Analysis of Thulium and Neodymium Mixtures by using a Photometric Derivative Graphical Model*

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The determination of rare earth elements (REE) at trace levels is still very difficult because they are so similar in nature [1]. Serious interference problems are encountered when using direct determination instrumental techniques, especially when the samples contain large amounts of several REE at different concentration levels. Several analytical techniques have been developed for the determination of these elements. Trace amounts of REE are usually analysed by neutron-activation analysis [2], or by mass spectrometry [3], atomic absorption spectrometry [4], X-ray fluorescence [5], inductively coupled plasma spectroscopy [6], etc. There are several reagents to determine spectrophotometrically the total REE, such as Xylenol Orange, Arsenazo I and III, PAN, etc. None of these is specific for REE and their selectivity is poor, because of considerable overlap between their broad absorption spectra. The derivative technique is a resolution enhancement technique to facilitate the discrimination of poorly resolved components of a complex spectrum and therefore it is useful in resolving difficult mixtures [7, 8].

The authors have attempted to find a method to determine in a simple sample a pair of REE whose absorption spectra strongly overlap. The graphical model is based on the first derivative amplitudes measured from the isodifferential points in the calibration graphs and it was applied to the determination of thulium and neodymium without prior separation. This model is simple and reproducible and it has been recently applied to determine fluorimetrically binary mixtures of aluminium and gallium [9].

Experimental

Apparatus

Spectral measurements were made with a Shimadzu UV-240 Graphicord recording spectro-

photometer in 1-cm quartz cells. The spectra were obtained with a spectral bandwidth of 0.5 nm, a scanning speed of 3 nm cm^{-1} and recording chart speed of 10 nm cm^{-1}. First derivative spectra were obtained with a Shimadzu derivative spectrum attachment optional program/interface model OPI-2 (1st to 4th derivatives, $\Delta\lambda$ 1, 2 and 4 nm). The conditions $\Delta\lambda = 4$ nm, medium scanning speed (3 nm cm^{-1}) and the response time associated with the derivative circuit give satisfactory results.

Reagents

Stock solutions containing thulium and neodymium (≈ 9 g/l) were prepared from their oxides (99.99%, Sigma Chemical Co.). The oxides were dissolved in concentrated hydrochloric acid. The pH was adjusted to 4–5 by the addition of an excess of oxide and subsequent filtration of the solution. These solutions were standardized with EDTA using Xylenol Orange as indicator.

1,4-Dihydroxyanthraquinone (quinizarin, from Aldrich Chemical Co.) was recrystallized in methanol and 10^{-3} M solutions were prepared in the same solvent. Methanol (analytical reagent grade) was used without further purification.

Procedure

An aliquot (≤ 0.1 ml) of a sample aqueous solution ($6.5 \geq$ pH ≤ 4.5) containing 0.40–1.20 μg ml^{-1} of thulium and 0.40–1.20 μg ml^{-1} of neodymium was placed in a 10-ml calibrated flask. Quinizarin (2 ml of 1 $\times$ 10^{-3} M) in methanol was added and the solution was diluted to the required volume with methanol and water to obtain a 99.99% v/v methanolic proportion. The first derivative spectra were recorded between 540 and 590 nm against a reagent blank, with the following instrumental parameters: $\Delta\lambda = 4$ nm, scanning speed 3 nm cm^{-1}. The first derivative analytical value was measured as the vertical difference in the dA scale from the corresponding isodifferential point ($\lambda_1 = 557$ nm for neodymium, $\lambda_2 = 559$ nm for thulium) to the break with the first derivative curve. The concentrations of neodymium and thulium in the sample were determined from the corresponding calibration graph previously run under conditions similar to those of the mixture.

Discussion and Results

Thulium and neodymium give red coloured reactions with quinizarin in methanolic medium (99% v/v) with absorption maximum at 557 nm and 559 nm, respectively (Fig. 1). The chelates so formed are stable for at least 4 h; their absorbance values are

constant in the apparent pH range 4.5–6.5, and a four-fold molar excess of ligand is enough for complete complexation. The stoichiometry of the complexes in both cases is 1:1.

Because of the considerable overlapping of the spectra and the proximity of the absorption maxima (2 nm difference between them, Fig. 1), the individual determination of each element in mixtures is impeded.

