTA (4.0×10^{-2} mol dm^{-3}), 4 cm^3 of DMA (7.0×10^{-2} mol dm^{-3}), 5 cm^3 of 2,4,6-trimethylpyridine (TMP) (1.5×10^{-1} mol dm^{-3}) and 3 cm^3 of ammonia (1.0 mol dm^{-3}) solutions are added. The pH of the solution is adjusted to 7.1 - 7.3 by adding 1.0 and/or 0.1 mol dm^{-3} hydrochloric acid using a pH meter. The solution is transferred to a 50-cm^3 volumetric flask. After adding a mixture of 3 cm^3 of MBTH solution (1.0×10^{-3} mol dm^{-3}) and 2 cm^3 of hydrogen peroxide solution (6.0 mol dm^{-3}), the solution is diluted to the mark with water, mixed well and kept at 45.0 ± 0.1°C in a thermostated bath to initiate the reaction. Exactly 50 minutes after immersing the solution in the bath, the reaction mixture is pipetted into a 10-mm glass cell. Then the absorbance at 590 nm is measured against a distilled water reference. The net absorbance is obtained by subtracting a blank absorbance.

The dye formed by the reaction of MBTH with DMA has an absorption maximum at 590 nm[8] in the pH range 6.0 - 8.5 and is thought to be 4-(3-methyl-2-benzothiazolylidenehydrazono)-2,5-cyclohexadiene-1-ylidenedimethylammonium as exemplified below:



The effect of pH on the color development for the uncatalyzed and catalyzed reactions was examined for a constant time of 50 minutes at 45°C. The maximal color development for the catalytic reaction was obtained at a pH around 7.2 as shown in Fig. 1. The reaction proceeded faster with an increase in temperature, but the reagent blank also increased at temperatures higher than 50°C. An increase in the reaction time also improved the sensitivity. For the sake of high sensitivity and reproducibility, a reaction time of 50 minutes at 45°C was selected. The possibility for further increase in the sensitivity of catalytic reaction is the application of activators. An activator for a catalytic reaction is defined as a substance which does not catalyze the reaction but strongly increases its rate in the presence of certain catalysts.[9] On the basis of this idea, the authors have found some activators for various elements.[10)-13] It is expected that EDTA acts as an activator for the catalytic action of chromium(III), because the chromium(III)-EDTA complex catalyzes the decomposition of hydrogen peroxide.[14),15] Therefore, the effect of EDTA as an activator was examined as shown in Fig. 2. The reaction rate increases at EDTA concentration higher than 1.0 x 10^{-6} mol dm^{-3} and the

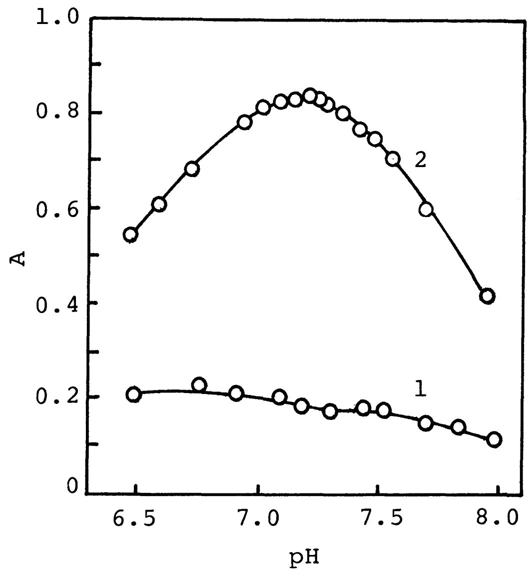


Fig. 1. Effect of pH
1: Reagent blank
2: 300 ng of chromium(III) per 50 cm^3

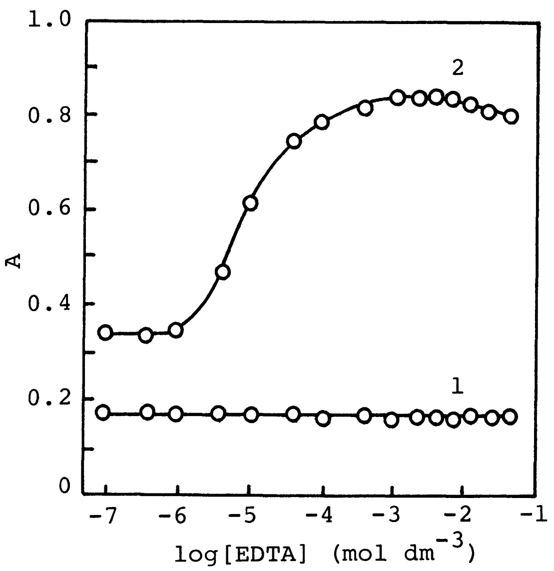


Fig. 2. Effect of EDTA concentration
1: Reagent blank
2: 300 ng of chromium(III) per 50 cm^3

maximal and constant absorbance is obtained in the EDTA concentration range 1.0×10^{-3} - 7.0×10^{-3} mol dm^{-3}. On the other hand, the blank absorbance remains constant over the EDTA concentration range examined.

