

Determination of Mixtures of Cobalt and Iron by First Derivative Spectrophotometry

M. INÉS TORAL, PABLO RICHTER,¹ LORENA SILVA, AND ANDREA SALINAS

Department of Chemistry, Faculty of Sciences, University of Chile, P.O. Box 653, Santiago, Chile

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Cobalt and iron can be determined simultaneously by first derivative spectrophotometry. The method does not require simultaneous equations to be resolved and it is based on the separation of the analytes, by liquid-liquid extraction, integrated reaction with 3-(4-phenyl-2-pyridinyl)-1,2,4-triazine, and perchlorate in dichloroethane and on the subsequent derivative spectrophotometric measurement using the graphical and the zero-crossing methods for determination of iron and cobalt, respectively. Cobalt and iron were thus determined in the range 57-1200 ng/ml and 2.0-120 ng/ml, respectively, in the presence of one another. The method has a high sensitivity and the detection limits (3σ) were calculated to be 17.1 ng/ml of cobalt and 0.6 ng/ml of iron. The relative standard deviations were in all instances less than 3.2%. The proposed method was successfully applied to the determination of both analytes in river water. © 1993 Academic Press, Inc.

INTRODUCTION

Despite the fact that a number of sensitive spectrophotometric methods have been described for the individual determination of cobalt and iron, considerably less attention has been paid to the simultaneous determination of both ions.

The spectrophotometric determination of both analytes in a mixture is often troublesome because of the appreciable overlap between their broad absorption spectra. However, DiTusa and Schilt (1) described a spectrophotometric multielement determination of cobalt-iron, and of cobalt-iron-nickel using 2,2'-dipyridylketone-2-pyridylhydrazone and isoquinoline-3-aldehyde-2-pyridylhydrazone, respectively. These reagents were selected on the basis of high absorptivities and spectral differences among their different metal chelates and the determination was carried out by using two or three simultaneous equations at different wavelengths, depending on the number of analytes in the sample. Similarly, Afeworki and Chandravanshi (2) reported a method for the separate and simultaneous determination of these analytes which were extracted into ethylacetate as 1:2:2 (Fe:SCN⁻:*N*-phenylcinnamohydroxamic acid) and 1:4 (Co:SCN⁻) complexes. Thus by measuring the absorbance of the organic extract at two wavelengths the concentration of the metals could be determined by solving simultaneous equations.

Alternatively, the analytical use of the kinetic of complex formation is also applicable for the determination of cobalt and iron in mixtures and it was proposed by Ballesteros and Perez-Bendito (3) using pyridoxal thiosemicarbazone (PT).

¹ To whom correspondence should be addressed.

This kinetic approach has good features and it was based on the differential reaction rate between PT and these metallic ions. However, the method needs a rigid control of experimental variables.

On the other hand, derivative spectrophotometry has received increasing attention with regard to the quantitation of multicomponent mixtures (4–10), because the information contained in the spectrum is presented in a potentially more useful form, increasing notably the spectral resolution. In this instance, derivative spectrophotometry has been used for the simultaneous determination of some inorganic species through the formation of their complexes with organic reagents. Accordingly, this paper reports on the analytical advantages and features of the derivative spectrophotometry for the simultaneous determination of cobalt and iron in mixtures using 3-(4-phenyl-2-pyridinyl)-1,2,4-triazine (PPT) and perchlorate as the reagents, and without the need to solve simultaneous equations or for rigid control of experimental variables.

MATERIALS AND METHODS

Apparatus

A Shimadzu UV-160 spectrophotometer with 10-mm cells was used for measurements of the absorbance and derivative absorption spectra. An Orion Research Model 701 digital ion analyzer with glass and saturated calomel electrodes was used for pH determinations.

Reagents

All reagents were of analytical reagent grade and the solutions were prepared with high-purity water from a Millipore Milli-Q water purification system device.

Standard Cobalt(II) Solution A 1000 $\mu\text{g/ml}$ solution was used (Titrisol Merck).