It is known that the major benefits of derivative techniques are the increased resolution of overlapping spectral bands and the enhancement of relatively minor spectral features, resulting in improved selectivity over ordinary spectrophotometry. Figure 2 shows the first derivative spectra of two series of solutions containing increasing amounts of neodymium and thulium. In the baseline can be observed two isodifferential points at 557 nm and 559 nm for thulium and neodymium, respectively (maximum absorption wavelength for each one). At
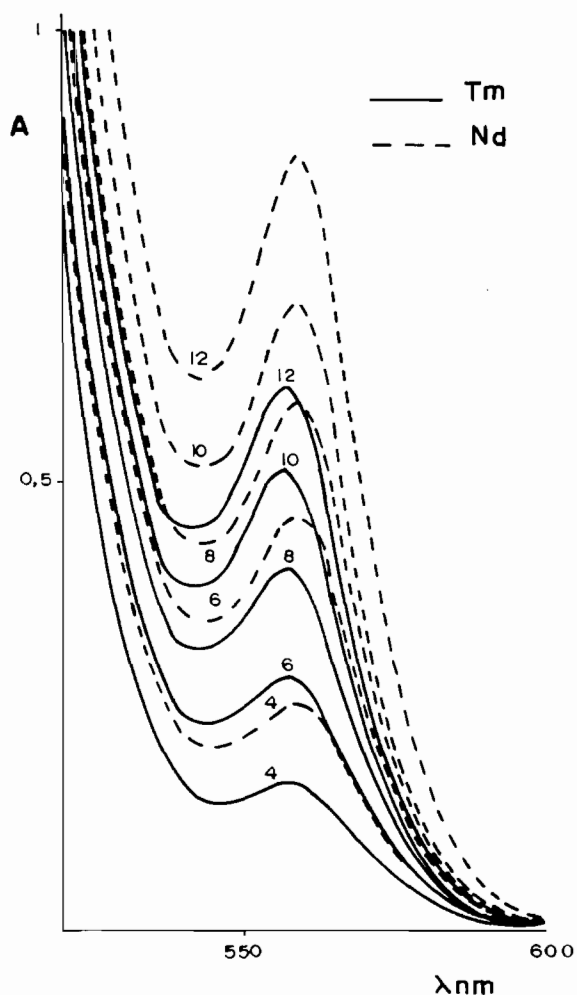
these wavelengths the change in the dA values with changing wavelengths arises from each chelate, so that the other compound can be determined without interference.

The model used in this paper to discriminate closely related spectral bands is based on the assumptions that Beer's Law is obeyed in the concentration range studied and that the derivative of a spectral band is equivalent to the sum of the derivatives of its component bands. Only a few data about the fundamental spectra of the compounds are needed to predict if two overlapping bands can be measured in good conditions by using the isodifferential derivative approach. These data are: maximum spectral intensity (Am), half-band width at half maximum intensity ($\frac{1}{2}B$) and separation between wavelength maxima of both compounds (C).

Assuming that the overlapping bands have a Gaussian profile, the absorbance of bands 1 and 2 are given as a function of wavelength (x)

$$A_1(x) = Am_1 \exp((-x - C_1)^2/2B_1^2)$$

$$A_2(x) = Am_2 \exp((-x - C_2)^2/2B_2^2)$$

The first derivative of band 1 is expressed as

$$\frac{dA_1(x)}{dx} = -\frac{Am_1(x - C_1)}{B_1^2} \exp\left(\frac{-(x - C_1)^2}{2B_1^2}\right)$$

and the second derivative of band 2 is

$$\frac{d^2A_2(x)}{dx} = \frac{Am_2}{B_2^2}\left(\frac{(x - C_2)^2}{B_2^2} - 1\right) \exp\left(\frac{-(x - C_2)^2}{2B_2^2}\right)$$

Maximum sensitivity and precision are obtained in the isodifferential derivative method when the first derivative amplitude of component 1 is zero at the same wavelength in which the second derivative of the component 2 is zero. The solutions for $d^2A_2(x)/dx^2 = 0$ and for $dA_1(x)/dx = 0$ are satisfied when $C_1 = x$ and $(x - C_2) = 1$, *i.e.* when $C_1 - C_2 = B_2$. This implies that the best conditions for evaluation of amplitude values of component 2 from the zero crossing of component 1 are obtained when the separation between maxima ($C_1 - C_2$) is equal to the band half-width at half maximum height of component 2, B_2. Inversely, $C_1 - C_2 = B_1$ from the isodifferential point of component 2 presents optimal conditions.

