

Simultaneous Determination of Cobalt and Nickel by First-derivative Spectrophotometry

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A method for the simultaneous determination of cobalt and nickel in mixtures by first-derivative spectrophotometry is described. The method is based on the red complexes formed by both metal ions with 1-hydroxy-2-carboxyanthraquinone in alkaline ethanol - water mixtures. The range of application is between 0.75 and 4.5 $\mu\text{g ml}^{-1}$ for cobalt and between 0.50 and 3.0 $\mu\text{g ml}^{-1}$ for nickel. A statistical evaluation of the experimental results is reported.

Keywords: Cobalt determination; nickel determination; 1-hydroxy-2-carboxyanthraquinone; derivative spectrophotometry; simultaneous determination

Derivative spectrophotometry offers a convenient solution to a number of well defined analytical problems, such as resolution of multi-component systems, removal of sample turbidity, matrix background and enhancement of spectral details.¹ One of the classic analytical problems for any worker in the field of ultraviolet - visible spectrophotometry is the resolution of a number of components in a mixture. Most reports concerning derivative spectrophotometry have featured the application of this technique to multi-component resolution, demonstrating the importance of this approach.

Derivative spectrophotometry has been used for the simultaneous determination of inorganic ions through the formation of their complexes with the same organic ligand. Some examples are the determination of beryllium and magnesium with 1-hydroxy-2-carboxyanthraquinone,² ruthenium and palladium³ and iron and copper⁴ with 2-thiobarbituric acid, osmium and palladium with allylthiourea,⁵ nitrate and nitrite before reduction to nitrogen monoxide,⁶ lutetium and praseodymium with 1,4-dihydroxyanthraquinone⁷ and cobalt and nickel with benzyl 2-pyridyl ketone 2-pyridylhydrazone.⁸

1-Hydroxy-2-carboxyanthraquinone has been proposed for the photometric determination of beryllium,⁹ nickel,¹⁰ cobalt¹¹ and magnesium,¹² separately. The sensitivity of the proposed method for the determination of magnesium with this reagent was increased by the use of first-derivative measurements.¹² This reagent can also be used as a metallo-chromic indicator for cobalt.¹¹

The determination of cobalt and nickel in mixtures is difficult as these two elements mutually interfere owing to a considerable overlap of the spectra of their respective 1-hydroxy-2-carboxyanthraquinone complexes.^{10,11} Recently, we reported a simple, sensitive and rapid method for the simultaneous determination of beryllium and magnesium by first-derivative spectrophotometry² and it was envisaged that this approach might be useful for cobalt and nickel. Accordingly, this paper describes the application of first-derivative spectrophotometry to the simultaneous determination of cobalt and nickel in mixtures using 1-hydroxy-2-carboxyanthraquinone as the reagent. A single sample can be used and no prior separation is required.

Experimental

Apparatus

A Shimadzu UV - visible recording spectrophotometer (Model UV-160) and 1-cm quartz cells were used for the normal and first-derivative spectrophotometric measurements.

Reagents

All experiments were performed with analytical-reagent grade chemicals and pure solvents. Doubly distilled water was used throughout.

1-Hydroxy-2-carboxyanthraquinone. Synthesised by diazotisation of 1-amino-2-carboxyanthraquinone, followed by hydrolysis, according to the method of Scholl¹³ and purified by recrystallisation from glacial acetic acid. The purity was checked by thin-layer chromatography. The melting-point found, 223–225 °C, was in agreement with that reported in the literature.¹³ A 2×10^{-3} M solution was prepared by dissolving an accurately weighed amount of 1-hydroxy-2-carboxyanthraquinone in the appropriate volume of absolute ethanol.

Cobalt(II) stock solution, 1 g l⁻¹. Prepared from Co(NO₃)₂·6H₂O (Merck). The exact cobalt content was determined gravimetrically by the pyrophosphate method.

Nickel(II) stock solution, 1 g l⁻¹. Prepared from Ni(NO₃)₂·6H₂O (Merck). The exact nickel content was determined gravimetrically with dimethylglyoxime.

