RESOLUTION OF BINARY MIXTURES OF METAL IONS BY FLOW INJECTION ANALYSIS

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Abstract

A selective FIA spectrophotometric method for the resolution of cobalt-nickel and cobalt-cadmium mixtures by use of a four-channel flow injection manifold and 4-phenyl-thiosemicarbazone as reagent was developed. The fourth manifold channel was used to insert a stream containing 30% perchloric acid or an acetic acid/acetate buffer of pH 5.2. By running a calibration graph for Co(II) in 30% $HClO_4$ and three others for Co(II), Ni(II) and Cd(II), respectively, in the HAcO/AcO⁻ buffer, the amount of Ni or Cd in a mixture with Co can be readily determined by difference. The physical and chemical variables of the process were all optimized. The proposed method allows the above three ions to be determined over the linear ranges 0.4–30 μg ml^{-1} for Co(II) and Ni(II), and 0.5–50 μg ml^{-1} for Cd(II). The method is quite tolerant to interferences and allows the resolution of Co–Ni mixtures in ratios between 30:1 and 1:30, and that of Co–Cd mixtures over the ratio range 8:1–1:7.

None of the FIA spectrophotometric methods for the determination of cobalt developed in the last few years allows for multicomponent analyses [1–5]. In fact, one simultaneous determination for cobalt and nickel with salicylaldehyde thiosemicarbazone relies on differential kinetic analysis [6].

In this work we developed a method for the resolution of cobalt-nickel and cobalt-cadmium mixtures using pyridoxal 4-phenyl-3-thiosemicarbazone (PPT) as reagent on the basis of the different stability of the complexes thus formed at various pH values.

EXPERIMENTAL

Apparatus

The experimental setup used consisted of a Gilson Minipuls 3 peristaltic pump, an HP 8452A diode array spectrophotometer, an HP Vectra QS/165 computer running HP 89531A UV/Vis software and an HP Laserjet IIP printer. A QS flow-cell and a variable-volume 4-way rotary valve were also used.

Reagents

Standard solutions of cobalt(II), nickel(II) and cadmium(II) containing 4.5065, 4.7826 and 1.000 g l^{-1}, respectively, of the ion concerned, were prepared from the respective nitrates (Merck) and standardized titrimetrically with EDTA.

A stock 0.1% PPT solution in N,N-dimethylformamide was used to prepare more dilute solutions as required. The reagent was synthesized as described elsewhere [7] and was identified by elemental analysis and IR and NMR spectroscopy.

Acetic acid/acetate buffers of various pH values were also used.

All solvents and reagents employed were of analytical grade.

Procedure

Sample volumes of 260 μl containing 0.4–30 μg ml^{-1} cobalt, 0.4–30 μg ml^{-1} nickel or 0.5–50 μg ml^{-1} cadmium were injected into the manifold depicted in Fig. 1. Another manifold channel was used to circulate a stream of the reagent in N,N-dimethylformamide containing 30% HClO$_4$ or HAcO/AcO$^-$ buffer of pH 5.2.

The optimal flow-rates of the streams were found to be as follows: 1.4 ml min⁻¹ (sample), 1.6 ml min⁻¹ (water), 0.7 ml min⁻¹ (PPT) and 1.1 ml min⁻¹ ($HClO_4$ or $HAcO/AcO^-$).

The absorption of the reaction medium was monitored spectrophotometrically by measuring the absorbance at 430 nm and 440 nm. Some calibration curves were previously constructed from standards containing accurately known concentrations of cobalt, nickel and cadmium.

For the determination of cobalt and nickel in catalysts, different amounts of sample (between 0.05-0.1 g) were dissolved in 4 ml of aqua regia in reflux. Excess acid was then evaporated by heating and the mixture was diluted to 100 ml with de-ionized water. Several aliquots were subsequently transferred to 25-ml volumetric flasks and made to the mark. The solutions thus obtained were used to inject 260-μl aliquots into the manifolds in order to determine cobalt and nickel as described above.
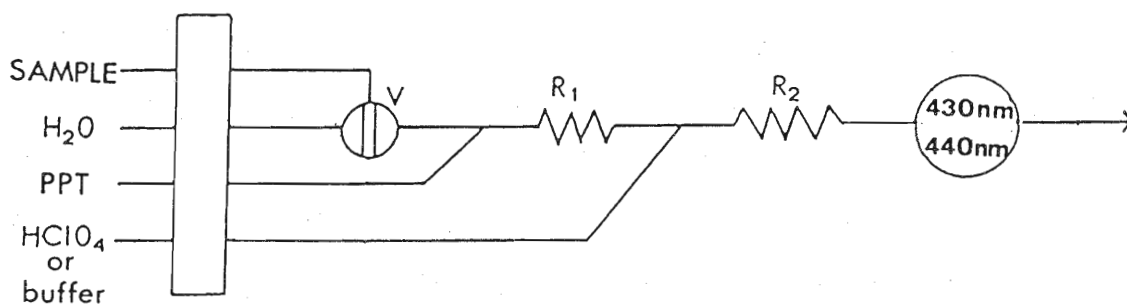

