

DETERMINATION OF COBALT WITH α -FURILMONOXIME

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On the basis of the data obtained previously on the conditions of the cobalt extraction with α -furilmonoxime, an extraction-photometric method for the determination of cobalt with this reagent has been developed. The detection limit is 0.1 p.p.m. and the relative standard deviation for determinations in cobalt(II) salt solutions is 2.5%. No interference is encountered in the determination from a 1000 : 1 excess of Mg, Ca, Sr, Ba, Pb(II), Zn and Cu(II) ions, a 500 : 1 excess of Mn(II) ions, a 250 : 1 excess of Cd ions, a 100 : 1 excess of Cr(III) and W(VI) ions, a 50 : 1 excess of Ni ions and a 25 : 1 excess of V(V) ions. Fe(III) (1000 : 1) and Al (500 : 1) ions can be masked with sodium fluoride. The colouration of the extract is stable for 1 hour. The method was applied to the determination of cobalt in technical iron.

Common and very selective methods for the determination of cobalt are often based on the formation of chemically inert, inner-orbital chelates of trivalent cobalt (*e.g.* the reaction with acetylacetone, 1-nitroso-2-naphthol, *etc.*). In contrast to the chelates of numerous other metals, trivalent cobalt chelates also resist media containing rather concentrated acids or hydroxides. These properties were employed on the extraction-photometric determination of cobalt with α -furilmonoxime¹. As poorer reproducibility was sometimes encountered in this determination, while the method has certain advantages compared with other common methods for the determination of small amounts of cobalt (simple elimination of the effect of other metal ions, relatively good stability of the extract colouration), we studied the extraction of cobalt with α -furilmonoxime in greater detail²⁻⁴.

In the present paper, knowledge obtained previously was utilized for the development of an extraction — photometric determination of cobalt in solutions of its salts and in technical iron.

EXPERIMENTAL AND RESULTS**Chemicals and Instruments Used**

Cobalt(II) perchlorate was prepared from *p.a.* cobalt(II) acetate by repeated evaporation with perchloric acid and recrystallization from water. The concentration of its solution was determined electrogravimetrically and chelometrically; the results of the two determinations were identical. Commercial *p.a.* α -furilmonoxime (Lachema, Brno) was employed.

The pH was measured using an OP-205 pH-meter (Radelkis, Budapest) with an OP-800 1/A combined electrode from the same manufacturer. The measuring cell was calibrated by standard

buffer solutions. Spectrophotometric measurements were carried out on a Spēkol instrument with an auxiliary amplifier (Zeiss, Jena).

The precision of the results was expressed in terms of the standard deviation s or relative standard deviation s_r . The accuracy of the results was evaluated by using the Lord test⁵. The detection limit was calculated using a procedure assuming a larger series of blank determinations and 2–3 determinations in the analysis itself⁶.

Determination of Cobalt in Cobalt(II) Salt Solutions

The solution of a cobalt(II) salts is brought to pH 2.5–7 (using *e.g.* methyl orange). To 5 ml of this solution (0.1–5 p.p.m. Co), 5 ml of a reagent solution in pyridine are added (1.5 g α -furylmonoxime are dissolved in 32 ml of pyridine and diluted with water to 100 ml), the mixture is stirred and allowed to stand for 15 min. The mixture is then extracted with 10 ml benzene until the equilibrium is established (c. 5 min). The benzene extract is separated and its absorbance is measured at 405–410 nm in a 1 cm cuvette against the blank. The colouration of the benzene extract is stable for one day. It was found that the blank absorbance at 405–410 nm is independent of the pH of the aqueous phase. The relative standard deviation, calculated from 15 analyses of a sample containing 2.36 p.p.m. of cobalt, is 2.5%.

In the presence of other metal ions (except Fe, Al, Pd and Pt), aqueous solutions of a cobalt salt must be acidified with 2 ml of concentrated hydrochloric acid before the extraction, stirred, and after 3–5 min standing extracted and then the procedure described in the previous paragraph is followed. If Fe(III) and Al ions are present, they are masked by adding a saturated solution of sodium fluoride. Palladium and platinum interfere in the determination.

The effect of some anions on the extraction — photometric determination of cobalt with α -furylmonoxime was further studied. The absorbance of benzene extracts from aqueous solutions containing various concentrations (0–0.6M) of sodium perchlorate, nitrate, sulphate or fluoride in addition to a cobalt(II) salt was measured. Perchlorate and nitrate exert the most pronounced effect (at $c < 0.3M$ and $c > 0.3M$, respectively) (Fig. 1).

The effect of some metal ions on the determination of cobalt with α -furylmonoxime was also followed (Fig. 2) in the absence of sodium fluoride and in its presence (Fig. 3). Metal salts were added to a cobalt(II) salt in the form of nitrates, tungsten as Na_2WO_4 and vanadium as NH_4VO_3 . The ionic strength of solutions containing cobalt(II) and another metal ion was maintained at 0.2 with sodium nitrate.