Standard iron(II) solution. A 1000 $\mu\text{g/ml}$ solution was prepared by dissolving 7.022 g of ammonium iron(II) sulfate hexahydrate in 10 ml of 9 M sulfuric acid and diluting to the volume in a 1000-ml standard flask. Solutions of 10 $\mu\text{g/ml}$ of the analytes were prepared by diluting these standard solutions and other ranges of concentrations were prepared by appropriate dilution.

3-(4-Phenyl-2-pyridinyl)-1,2,4-triazine solution. A 5×10^{-3} M solution was prepared by dissolving 1.5520 g of the compound in 100 ml of dichloroethane (DCE).

Sodium perchlorate solution. A 1 M solution was prepared by dissolving 122.4 g in 1000 ml of water.

Hydroxylamine hydrochloride solution. This solution was prepared by dissolving 100 g of the salt in 1000 ml of water.

Sodium acetate–acetic acid buffer solution (pH 5). Prepared by adding acetic acid to 2.0 M sodium acetate solution until pH 5 was reached.

Foreign ion solutions. Solutions of diverse ions for the interference studies were prepared by dissolving the calculated amount of each compound in order to give 10–1000 $\mu\text{g/ml}$ solutions of each species.

All these solutions were stored in polyethylene containers.

1,2-Dichloroethane. This was used in extrapure grade (sp gr 1.25).

Procedure

Ordinary spectrophotometry. To an aliquot of sample solution containing less than 1.2 and 0.12 μg of cobalt and iron, respectively in a 250-ml separating funnel, add 1 ml of the buffer solution, 1 ml of hydroxylamine solution, and 6 ml of 1 M sodium perchlorate solution and adjust the total volume to 100 ml. Mix and set aside for 2 min. Then add 5 ml of 5×10^{-3} M PPT solution in dichloroethane and shake the funnel for 2 min. Allow the phases to separate and run the organic layer into a dry flask. Record the spectra of the DCE extract over the range from 650 to 400 nm against a reagent blank prepared under the same experimental conditions, using 10-mm cells.

Derivative spectrophotometry. Prepare the extract as above and record the first derivative spectra from 650 to 500 nm against a reagent blank at a scan speed of 480 nm/min with $\Delta\lambda 1.6$ nm.

RESULTS AND DISCUSSION

Spectral Characteristics

Under the experimental conditions described above Fe(II) and Co(II) can be extracted, as the perchlorate ion pairs, into an organic phase containing PPT in DCE to form the ion-associated complexes Fe-PPT-ClO₄ and Co-PPT-ClO₄.

It can be seen in Fig. 1 that the spectro for iron and cobalt complexes do not show prominent peaks which can be used for reliable direct absorbance measurement. Incorrect results were obtained by solving simultaneous equations for two wavelengths. In this respect derivative spectrophotometry provides additional possibilities, because it enhances the detectability of minor spectral features.

The first derivative spectra of the two complexes show significant differences in some areas (Fig. 2) and this approach offers a valuable means of simultaneously determining both metals in a mixture.

Figure 3a shows a series of first derivative spectra of mixtures of 0.6 $\mu\text{g}/\text{ml}$ cobalt and increasing concentrations of iron ranging from 0.02 to 0.1 $\mu\text{g}/\text{ml}$. Similarly, Fig. 3b shows the first derivative spectra of mixtures of 0.06 $\mu\text{g}/\text{ml}$ iron and increasing concentrations of cobalt from 0.2 to 1.0 $\mu\text{g}/\text{ml}$. In this instance, the graphical method can be used for the determination of iron because the peak at 600 nm is only proportional to the concentration of this analyte. In contrast, the

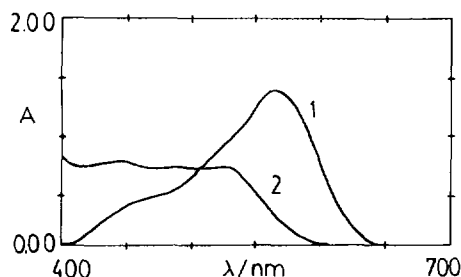


FIG. 1. Absorption spectra of DCE extract of the metal-PPT-perchlorate complexes measured against DCE. (1) 100 ng/ml iron. (2) 400 ng/ml cobalt. All other conditions as in text.