Figure 1 – Scheme of the FIA manifold used. Reagent: 0.1% PPT in DMF, 3 M $HClO_4$. Buffer: $HAcO/AcO^-$, pH 5.2. V: sample injection valve (V_i = 260 μl). R_1 and R_2: reaction coils, 116 and 150 cm long, 0.5 mm ID.

RESULTS AND DISCUSSION

Features of the Co(II)–PPT, Ni(II)–PPT and Cd(II)–PPT complexes

Cobalt forms a yellow complex with PPT (λ_{max} = 430 nm, ϵ = 1.35×10^4 l mol⁻¹ cm⁻¹) that is stable in $HClO_4$, where most of the metal complexes of PPT are not formed.

Nickel also forms a yellow complex with PPT (λ_{max} = 430 nm, ϵ = 1.9×10^4 l mol^{-1} cm^{-1}) at pH 4–6. Cadmium also reacts with PPT to form a yellow complex (λ_{max} = 405 nm, ϵ = 8.6×10^3 l mol^{-1} cm^{-1}) at pH 4.5–5.5.

Figure 2 shows the influence of pH on the absorbance of the above three complexes. As can be seen, the Co–PPT complex is not destroyed by the acid medium, whereas those of Ni and Cd absorb maximally at pH 4–6. Thus, by injecting a Co–Ni or a Co–Cd mixture into the manifold depicted in Fig. 1 and circulating HClO$_4$ or HAcO/AcO$^-$ through its fourth channel one will obtain a first FIA peak that will correspond to cobalt in the former case and to the sum of the mixture in question in the latter, so nickel (or cadmium) can be readily determined by difference.
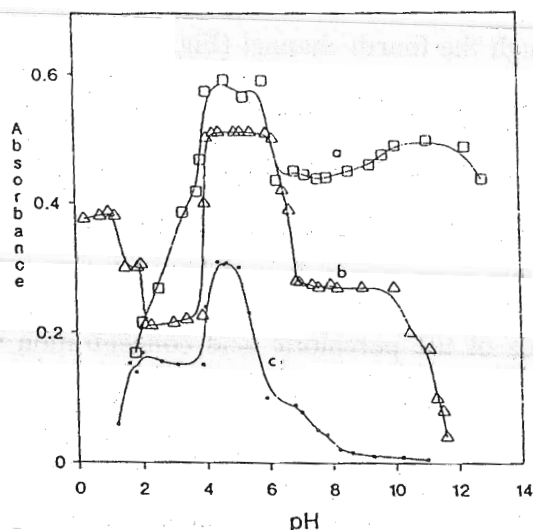

Figure 2 — Influence of pH on the absorbance of the PPT complexes of Co, Ni and Cd. [Co(II)] = [Ni(II)] = 2 μg ml^{-1}, [Cd(II)] = 4 μg ml^{-1}. (a) PPT-Ni, (b) PPT-Co, (c) PPT-Cd system

Optimization of the FIA manifold

Various FIA manifold designs, reactant addition sequences and mixing coil lengths were assayed. The sample solution was previously merged with a water stream in order to avoid signals arising from changes in the refractive index on each injection.

The lengths of reactors R_1 and R_2 were optimized from the results (peak heights) obtained by triplicate injection of a fixed concentration of cobalt in $HClO_4$ or Co + Ni in HAcO/AcO$^-$. The best results were obtained for R_1 = 116 cm and R_2 = 150 cm. The inner diameter of the two reactors was 0.5 mm. The selected injection loop volume was 260 μl. Under these conditions, the FIA manifold used (Fig. 1) provided a residence time [8] of 34 s and a maximum throughput of 72 samples h^{-1}.

Influence of the reagent, perchloric acid and buffer concentrations

The influence of the PPT concentration in DMF on the analytical signal was investigated by using a mixture of 5 μg ml^{-1} Co and 5 μg ml^{-1} Ni and circulating $HClO_4$ or HAcO/AcO$^-$ through the fourth channel (Fig. 3).

