Simultaneous Determination of Nickel, Zinc and Copper by Second-derivative Spectrophotometry Using 1-(2-Pyridylazo)-2-naphthol as Reagent

A. Gallardo Melgarejo, A. Gallardo Cespedes and J. M. Cano Pavón*
Department of Analytical Chemistry, Faculty of Sciences, University of Málaga, 29071 Málaga, Spain

A derivative spectrophotometric method, based on the use of second-derivative absorption spectra, has been developed for the simultaneous determination of microgram amounts of nickel, zinc and copper in an aqueous ethanolic medium. The peak to base line measurement technique has been used with good results. Using the proposed method, nickel (0.3–2.0 p.p.m.), zinc (0.5–3.0 p.p.m.) and copper (0.5–3.0 p.p.m.) in various ratios have been determined with good precision and accuracy.

Keywords: Derivative spectrophotometry; second-derivative spectra; nickel determination; zinc determination; copper determination

Derivative spectrophotometry is an analytical technique of great utility for extracting both qualitative and quantitative information from spectral curves composed of unresolved bands. In general, the derivative process discriminates against broad bands while emphasising sharper features to an extent that increases with increasing derivative order. However, the use of higher-order spectra is not recommended as a general procedure because the signal to noise ratio becomes progressively larger.1-5

Derivative techniques have been used in pharmaceutical analysis,6 environmental analysis7 and in the fingerprint analysis of proteins,8 but few data have been published on the determination of mixtures of inorganic ions. Using fifth-derivative spectrophotometry it is possible to determine calcium and zinc9 and palladium and platinum.9 A method has been developed for the rapid determination of small amounts of Nd, Ho, Er and Tm in a mixture of lanthanides by third-derivative spectrophotometry with thioyltrifluorocarbene.10 The analysis of a mixture of Sm and Eu has also been described11 in addition to the determination of zirconium in the presence of hafnium with picramine E.12

This paper describes the simultaneous determination of nickel, zinc and copper ions using 1-(2-pyridylazo)-2-naphthol (PAN) as the reagent; the prior separation of these metal ions is not necessary. In the normal spectra the bands due to these metal complexes show appreciable overlapping, which precludes their simultaneous determination. However, in the second-derivative spectra each complex shows a separate band.

The use of PAN as a reagent in normal spectrophotometry was first described more than 30 years ago; details of this work can be found elsewhere.13-15

Reagents
All chemicals used were of analytical-reagent grade. Standard solutions of nickel, zinc and copper. Prepared from nickel(II) nitrate hexahydrate, zinc(II) sulphate heptahydrate and copper(II) sulphate pentahydrate, respectively, in distilled, de-ionised water. These solutions were standardised titrimetrically with ethylenediaminetetraacetic acid (EDTA).

1-(2-Pyridylazo)-2-naphthol, 0.1% solution in ethanol.
Buffer solution, pH 4.8. Prepared by mixing 56.0 g of sodium acetate trihydrate and 25.0 ml of glacial acetic acid and diluting to 1 l with distilled water.
Buffer solution, pH 10.0. Prepared by mixing 67.5 g of ammonium chloride and 570 ml of concentrated ammonia and diluting to 1 l with distilled water.

Recommended Procedure
To an aliquot of the sample solution, containing 15–50 µg of nickel, 15–60 µg of zinc and 15–75 µg of copper, in a calibrated flask, add 5 ml of 0.1% PAN solution in ethanol, 10 ml of ethanol and 5 ml of the pH 4.8 acetic acid - sodium acetate buffer and dilute to the mark with distilled water. Record the second-derivative absorption spectra in the range 500–610 nm against a blank solution prepared in the same way. Measure the distances between the base line and the peaks of the derivative curves corresponding to nickel, zinc and copper at 545, 557 and 595 nm, respectively. For preparation of the calibration graphs, record the second-derivative absorption spectra for various known amounts of nickel, zinc and copper under the conditions given above. Construct the graphs as shown in Fig. 3.

Results and Discussion

Experimental

Apparatus
The absorption and derivative spectra were recorded on a Bausch Lomb Spectronic 2000 UV - visible spectrophotometer with 1-cm cells. Derivative spectra were generated by electronic differentiation; the spectrophotometer used had an adequate derivative module so that the first- and second-derivative spectra could be obtained directly. For the pH measurements, a Kilab 1001 potentiometer with a combined glass - calomel electrode was used.

* To whom correspondence should be addressed.
The characteristics of derivative spectra, such as peak height and noise level, depend on the choice of parameters such as scan speed and integration time during recording of the spectra. The optimum parameters were chosen from results of preliminary experiments. The best results were obtained with a scale range of 0.8, an average signal of 8, a wavelength interval of 1 nm and a scan speed of 50 nm min⁻¹.

The absorption spectra shown in Fig. 1 are for mixtures of the nickel, zinc and copper complexes at a concentration of 1 p.p.m. of each ion. Fig. 2 shows the spectra obtained for mixtures containing different concentrations of each ion. The intensity of the signals at 545 (distance OA), 557 (distance OB) and 595 nm (distance OC) are directly proportional to the amounts of nickel, zinc and copper present, respectively.

**Analytical Determination**

Nickel, zinc and copper can be determined on the basis of the peak heights at 545, 557 and 595 nm, respectively. In all instances the distances between the base line and the corresponding peaks are measured; good results were obtained (Fig. 2). This method is easier to use than the peak to peak method.

The metal complexes of PAN are only sparingly soluble in water so the use of a certain percentage of ethanol is necessary to prevent precipitation. A 3 + 2 ethanol - water medium was selected for all subsequent work.

The absorbance of the metal - PAN complexes is affected by pH; a constant zone (i.e., no variation in absorbance) is observed in acidic media. The use of an acetic acid - sodium acetate buffer (pH 4.8) is convenient.

The calibration graphs obtained show a linear relationship between the distances measured and the concentrations of the metal ions in the range 0.3-2.0 p.p.m. of nickel(II), 0.5-2.5 p.p.m. of zinc(II) and 0.5-3.0 p.p.m. of copper(II) (Fig. 3); the corresponding correlation coefficients are 0.998, 0.999 and 0.985. The sensitivity of the method is 0.2, 0.3 and 0.5 p.p.m. for nickel(II), zinc(II) and copper(II), respectively. Measurements on 11 solutions containing 1.0 p.p.m. of nickel, 2.0 p.p.m. of zinc and 2.0 p.p.m. of copper gave relative standard deviations of 3.7, 2.7 and 3.0%, respectively.

Table 1 gives the results of the simultaneous determination of nickel, zinc and copper, carried out as described under Recommended Procedure. It can be seen that the determination of these metal ions is feasible using peak to base line measurements.

An interference study showed that the influence of foreign ions on the determinations was similar to that reported in the literature for normal spectrophotometry. Hence, cobalt(II), iron(II), EDTA, phosphate, cyanide and citrate interfere at concentrations greater than 1.5 p.p.m. No mutual interference between nickel, zinc and copper was observed in the concentration ranges studied.
References


Received March 15th, 1988
Accepted July 19th, 1988