Determination of Cobalt in Technical Iron Samples

The sample is dissolved in concentrated hydrochloric acid (20–30 ml) and after oxidation by 5 ml of nitric acid the solution is evaporated to a volume of c. 5 ml. The sample weight and the aliquot part (see below) taken for the determination are selected as follows:

% Co	Sample, g	Aliquot part, ml
0.04–0.3	2.5	25
0.3–1	1	10

The sample can also be dissolved in other acids, *e.g.* in a 1 : 1 mixture of concentrated nitric and perchloric acids, evaporated to the appearance of perchloric acid fumes and the residue heated for another 10 min. After cooling, the residue is diluted with water to about 50 ml and filtered if a precipitate is present (graphite, silicic acid). The filter is washed with c. 100 ml of boiling water, 100 ml of boiling dilute hydrochloric acid (1 : 100) and finally with 50 ml of hot water. The trans-

parent filtrate is diluted to 500 ml after cooling. An aliquot part of the solution is measured into a 100 ml volumetric flask, 20 ml of a saturated sodium fluoride solution are added, the solution is neutralized with a sodium hydroxide solution using methyl orange and diluted with water to the mark. 5 ml are measured from this solution, 5 ml of pyridine reagent solution are added, the mixture is stirred, allowed to stand 15 min, 2 ml of concentrated hydrochloric acid are added

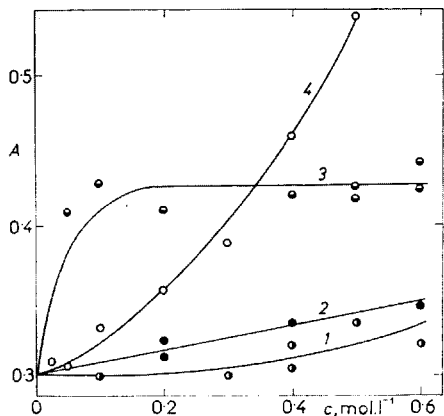


FIG. 1

Dependence of the Organic Phase Absorbance in the Extraction of Cobalt Complex with α -Furilmonoxime into Benzene on the Molar Concentrations of Some Anions in the Aqueous Phase

The Effect of 1 Na_2SO_4 , 2 NaF , 3 NaClO_4 , 4 NaNO_3 . 410 nm $c_{\text{Co}} = 3.4 \cdot 10^{-5} \text{M}$ (i.e. 2 p.p.m.).

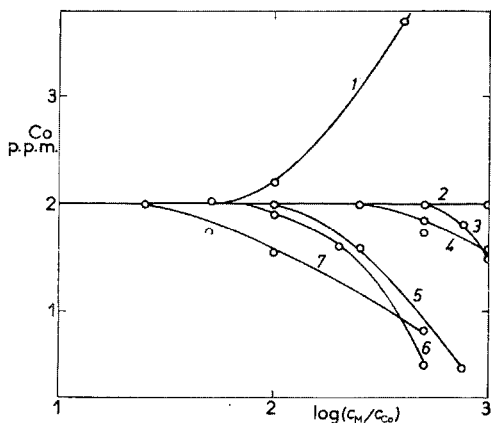


FIG. 2

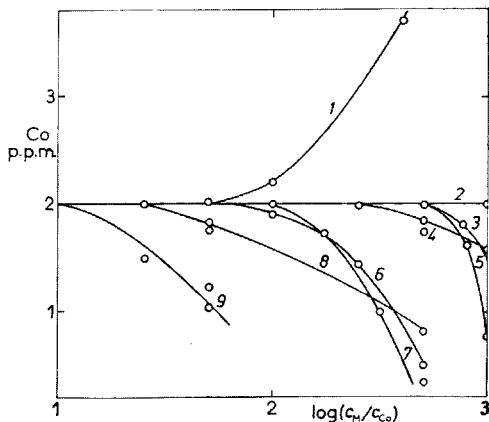
The Effect of the Presence of Some Cations on the Determination of Cobalt with α -Furilmonoxime

1 Ni, 2 Mg, Ca, Sr, Ba, Cu, Zn, Pb, 3 Mn, 4 Cd, 5 Cr, 6 W, 7 V. 410 nm, $c_{\text{Co}} = 2$ p.p.m.

FIG. 3

The Effect of the Presence of Some Cations on the Determination of Cobalt with α -Furilmonoxime in the Presence of Sodium Fluoride

1 Ni, 2 Fe, Cu, Zn, 3 Mn, 4 Cd, 5 Al, 6 W, 7 Cr, 8 V, 9 Mg. 410 nm, $c_{\text{Co}} = 2$ p.p.m.



the mixture is stirred again and after 3–5 min is extracted with 10 ml benzene until equilibrium is established. The absorbance of the benzene extract is measured at 405–410 nm in a 1 cm cuvette against the blank. The colouration is stable for 1 h and then slowly becomes weaker. The precision and accuracy of the determination are evident from Table I.