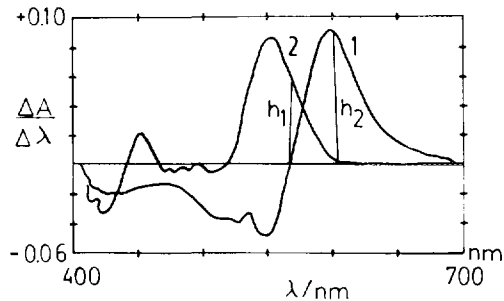


FIG. 2. First derivative spectra of the metal-PPT-perchlorate complexes. (1) 0.160 $\mu\text{g/ml}$ iron. (2) 1.60 $\mu\text{g/ml}$ cobalt. All other conditions as in text.

measurement of the derivative spectrum at an abscissa value of 566 nm corresponding to the zero-crossing point of the derivative spectrum of Fe-PPT-ClO₄ (Fig. 2) was used satisfactorily to determine cobalt.

Study of the Experimental Variables

Variables were optimized by the univariate method, for each analyte separately. Table 1 shows the optimum values found for the chemical and spectral variables and the range over which they were studied. It can be seen in Table 1 that working values for the reagent concentration were selected taking into account not only the presence of both analytes but also that foreign cations can be present in the sample with the evident consumption of reagents. A buffer system pH of 5 was chosen for all subsequent experiments, in order to keep the pH in the center of the optimum range.

The aqueous/organic phase volume ratio was chosen to obtain the maximum enrichment factor. A value of 20 was determined as optimum because miscibility of the phases occurred when higher ratios were selected.

The main spectral variables affecting the shape of the spectra was the order of the derivative and the $\Delta\lambda$ value. Cobalt was the determining analyte in the selection of the instrumental variables because only the zero-crossing first derivative

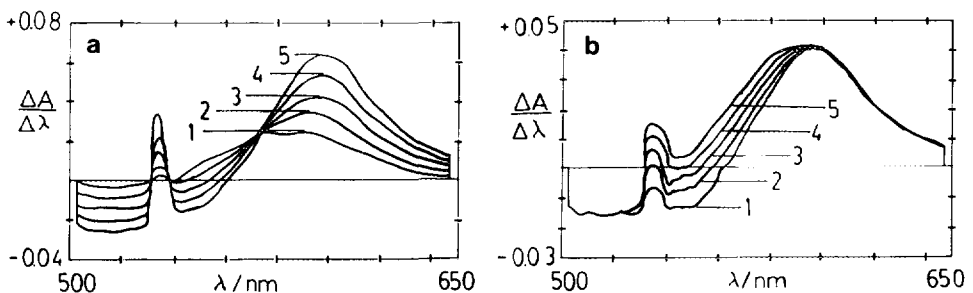


FIG. 3. First derivative spectra of mixtures of cobalt and iron. (a) Cobalt: 600 ng/ml; iron: (1) 20, (2) 40, (3) 60, (4) 80, and (5) 100 ng/ml. (b) Iron: 60 ng/ml; cobalt: (1) 200, (2) 400, (3) 600, (4) 800, and (5) 1000 ng/ml. All other conditions as in text.

TABLE I
Study of Variables

Variable	Cation	Range studied	Optimum range	Working value
<i>Chemical</i>				
pH	Cobalt	1.0–12.0	2.5–9.0	5.0
	Iron	1.0–12.0	3.0–7.0	
PPT solution/ $1 \times 10^{-4} M$	Cobalt	0.6–12.0	3.0–12.0	10.0
	Iron	0.6–12.0	2.0–12.0	
1 M sodium perchlorate solution/ml	Cobalt	1.0–10.0	4.0–10.0	6.0
	Iron	1.0–10.0	2.0–10.0	
Aqueous/organic phase ratio	Cobalt	2–24		20
	Iron	2–24		
<i>Spectral</i>				
Derivative order	Cobalt	0–4		1
	Iron	0–4		
$\Delta\lambda/\text{nm}$	Cobalt	0.8–8.0	0.8–2.4	1.6
	Iron	0.8–8.0	0.8–2.4	
Analytical wavelength/nm	Cobalt	400–700		566
	Iron	400–700		600