Procedure

Place an aliquot of the sample or standard solution containing between 7.5 and 45 μg of cobalt and between 5.0 and 30 μg of nickel in a 10-ml calibrated flask and add enough water to ensure a final water content of 50% V/V. Then add 4.0 ml of a 2.0×10^{-3} M ethanolic 1-hydroxy-2-carboxyanthraquinone solution and 0.40 ml of 2.0 M ammonia solution and dilute the mixture to the mark with ethanol. Record the first-derivative absorption spectra against a reagent blank. Determine the cobalt content from the first-derivative spectrum by measuring the first-derivative signal at the zero-crossing point for nickel (510.5 nm) and comparing the value with an appropriate calibration graph. Determine the nickel content by measuring the first-derivative signal at the zero-crossing point for cobalt (494.5 nm) and comparing the value with the appropriate calibration graph. The wavelengths of the zero-crossing points quoted are those obtained in this work but these values should be established independently for other instruments as part of the calibration procedure.

Results and Discussion

Effect of Experimental Variables

1-Hydroxy-2-carboxyanthraquinone forms red complexes with cobalt and nickel in basic media. In earlier work, these complexes were studied spectrophotometrically and pro-

cedures for the separate determination of both ions were reported.^{10,11}

The maximum absorbances of both complexes are obtained when the ammonia concentration in the medium is 0.08 M. The ethanol content of the medium also affects the absorbance of the complexes. An ethanol content of 50% V/V was selected as the optimum.

The absorbances are further affected by changes in the order of addition of reagents. The best results for analytical purposes are obtained when the ammonia is added after the metal ions and the anthraquinone reagent. An 8.0×10^{-4} M reagent concentration was selected as the optimum for the determination of cobalt and nickel in mixtures to ensure a sufficient excess of the anthraquinone. Under these conditions, complex formation is instantaneous and the absorbances remain stable for at least 3 h.

Spectrophotometric Measurements

Fig. 1 shows the absorption spectrum of the cobalt complex which has an absorption maximum at 494.5 nm, the corresponding spectrum of the nickel complex, with an absorption maximum at 510.5 nm and the total spectrum of a mixture of

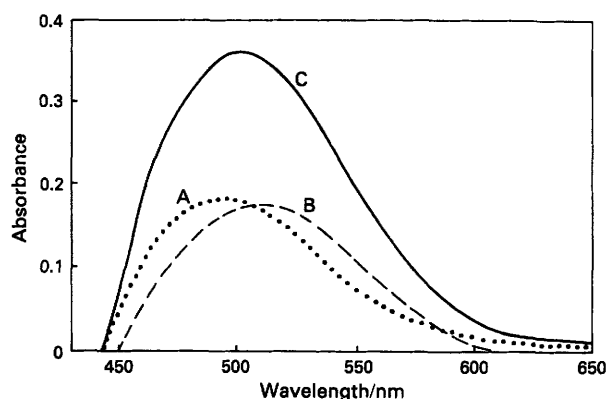


Fig. 1. Absorption spectra of (A) cobalt complex; (B) nickel complex; and (C) mixture of cobalt and nickel complexes. $[\text{Co}^{II}] = 3.0 \mu\text{g ml}^{-1}$; $[\text{Ni}^{II}] = 2.0 \mu\text{g ml}^{-1}$; reference, reagent blank

