Spectrophotometric Determination of Chromium as the Chromium-Peroxo-4-(2-pyridylazo)resorcinol Complex

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Summary. The ternary complex chromium-peroxo-PAR exhibits an apparent molar absorptivity of 6280 1 mol⁻¹ cm⁻¹ when extracted into ethyl acetate from 0.1 M sulfuric acid solution. Beer's law is followed for solutions containing up to 6.0 μg Cr ml⁻¹. Conditions for optimum color formation, complex composition, effects of diverse ions, and application to the determination of chromium in steels are described.

Key words: Best. von Chrom; Spektralphotometrie; Peroxopyridylazoresorcin-Komplex

Spectrophotometric determination of chromium(VI) as the familiar blue chromium-peroxo complex is well known [3, 9, 10]. The methods, however, lack sensitivity. To improve the detection limit while at the same time increasing the stability of the chromium-peroxo complex, attention was directed to the effect of complexation upon the spectrum of an auxiliary ligand. A procedure utilizing this approach with 2,2'-bipyridine has been reported [5]. In an attempt to further improve the detection limit for chromium, additional ligands containing electron donating groups were studied. One of these PAR, 4-(2-pyridylazo)resorcinol, proved to be satisfactory. This paper describes optimum experimental conditions for the formation of a 1:1 adduct between the chromium-peroxo complex and PAR and its utility as an analytical procedure for chromium(VI).

1. Experimental

Reagents and Apparatus. All absorbance values were measured using a Cary Model 14 spectrophotometer with 1.00-cm silica cells. A standard chromium(VI) solution (25.0 μg Cr ml⁻¹) was prepared by dissolving dried, reagent-grade potassium dichromate, K₂Cr₂O₇, in distilled deionized water. A 0.01% (w/v), aqueous solution of PAR, 4-(2-pyridylazo)resorcinol, from Eastman Organic Chemicals was used without further purification. All other chemicals were of reagent grade quality.

Procedure. Transfer a sample aliquot, 1–10 ml of solution containing up to 150 μg chromium, to a 125-ml separatory funnel. Add 1.0 ml of 2.0 M sulfuric acid and sufficient water to reach a final volume of about 20 ml. Add 20 ml of ethyl acetate. Cool the funnel and its contents in an ice-water bath at 10°C for 30 min. All reagents added beyond this point are also cooled to 10°C. Add 3.0 ml of 3.0% (v/v) hydrogen peroxide. Shake the funnel vigorously for 30 s, allow for layer separation, and discard the aqueous phase. Add 10 ml 0.01% (w/v) PAR. Again extract for 30 s, allow for layer separation, and discard the aqueous phase. Transfer the organic phases to a 25-ml volumetric flask, warm to room temperature, and add sufficient additional ethyl acetate to achieve a volume of exactly 25 ml. Measure the absorbance of this solution at 470 nm against a reagent blank prepared in the same manner but containing no chromium.

2. Results and Discussion

The absorbance spectrum of this complex (Fig.1) exhibits a sharp peak at 470 nm and then quickly falls to zero absorbance at shorter wavelengths due to excess free PAR in the reference cell of the spectrophotometer. Molar absorptivity for the complex is 6280 1 mol⁻¹ cm⁻¹. Beer's law is obeyed up to a concentration of 6.0 μg Cr ml⁻¹. Optimum concentration for chromium,
as determined by Ringbom's method [7] is 4.0 to 6.0 μg Cr ml⁻¹. Repetitive measurement, at 470 nm of twenty samples each containing 5.0 μg Cr ml⁻¹, resulted in a mean absorbance reading and standard deviation of 0.596 ± 0.016. The sensitivity index of this procedure, as defined by Sandell [8] is 0.0083 μg Cr cm⁻².

Optimum conditions for color development of the complex included a 0.1-0.3 molar, sulfuric acid solution and addition of 2-3 ml of 3% (v/v) hydrogen peroxide solution. The absorbance for the complex increases with increasing amounts of PAR. To avoid excessive PAR in the reference sample 10 ml of 0.01% (w/v) PAR was selected. The chromium-peroxo complex itself is moderately stable in water solution at or below 10°C and at higher temperatures in the presence of an auxiliary ligand. It is essential that the sample solution and reagents be kept at 10°C when the chromium-peroxo complex is initially formed. The chromium-peroxo-PAR complex is sufficiently stable at ambient temperature for spectrophotometric measurements although readings should be made as soon as conveniently possible after the complex is formed. Absorbance values decreased by approximately 6% for samples which stood for 1 h. Ethyl acetate is a suitable organic solvent for extracting the complex. No extraction took place when benzene, chloroform, cyclohexane, or hexane were used. Partial extraction occurred with methyl isobutyl ketone. Eighteen hiterto unreported ligands were studied as possible adducts. They are: aluminon, arsenazo III, benzoin α-oxime, brucine, o-diaminobenzene, p-diaminobenzene, dimethylglyoxime, 1,5-diphenylcarbohydrazine, eriochrome black T, 8-hydroxyquinoline, phenyl-2-pyrind ketoxime, 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine, 1-(2-pyridylazo)-2-naphthol, 4-(2-pyridylazo)resorcinol, tetraphenylarsonium chloride, 2,2',2''-tripyridine, 2,4,6-tripyridyl-5-triazine, and zincon. PAR proved to be the most satisfactory ligand.