approach permits the reproducible determination of this species simultaneously with iron. Higher derivative orders yield very high yet irreproducible signals for cobalt. Analogously, as can be seen in Fig. 4 a $\Delta\lambda$ value less than 2.4 nm was mandatory to be used because over this value the derivative value at the zero-

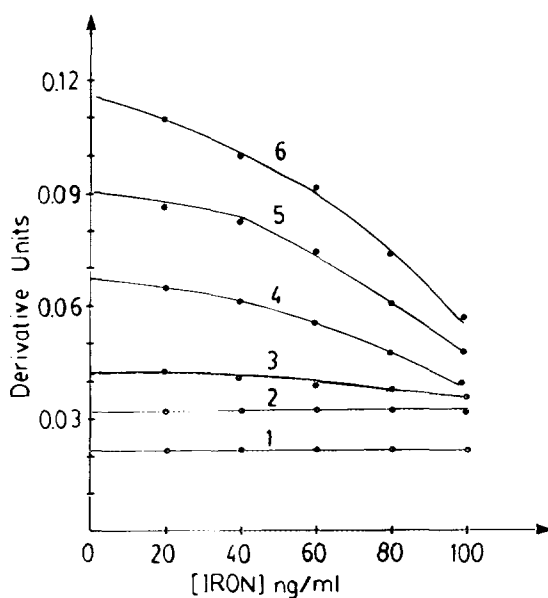


Fig. 4. Influence of the iron concentration on the cobalt signal (566 nm) at different $\Delta\lambda$ values. Cobalt: 600 ng/ml. $\Delta\lambda$ values: (1) 1.6, (2) 2.4, (3) 3.2, (4) 4.8, (5) 6.4, and (6) 8.0 nm. All other conditions as in text.

TABLE 2
Features of the Method

	Slope (DU/ppm) ^a	Intercept	Coefficient correlation	Detection limit (ppb)	Determination range (ppb)	Relative standard deviation (%)
Cobalt	0.035	1×10^{-5}	0.9989	17.1	57–2000	3.2
Iron	0.54	1×10^{-3}	0.9998	0.6	2.0–200	0.94

^a DU, derivative units.

crossing wavelength begins to be a function of the iron concentration. A $\Delta\lambda$ value of 1.6 was selected as optimum.

The wavelength scanning speed had no influence on the signal, because the differentiation is obtained digitally. Hence, a fast value of 480 nm/min was selected.

Features of the Method

The calibration graphs were obtained by plotting the first derivative value $h1$ for cobalt and $h2$ for iron with $\Delta\lambda = 1.6$ nm, versus the analyte concentrations.

The results of linear regression equations calculated for mixtures of cobalt and iron are shown in Table 2, together with the correlation coefficients, the determination ranges, the detection limits (calculated by using the 3σ recommendation), and the relative standard deviations for 11 standard samples. The results indicate the valuable analytical features achieved.

Interference Studies

The effects of several foreign ions on the simultaneous determination of cobalt and iron were studied by adding known quantities of a desired foreign ion to solutions of 200 and 50 ng/ml cobalt and iron, respectively. A deviation of more than 5% of the signal was taken as a sign of interference. Table 3 shows the tolerance limits for various species. It can be seen that cationic species that are