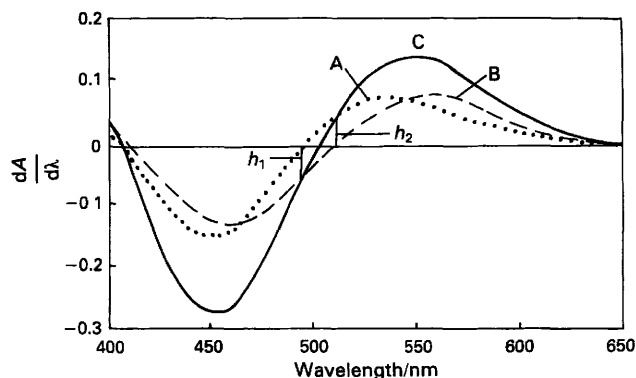


Fig. 2. First-derivative spectra of (A) cobalt complex; (B) nickel complex; and (C) mixture of cobalt and nickel complexes. $[\text{Co}^{II}] = 3.0 \mu\text{g ml}^{-1}$; $[\text{Ni}^{II}] = 2.0 \mu\text{g ml}^{-1}$; reference, reagent blank

both complexes with a maximum at 501 nm, located between the absorption maxima of the two components. All measurements were performed against a reagent blank because the reagent absorbs around these wavelengths.

As can be seen from Fig. 1, because of a large overlap between the two spectra, significant difficulties arise in the spectrophotometric determination of these ions when they are present in the same sample. To overcome this problem, derivative spectrophotometry can be used; this involves the differentiation of a normal spectrum with respect to wavelength.

Fig. 2 shows the first-derivative absorption spectra of the complexes of Co^{II} and Ni^{II} with 1-hydroxy-2-carboxyanthraquinone and of a mixture of both complexes. It can be seen that, because of the closeness of the two overlapping spectra of the cobalt and nickel complexes, these spectra are not sufficiently resolved to give two distinct peaks in the first-derivative spectrum of the mixture of both complexes; the first-derivative spectrum shows a maximum and a minimum at 453 and 545 nm, respectively [Fig. 2, curve (C)].

The two most commonly used techniques in derivative spectrophotometry¹⁴ are generally termed the "graphical method," which involves graphical construction on a chart recording of the spectrum, and the "zero-crossing method," which involves the measurement of the absolute value of the total derivative spectrum at a wavelength corresponding to the zero-crossing point of the derivative spectrum of the interfering component. In this instance, the graphical method cannot be used, because of the closeness of the overlapping spectra, which results in poor resolution of the spectrum of the mixture, *i.e.*, it is not possible to obtain two distinct peaks or shoulders proportional to, but independent of, the cobalt and nickel concentrations. In contrast, the zero-crossing method was used in this work with satisfactory results.

The zero-crossing method involves the measurement of the absolute value of the total derivative spectrum at an abscissa value (wavelength) corresponding to the zero-crossing point of the derivative spectrum of the interfering component. At this wavelength, the amplitude of the derivative signal of one of the two components passes through zero; measurement of the value of the derivative spectrum of a mixture, made at the zero-crossing point of the derivative spectrum of one of the two components, is, therefore, a function only of the concentration of the other component. Hence, the heights h_1 and h_2 in the first-derivative spectrum of the mixture [Fig. 2, curve (C)], corresponding to the values taken at 494.5 and 510.5 nm, are proportional to the nickel and cobalt concentrations, respectively.

Selection of Optimum Instrumental Conditions

The main instrumental parameters affecting the shape of the derivative spectra are the wavelength scanning speed, the wavelength increment over which the derivative is obtained ($\Delta\lambda$) and the response time. These parameters need to be optimised to give a well resolved large peak, *i.e.*, to give good selectivity and higher sensitivity in the determination.

In our spectrophotometer the derivative spectra are obtained by digital differentiation (convolution method) with 17–25 data points around each wavelength.

Table 1. Statistical analysis of the determination of cobalt ($0.75\text{--}4.5 \mu\text{g ml}^{-1}$) and nickel ($0.50\text{--}3.0 \mu\text{g ml}^{-1}$) in mixtures by first-derivative spectrophotometry

Element determined	Other element present		Slope	Intercept	Correlation coefficient	Standard deviation/ $\mu\text{g ml}^{-1}$
	Element	Concentration/ $\mu\text{g ml}^{-1}$				
Co^{II}	Ni^{II}	1.5	15.7×10^{-3}	-0.75×10^{-3}	0.999	0.059
		3.0	15.6×10^{-3}	-1.10×10^{-3}	0.998	0.066
Ni^{II}	Co^{II}	2.25	20.6×10^{-3}	0.25×10^{-3}	0.998	0.044
		4.50	20.2×10^{-3}	-0.31×10^{-3}	0.999	0.033

