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Study of Cr(VI)-2-Oximinodimedone Dithiosemicarbazone Reaction and Simultaneous Determination of Cr(VI) and Fe(III)

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With 2 Figures

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No bibliographic data have been found about the 2-oximinodimedone dithiosemicarbazone (5,5-dimethyl-1,2,3-cyclohexanetrione-2-oxime-1,3-dithiosemicarbazone) (ODDT) that we have obtained, characterized and applied to the determination of iron. The most frequently employed and recently developed photometric method for the determination of chromium have been summarized in the literature. Most of the methods involve heating the reaction mixture and some require extraction procedures.

In this paper, the reaction of Cr(VI) with ODDT has been studied and applied to the determination of Cr(VI)-Fe(III) mixtures in ceramic materials.

Experimental

Reagents

2-oximinodimedone dithiosemicarbazone has been obtained by the following method: 2 g of dimedone were dissolved in a solution of 10 g of NaOH in 30 ml of water and 30 ml of ethanol; 0.986 g of NaNO₂ were then added and while the solution was cooled in a freezing mixture and stirred, hydrochloric acid (1:1) was slowly added. To this solution 2.6 g of thiosemicarbazide in 100 ml of water and 200 ml of ethanol and sodium acetate up to pH 5 were added. The solution was stored for 2—3 days in
the refrigerator and the solvent then removed at 30°C under diminished pressure. Yellow crystals were separated and washed with ethanol and with water (m. p. 182-4; yield = 50-70%). Solutions of this reagent in DMF of different concentrations were used.

Cr(VI) solutions of different concentrations were prepared by exactly diluting of a 1.000 g/1 solution prepared of K₂Cr₂O₇ and Fe(III) solutions of different concentrations were prepared by exactly diluting of a Fe(III) 0.984 g/l solution prepared from Fe(NO₃)₃·9H₂O and standardized gravimetrically as the oxide.

All experiments were performed with analytical-reagent grade chemicals and pure solvents.

Apparatus

All photometric measurements were performed on a Beckman mod. 25 spectrophotometer, equipped with 1.0 cm glass cells.

Procedure for the Determination of Chromium(VI)

To a solution containing 10-240 µg of Cr(VI) in a 25 ml calibrated flask, add 7 ml of a 0.08% solution of ODDT in DMF, dilute the mixture and add 1.5 ml of HClO₄ (70%). Dilute the mixture to the mark with deionized water. Measure the absorbance at 485 nm against a reagent blank prepared in a similar way without Cr(VI) between ½ and 2 hours after the preparation.

Procedure for the Determination of Chromium(VI)-Iron(III) Mixtures

A. The procedure of determination of the total Cr(VI)-Fe(III) content is the same that of determination of Cr(VI) described, but the absorbance is measured at 500 nm between ¾ and 2 h after the preparation. It has been applied to samples containing 10-240 µg of Cr(VI) and 10-200 µg of Fe(III).

B. To determine the Fe(III) content add to another aliquot of the same solution containing 4.5-125 µg of Fe(III), in a 25 ml calibrated flask, 2 ml of ascorbic acid solution of 100 g/l, 3 ml of HClO₄ (70%), 7 ml of 0.08% solution of ODDT in DMF. Dilute the mixture to the mark and measure the absorbance at 565 nm.

Results and Discussion

Reaction with Chromium(VI). ODDT gives orange coloured solutions with Cr(VI) in strongly acid medium. The absorption spectrum of these solutions shows a maximum at 485 nm (Fig. 1).