Simultaneous Determination of Cobalt(III)-Copper(II) and Cobalt(III)-Nickel(II) Mixtures by Differential Kinetic Methods

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Abstract. A procedure is reported for the simultaneous determination of binary mixtures of cobalt(III)-copper(II) and cobalt(III)-nickel(II) by differential kinetic methods based on complex formation reactions with 3-(1'H-1',2',4'-triazolyl-3'-azo)-2,6-diaminotoluene. The single-point method is used in both cases. The simultaneous determination of Co-Cu and Co-Ni is possible in the concentration range from 10/1 to 1/1. The interference caused by various ions is also studied. The method has been used to determine cobalt-copper and cobalt-nickel mixtures in synthetic samples, hydrofining catalysts and low alloy steels.

Key words: differential kinetic, single-point method, cobalt-copper and cobalt-nickel simultaneous determination.

Kinetic methods have become very important in recent years [1, 2], mainly because of their sensitivity and, in many cases, because of their selectivity. Especially noteworthy are the differential methods which allow mixtures of similar species to be resolved.

In this regard, the most studied reactions are those of substitution or exchange of ligands, which include the determination of binary mixtures of copper-cobalt, copper-zinc, copper-magnesium or ternary mixtures of copper-magnesium-zinc or nickel-magnesium-zinc [3—5]. More recently, simultaneous determinations based on complexation reactions have been described, mixtures of iron-copper, iron-nickel [6, 7], iron-cobalt [8], copper-zinc [9], copper-nickel [10] being analyzed.

On the other hand, azo dyes have been used intensively for the spectrophotometric determination of many metal ions [11, 12]. However, despite the fact that the rate of formation of the corresponding complexes is not

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always instantaneous, few works using kinetic methods to determine inor-
ganic species have been reported.

The present paper is a kinetic study of the complexation reaction of
cobalt with 3-(1'H-1',2',4'-triazolyl-3'-azo)-2,6-diaminotoluene (TrADAT),
and methods are proposed for the determination of cobalt, cobalt-nickel,
and cobalt-copper mixtures.

**Experimental**

**Apparatus**

Beckman 25 and Hitachi Perkin-Elmer 200 recording spectrophotometers with 1-cm ther-
mostated cells. Radiometer PHM64 digital pH meter with glass and saturated calomel elec-
trodes. Selecta Frigitherm S328 thermostat-cryostat.

**Solutions**

10⁻³ M solution of TrADAT in absolute ethanol. Standard 10⁻¹ M solutions of copper,
cobalt and nickel perchlorates, prepared from the corresponding nitrates by perchloric acid
treatment and standardized complexometrically. The ionic strength was adjusted to 0.25 by
addition of suitable volumes of 0.25 M sodium perchlorate. Hexamine-HClO₄ pH 6.10 buffer
solution.

**Procedure for Measuring the Rate of the Complexation Reaction Cobalt-TrADAT**

Into 25-ml measuring flask are added, in the following order, 2.5 ml of NaClO₄ 2.5 M, 5.0 ml
of pH 6.10 buffer solution and amounts of cobalt comprised between 3.0 and 28.0 µg. These
flasks together with one containing a 10⁻³ M solution of TrADAT are thermostated for
10 min at 25±0.1°C. The complexation reaction is started by adding 3 ml of the 10⁻³ M
solution of TrADAT to the flasks containing the cobalt solution, which are then made up
with distilled water, homogenized, and the variation in absorbance is recorded at 490 nm, as
a time function. The initial rates are calculated from these absorbance-time curves and the
curve of calibration is constructed.

**Procedure for the Simultaneous Determination of Copper and Cobalt by the Single Point Method**

Solutions are prepared as described in the preceding paragraph, containing 17.68—58.93 µg
of cobalt and 6.35—19.06 µg of copper. Absorbances are measured, after shaking the solu-
tions for 30 s, against a reagent blank. Finally, the samples are left until total complexation
(30 min) in order to obtain Aᵦₑ.

**Procedure for the Simultaneous Determination of Cobalt and Nickel by the Single Point Method**

The procedure described above is followed, the amounts of cobalt and nickel in the case
being comprised between 2.94 and 27.99 µg, and 1.46 and 26.42 µg, respectively.

**Procedure for the Simultaneous Determination of Cobalt and Copper
in Hydrofining Catalysts**

Weigh accurately 0.5—1.0 g amounts of the catalysts and dissolve it in 30 ml
of 6 M HCl, heating in a water bath. Then take it almost to dryness and