Generally, the noise level decreases with an increase in $\Delta\lambda$, thus decreasing the fluctuation in the derivative spectrum. However, if the value of $\Delta\lambda$ is too large, the spectral resolution deteriorates. Therefore, the optimum value of $\Delta\lambda$ should be determined by taking into account the noise level, the resolution of the spectrum and the sample concentration. Various values of $\Delta\lambda$ were tested and 17 nm was selected as the optimum, in order to give a satisfactory signal to noise ratio.

The scan speed of the monochromator has virtually no effect on the derivative signal obtained, because the differentiation is obtained digitally. Hence, a fast wavelength scanning speed (*ca.* 2400 nm min⁻¹) was selected. The response time is automatically selected by the spectrophotometer in accordance with the optical energy and the scanning speed.

Determination of Cobalt and Nickel in Mixtures: Statistical Analysis of the Results

In order to test the mutual independence of the analytical signals of cobalt and nickel, *i.e.*, to show that h_1 and h_2 are independent of the cobalt and nickel concentrations, respectively, the following experiments were performed.

Two calibration graphs were constructed from first-derivative signals for standards containing between 0.75 and 4.5 $\mu\text{g ml}^{-1}$ of cobalt, in the presence of 1.5–3.0 $\mu\text{g ml}^{-1}$ of nickel. Similarly, two calibration graphs were prepared for standards containing between 0.50 and 3.0 $\mu\text{g ml}^{-1}$ of nickel in the presence of 2.25–4.50 $\mu\text{g ml}^{-1}$ of cobalt.

A critical evaluation of the proposed method was performed by assessing the results of the statistical analysis of the experimental data. The slope, intercept, correlation coefficient and standard deviation (S_0) obtained are summarised in Table 1. The linearity of the calibration graphs and the adherence of the systems to Beer's law is validated by the high value for the correlation coefficient of the regression equation and by the value of the intercept on the y-axis, which is close to zero.

From Table 1, it can be seen that the slope of the calibration graph for cobalt is virtually independent of the nickel concentration. Similarly, the slope of the calibration graph for nickel is independent of the cobalt concentration. Therefore, it can be deduced that the amplitude of the derivative signal of the mixture, measured at the zero-crossing point of the derivative spectrum of one of the two components, is a function only of the concentration of the other component, in accordance with the theoretical predictions.

Statistical analysis of the calibration graphs permits calculation of the error, S_c , in the determination of a given concentration, c , of a component by using the following equation¹⁵:

$$S_c = \frac{S_0}{b} \left[1 + \frac{1}{n} + \frac{(D - \bar{D})^2}{b^2(\sum c^2 - nc^2)} \right]^{\frac{1}{2}}$$

where $S_0 = \sqrt{\sum (D - \bar{D})^2 / n - 2}$; D = experimental value of the first derivative; D' = first-derivative value calculated from the regression equation; b = angular coefficient of the regression line; and \bar{c} and \bar{D} are the average concentration and first-derivative value, respectively, for n standard specimens. The graphs of S_c versus cobalt and nickel concentrations are shown in Figs. 3 and 4, respectively, in the form of histograms.