TABLE 3
Effect of Foreign Ions: Cobalt 200 ng/ml and Iron 50 ng/ml

Foreign species	Tolerance limit (ng/ml)	Foreign species	Tolerance limit (ng/ml)
Al ³⁺ , Mg ²⁺ , Na ⁺		Cl ⁻ , SO ₄ ²⁻ , SO ₃ ²⁻ ,	
Ca ²⁺ , Sr ²⁺ , K ⁺		NO ₃ ⁻ , CH ₃ COO ⁻	
Mn ²⁺ , Zn ²⁺		S ₂ O ₃ ²⁻ , tartrate, Br ⁻	10 ^{6a}
Cd ²⁺ , Cu ²⁺ , Bi ³⁺	10,000 ^a		
Hg ²⁺	4,800	NO ₂ ⁻ , F ⁻ , SCN ⁻	10 ⁵
Ni ²⁺ , Cr ³⁺	1,600	Oxalate, citrate	10 ⁴
		P ₂ O ₇ ⁼ , PO ₄ ³⁻	5000
		CN ⁻	200
		EDTA	10

^a Maximum tested.

TABLE 4
Determination of Mixtures of Cobalt and Iron in River Water

Sample	Found (ppb)		Added (ppb)		Found ^a (ppb)		Recovery (%)	
	Iron	Cobalt	Iron	Cobalt	Iron	Cobalt	Iron	Cobalt
					(RSD, %)	(RSD, %)		
1	50.1	—	40.0	300.0	90.6 (0.9)	295.5 (1.9)	100.5	99.5
2	48.2	—	40.0	300.0	88.7 (0.8)	303.9 (2.0)	100.6	101.3
3	50.3	—	40.0	300.0	89.5 (0.9)	296.1 (2.0)	99.1	98.7
4	45.3	—	40.0	300.0	86.1 (0.7)	304.2 (2.0)	100.9	101.4
5	49.0	—	40.0	300.0	88.3 (0.9)	303.0 (1.9)	99.2	101.0

^a Average of eight determinations. RSD, relative standard deviation.

known to react with PPT (11) are largely tolerated when derivative spectrophotometry is used. Contrarily EDTA and CN^- interfere negatively by inhibition of the complex formation reactions. However, the method proposed here is more selective than most of those reported in the literature.

Application of the Method

In order to test the analytical validity of this approach, the method has been applied to the analysis of cobalt and iron in river water. Since the proposed method is less sensitive for cobalt, which is also a minor component, the samples were spiked with a known quantity of cobalt.

The water samples were collected at the Maipo river in Santiago, Chile (in July 1992). They were instantly drawn through a membrane filter (pore size 0.45 μm .). The determination of iron and cobalt (spiked) of the filtrate was carried out using the proposed method (Table 4).

Conclusions

The simultaneous determination of cobalt and iron by the derivative technique permits both ions to be determined with good accuracy and precision and without the need to solve simultaneous equations. The proposed method is more selective than most of those reported in the literature. Cationic species were largely tolerated and only EDTA and cyanide interfered. The valuable analytical features of the method allow its application to real samples. In this context, the method can be used alternatively to the more expensive atomic absorption spectroscopy in the determination of both ions in water samples.

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REFERENCES

1. DiTusa, M. R.; Schilt, A. A. *Microchem. J.*, 1985, **32**, 44–49.
2. Afeworki, S; Chandravanshi, B. S. *Mikrochim. Acta*, 1987, **II**, 143–152.
3. Ballesteros, L.; Pérez-Bendito, D. *Analyst*, 1983, **108**, 443–451.
4. Garcia-Sanchez, F.; Hernandez-López, M.; Marquez-Gomez, J. C. *Anal. Chim. Acta*, 1987, **197**, 275–280.
5. Morelli, B. *Analyst*, 1983, **108**, 870–879.
6. Morelli, B. *Analyst*, 1983, **108**, 1506–1510.
7. Morelli, B. *Anal. Chim. Acta*, 1988, **209**, 175–184.
8. Morelli, B. *J. Pharm. Sci.*, 1988, **77**, 1042–1046.
9. Levillain, P.; Fompeydie, D. *Analusis*, 1986, **14**, 1–16.
10. Jiménez, A. I.; Jiménez, F; Arias, J. J. *Analyst*, 1989, **114**, 93–96.
11. Schilt, A. A.; Yang, T. A.; Wu, J. F.; Nitzki, M. *Talanta*, 1977, **24**, 685–687.