The effect of the reagent concentrations was examined. As the concentration of MBTH and DMA increased, the reaction proceeded faster and almost constant absorbances were obtained at the concentrations higher than 4.0×10^{-5} mol dm^{-3} MBTH and 4.2×10^{-3} mol dm^{-3} DMA, respectively. Thus the concentrations of MBTH and DMA were selected as 6.0×10^{-5} and 5.6×10^{-3} mol dm^{-3}, respectively. The effect of hydrogen peroxide concentration was also examined. The color development was maximal and almost constant over the range 2.0×10^{-1} - 3.6×10^{-1} mol dm^{-3}, while the blank absorbance was kept low. A 2.4×10^{-1} mol dm^{-3} hydrogen peroxide concentration was chosen for the procedure. The reaction rate for the catalytic reaction sometimes depends on the buffer used to control the pH. The buffers examined include TMP, piperazine-N,N-bis(2-ethanesulfonic acid) (PIPES), 3-(N-morphorino)-propanesulfonic acid (MOPOS), imidazole and phosphate. Among them TMP, PIPES and MOPOS were found the suitable buffers because of no effect on the reaction rate. TMP was used as buffer with consideration to its buffer capacity and low cost. A 1.5×10^{-2} mol dm^{-3} TMP concentration was used for the procedure.

The typical working curve over the range 20 - 500 ng of chromium(III) per 50 cm^3 by the recommended procedure is shown in Fig. 3. Although the working curve is not linear, the reproducibility of the method is satisfactory with the relative standard deviations of 3.8, 3.5 and 3.7 % for eight determinations of 100, 200 and 500 ng of chromium(III) per 50 cm^3, respectively. Chromium(III) concentration as low as 10^{-8} mol dm^{-3} can be determined. Chromium(VI) showed a little catalytic effect on this reaction, possibly because chromium(VI) reacted with hydrogen peroxide to form chromium(III) via peroxochromium(VI) complexes,[16)] but the rate of chromium(III) formation was very slow under the reaction pH. In the case of determining chromium(VI), this ion should be reduced to chromium(III) with ethanol (Table 1).

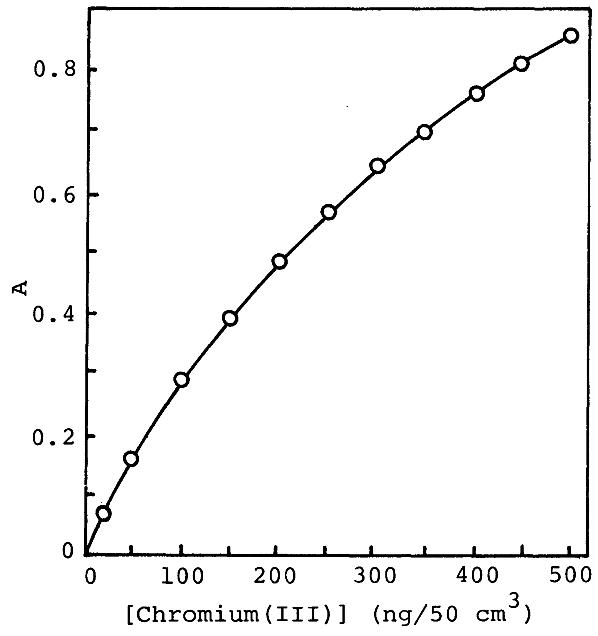


Fig. 3. Working curve for chromium(III)

Table 1. Determination of Cr(VI)

Cr(VI) added (ng)	Cr(III) added (ng)	Cr(III) found (ng)
100	0	33
200	0	63
200	0	206[a]
100	100	137
100	100	202[a]

[a] The values were obtained after the reduction of chromium(VI) to chromium(III) with ethanol.

The effect of diverse ions on the determination of 200 ng of chromium(III) per 50 cm^3 of the working solution was examined. The following ions and compounds caused no interference at least up to the specified amounts: 10 mg of F^-, sodium chloride, potassium chloride, sodium nitrate and sodium sulfate; 1 mg of Ba(II), Bi(III), Ca(II), Cd(II), Hg(II), Pb(II), Sr(II), Ti(IV), Zn(II) and Br^-; 100 μg of Ag(I), Al(III), As(III), As(V), Cu(II), Sn(IV), ClO_4^- and PO_4^{3-}; 10 μg of Mg(II), Ni(II), Se(IV), Sn(II) and W(VI); 5 μg of Co(II) and Mn(II); 1 μg of Mo(VI), Te(IV), V(V) and I^-.

Positive interferences were observed for iron(II) and iron(III) in amounts of 1 μg. These ions or iron(III)-EDTA complex seem to catalyze the reaction. Iron should be separated by solvent extraction or ion exchange.

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