The quantity S_c also allows the determination of confidence limits¹⁵ at the selected level of significance for the determination of unknown concentrations. These results are shown in Fig. 5 in the form of uncertainty per cent. in the concentration ($t_p S_c / c$) for all the calibration graphs, where t_p is the value of the Student's quantity at the 0.05 level of significance (95% probability) for $n - 2$ degrees of freedom. This is a useful way of representing confidence limits because it allows a direct calculation of the relative uncertainty in concentration over

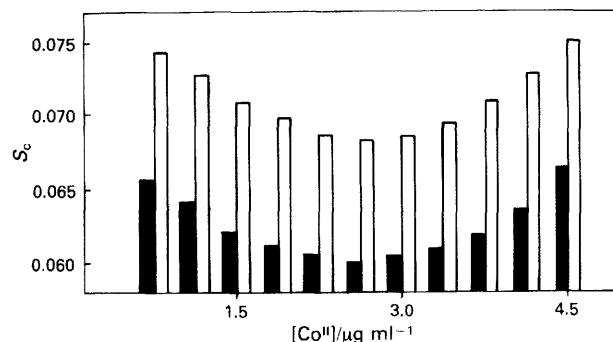


Fig. 3. Histograms of the error in the determination of the concentration of Co^{II}. Shaded area, in the presence of 1.5 $\mu\text{g ml}^{-1}$ of Ni^{II}; and unshaded area, in the presence of 3.0 $\mu\text{g ml}^{-1}$ of Ni^{II}.

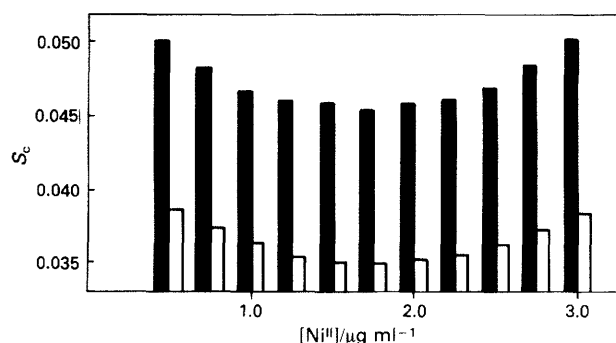


Fig. 4. Histograms of the error in the determination of the concentration of Ni^{II}. Shaded area, in the presence of 2.25 $\mu\text{g ml}^{-1}$ of Co^{II}; and unshaded area, in the presence of 4.5 $\mu\text{g ml}^{-1}$ of Co^{II}.

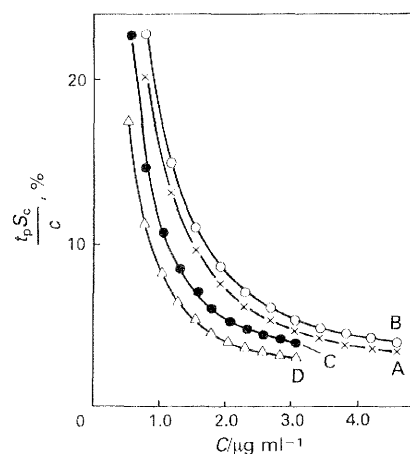


Fig. 5. Variation of the confidence limit at a level of significance of $p = 0.05$ (95% probability) in the form of uncertainty per cent. in the concentration of Co^{II} and Ni^{II}. (A) [Ni^{II}] = 1.5 $\mu\text{g ml}^{-1}$; (B) [Ni^{II}] = 3.0 $\mu\text{g ml}^{-1}$; (C) [Co^{II}] = 2.25 $\mu\text{g ml}^{-1}$; and (D) [Co^{II}] = 4.5 $\mu\text{g ml}^{-1}$.

the full range of concentrations tested, and hence it is a guide to the level of precision that may be expected from the application of the proposed analytical procedure.

In conclusion, a general procedure for the analysis of cobalt and nickel mixtures by first-derivative spectrophotometry using 1-hydroxy-2-carboxyanthraquinone as reagent is proposed and the usefulness of derivative spectrophotometry in this field is discussed. The proposed method permits the simultaneous determination of cobalt and nickel mixtures in the range 0.75–4.5 $\mu\text{g ml}^{-1}$ of Co^{II} and 0.50–3.0 $\mu\text{g ml}^{-1}$ of Ni^{II} without the need for tedious and time-consuming separation procedures. The method, based on the “zero-crossing measurement” technique, gives satisfactory levels of precision and accuracy.

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