Both 0.05% and 0.1% PPT in DMF yielded the maximum possible peak height with HAcO/AcO$^-$, so we chose 0.1% PPT for all subsequent experiments in order to maximize the reagent concentration available for the determination of the sum of Co and Ni or Cd.

The influence of the perchloric acid concentration was also studied and 30% $HClO_4$ was found to provide the maximum FIA peak height.

On the other hand, HAcO/AcO$^-$ buffers of various pH values between 4.8 and 5.6 were found to have no appreciable influence on the analytical signal, so a pH of 5.2 was chosen for further experiments.

Calibration curves and precision

In order to establish the optimal range for the determination of the three ions we used injections of variable concentrations of each ion plus 0.1% PPT and 30% $HClO_4$ or HAcO/AcO$^-$ buffer of pH 5.2. We also used a blank containing none of the analytes.

The linear range and reproducibility of the proposed method for each ion at 430 and 440 nm in HAcO/AcO$^-$ and $HClO_4$, respectively, are listed in Table 1.
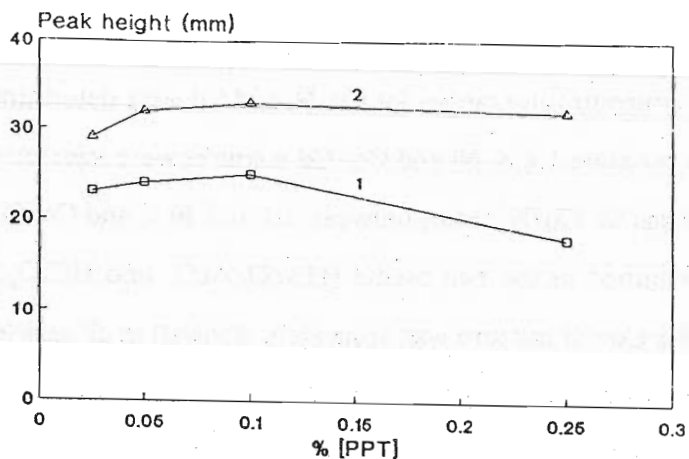
Figure 3 – Influence of the PPT concentration on the peak height. [Co(II)] = [Ni(II)] = 5 μg ml^{-1}. HAcO/AcO$^-$ buffer. 1-430 nm, 2-440 nm.

TABLE 1

Figures of merit of the determination of Co, Ni and Cd

ion	λ nm	linear range (μg/ml) 30% HClO$_4$	HAc/Ac$^-$	μg/ml	N	% R.S.D.
Co	430	0.4-30.0		5.0	12	0.39
Co	440	0.4-30.0		5.0	12	0.59
Co	430		0.4-30.0	5.0	12	0.68
Co	440		0.4-30.0	5.0	12	0.54
Ni	430		0.4-30.0	5.0	12	1.00
Ni	440		0.4-30.0	5.0	9	1.02
Cd	430		0.5-50.0	2.0	7	4.90
				5.0	7	3.54
Cd	440		0.5-50.0	2.0	7	4.23
				5.0	7	2.50

Resolution of mixtures

After the linear concentration ranges for Co, Ni and Cd were determined and the height of the FIA peak measured, Co–Ni and Co–Cd mixtures were injected into the manifold and FIA recordings for Co/Ni ratios between 1:1 and 30:1, and Co/Cd ratios from 1:30 to 30:1, were obtained in the two media ($HAcO/AcO^-$ and $HClO_4$). As can be seen from Table 2, the Co–Ni mixture was accurately resolved at all assayed ratios, whereas the Co–Cd mixture was properly resolved for Co at all ratios, yet the Cd concentration was subject to a negative error at ratios below 1:6 and above 8:1.