DISCUSSION

From the results of the previous work⁴ it follows that the α -furylmonoxime concentration in the aqueous phase should be $\approx 3 \cdot 10^{-2} \text{M}$ (0.7%) and that of pyridine 2–3M (16–24%) in order to achieve a suitable extraction recovery and for the reaction to take place in the pH-range in which the cobalt distribution ratio is constant. If the required pH is to be attained by addition of pyridine, the pH of the aqueous solution of the cobalt(II) salt must be 2.5–7 before the addition of the reagent pyridine solution. Under these conditions the cobalt distribution ratio is approximately 1.25 (ref.⁴).

Some excess ions do not interfere in the determination of cobalt, namely Mg, Ca, Sr, Ba, Pb(II), Zn, Cu(II) (1000 : 1), Mn(II) (500 : 1), Cd (250 : 1), Cr(III), W(VI) (100 : 1), Ni (50 : 1) and V(V) (25 : 1). Fe(III) and Al ions must be masked with sodium fluoride; ions that form sparingly soluble fluorides (Mg, Ca, Sr, Ba, Pb) and give rise to precipitates in the aqueous phase also interfere (only the Mg curve is given in Fig. 3 for the sake of illustration). The effect of other ions is not changed in the presence of fluoride ions. Fe(III) and Al ions do not interfere, even if present in an excess of 1000 : 1 and 500 : 1, respectively.

TABLE I

Accuracy and Precision of the Results of Analyses of Technical Iron Samples

Co, %		Number of determinations	u_0^a	$u_{0,k}^b$	s	$s_r, \%$
Declared	determined (arithmetical mean)					
0.085 ^c	0.090	5	0.061	0.507	0.013	15.3
0.095 ^d	0.098	4	0.091	0.717	0.016	16.9
0.140 ^c	0.136	9	0.087	0.255	0.016	11.4
0.155 ^c	0.168	4	0.620	0.717	0.010	6.6
0.250 ^e	0.256	10	0.182	0.230	0.011	4.4

^a Lord test value, ^b Lord test critical value, ^c ČKD Stalingrad standard sample, ^d VŽKG standard sample, ^e British Chemical Standard.

This extraction-photometric method for the determination of cobalt is sensitive and its detection limit (0.1 p.p.m.) is comparable with those of the thiocyanate⁷ (0.2 p.p.m.), nitroso-R-salt⁸ (0.1 p.p.m.) and 2-nitroso-1-naphthol⁹ (0.2 p.p.m.) methods. Compared with the thiocyanate or 2-nitroso-1-naphthol methods, the present method has an advantage in simple elimination of the influence of other metal ions and compared with the nitroso-R-salt method it exhibits better stability of the extract colouration.

It is important to maintain the initial volumes of the aqueous and organic phases during the extraction of the complex formed from the aqueous phase, because of the relatively low value of the cobalt distribution ratio ($D = 1.25$). Further, care must be exercised that the sample and standard solutions contain approximately equal amounts of salts, as these affect the cobalt extraction recovery through ionic strength variations (Fig. 1).

The suitability of the procedure proposed for the determination of cobalt in technical iron was verified by analyses of standard samples. The accuracy of the analyses was checked using the Lord test. In all cases the calculated test values were lower than the critical values (for 95% probability) (Table I), so that the difference between the determined and declared content has a low statistical significance. The standard deviation is lower in all cases than the permitted precision value specified in the valid standard for the determination of cobalt in technical iron using the nitroso-R-salt (ČSN 420521), which is $0.02 + 0.04\%$ for cobalt contents from 0.05 to 1%. The considerable difference in the precision of the determination of cobalt in a pure salt solution and in technical iron with a low cobalt content (samples c, d) may be caused by sample inhomogeneity.

REFERENCES

1. Martínek J., Hovorka V.: *Chem. Listy* 50, 1450 (1956).
2. Jehličková A., Vlášil F.: *This Journal* 38, 1027 (1973).
3. Jehličková A., Vlášil F.: *This Journal* 38, 3395 (1973).
4. Vlášil F., Jehličková A.: *This Journal* 40, 539 (1975).
5. Eckschlager K.: *Chyby chemických rozborů*, 2nd Ed., p. 113, 143. Published by Nakladatelství SNTL, Prague 1971.
6. Doerffel K.: *Statistik in der Analytischen Chemie*, p. 72. Deutscher Verlag für Grundstoffindustrie, Leipzig 1966.
7. Zimmermann H., Hoyme H., Tryonald A.: *Faserforsch. Textiltech.* 21, 33 (1970).
8. Koch K. H., Ohls K., Sebastiani E., Riemer G.: *Fresenius' Z. Anal. Chem.* 249, 307 (1970).
9. Funke A., Laukner H. J.: *Fresenius' Z. Anal. Chm.* 249, 26 (1970).

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