TABLE 2

Resolution of binary mixtures

Co:Ni ratio	present ppm		found ppm		Co:Ni ratio	present ppm		found ppm	
	Co	Ni	Co	Ni		Co	Ni	Co	Ni
1:1	3.0	3.0	3.0	3.0	2:1	6.0	3.0	6.0	3.0
1:2	3.0	6.0	3.0	6.0	3:1	9.0	3.0	9.2	3.0
1:3	3.0	9.0	3.0	9.0	4:1	12.0	3.0	12.2	3.0
1:4	3.0	12.0	3.0	12.0	5:1	15.0	3.0	15.0	3.0
1:5	3.0	15.0	3.0	15.0	6:1	18.0	3.0	18.0	3.3
1:6	3.0	18.0	3.0	17.0	7:1	21.0	3.0	20.8	3.0
1:7	3.0	21.0	3.0	21.0	8:1	24.3	3.0	25.2	3.6
1:8	3.0	24.0	3.0	24.0	9:1	27.0	3.0	27.3	3.0
1:9	3.0	27.0	3.0	27.2	10:1	30.0	3.0	29.4	3.0
1:10	3.0	30.0	3.0	30.0	15:1	15.0	1.0	15.0	1.0
1:15	1.0	15.0	1.0	15.0	20:1	20.0	1.0	20.0	1.0
1:20	1.0	20.0	1.0	20.0	25:1	25.0	1.0	25.0	1.0
1:25	1.0	25.0	1.0	25.0	30:1	30.0	1.0	29.0	1.0
1:30	1.0	30.0	1.0	30.0					

TABLE 2 (Continuation)

Co:Cd ratio	present ppm Co	present ppm Cd	found ppm Co	found ppm Cd	Co:Cd ratio	present ppm Co	present ppm Cd	found ppm Co	found ppm Cd
1:1	3.6	3.6	3.6	3.6	2:1	7.2	3.6	7.4	4.0
1:2	3.6	7.2	3.6	6.0	3:1	10.8	3.6	10.8	5.0
1:3	3.6	10.8	3.6	10.0	4:1	14.4	3.6	14.6	4.0
1:4	3.6	14.4	3.6	14.5	5:1	18.0	3.6	18.0	4.0
1:5	3.6	18.0	3.6	18.0	6:1	21.6	3.6	21.8	5.0
1:6	3.6	21.6	3.6	21.0	7:1	25.2	3.6	24.0	5.0
1:7	3.6	25.2	3.6	20.0	8:1	28.8	3.6	26.8	3.6
1:8	3.6	28.8	3.6	25.0	9:1	32.4	3.6	28.0	8.0
1:9	3.6	32.4	3.6	26.0	10:1	36.0	3.6	28.4	3.6
1:10	3.6	36.0	3.6	33.0	15:1	30.0	2.0	26.0	11.0
1:15	2.0	30.0	2.0	24.0					
1:20	2.0	40.0	2.0	30.0					

Interferences

The effect of potential interferents with the determination of cobalt and nickel by the proposed method was studied by using 3.6 μg ml^{-1} Co(II) and 3.8 μg ml^{-1} Ni(II) plus variable concentrations of each foreign ion assayed up to a maximum ion-to-cobalt or ion-to-nickel ratio of 225:1. A given species was considered to interfere if its presence resulted in a ± 3% variation in the average FIA signal determined for the set concentrations of cobalt and nickel. The results obtained are listed in Table 3.

Interfering effects on cobalt and cadmium were similar as the pH used for the two was the same.

Applications

The proposed method was applied to the determination of cobalt and nickel in catalysts that were supplied by the Spanish oil product manufacturer CEPSA. The results are given in Table 4 as the average of three determinations. As can be seen, they were quite consistent with the manufacturer's certified values.

TABLE 3

Interference of foreign ions

Ion	Tolerated ratio(w/w)
Li(I), $PO_4^=$, Cl^-, $SO_4^=$, $C_2O_4^=$, ascorbic acid, F^-, citrate, tartrate, BrO_3^-, Mg(II), Br^-, I^-, Ba(II), Ca(II), Sr(II), Na(I), K(I)	$>$ 225
$WO_4^=$, $B_4O_7^=$,	150
Mn(II), Zr(IV), Mo(VI)	100
Cr(III)	50
AsO_4^{3-}	25
Pb(II), UO_2^{2+}, Hg_2^{2+}, Al(III)	10
AsO_3^{3-}	5
Ag(I)	4
VO_3^-, Cu(II), Bi(III)	1
Fe(III), Sb(III), Zn(II)	$<$ 1

TABLE 4

Determination of Co and Ni in catalysts

Sample	% Co present	% Ni present	430nm		440 nm	
			% Co found	% Ni found	% Co found	% Ni found
1	2.30		2.25 ± 0.02		2.16 ± 0.02	
2		3.00		3.10 ± 0.02		3.14 ± 0.02
3	1.14	1.51	1.09 ± 0.02	1.44 ± 0.02	1.07 ± 0.02	1.67 ± 0.02
4	0.74	2.04	0.74 ± 0.02	2.01 ± 0.02	0.75 ± 0.02	1.97 ± 0.03

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