Quantitative Analysis

The calibration graphs obtained by plotting absorbance and dA *versus* thulium and neodymium concentrations were linear for 0–12 μg/ml in both cases. The equations obtained by the least-squares method were

Fig. 1. Absorption spectra of two series of thulium and neodymium complexes covering the concentration range indicated in the curves (in μg/ml); [R] = 2 × 10^{-4} M.
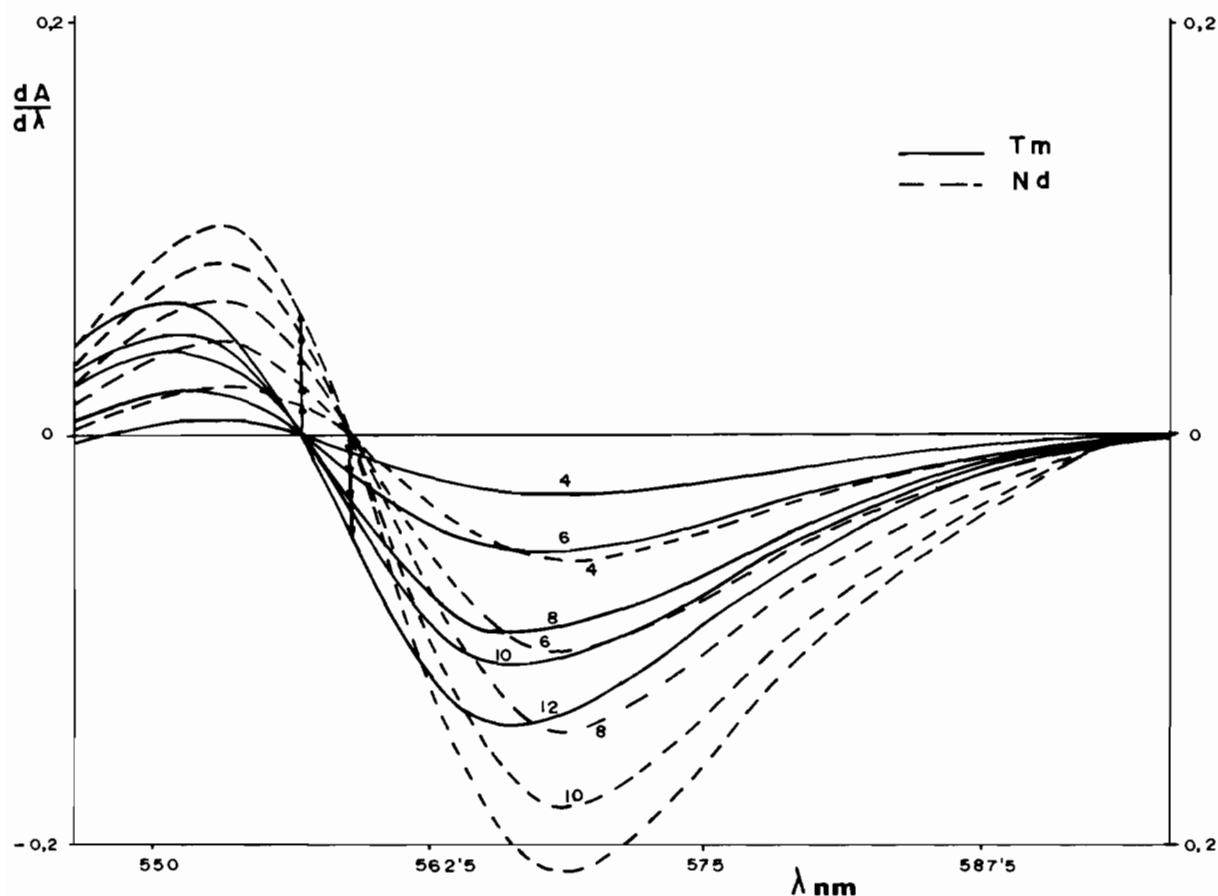
Fig. 2. Superimposed first derivative spectra of two series of thulium and neodymium complexes covering the concentration range indicated in the curves (in $\mu g/ml$); [R] = 2 × 10^{-4} M.

TABLE I. Analysis of Binary Mixtures of Thulium and Neodymium

	Ratio Nd:Tm (w/w)	Neodymium amount (g/ml)		Error (%)	Thulium amount (g/ml)		Error (%)
		Taken	Found[a]		Taken	Found[a]	
1st derivative	1:1	4.00	3.80 ± 0.18	−5.0			
	1:1	6.00	6.15 ± 0.10	+2.5			
	1:2	4.00	4.04 ± 0.05	+1.1			
	1.5:1	6.00	6.15 ± 0.18	+2.5			
	2:1	8.00	7.57 ± 0.30	−5.0			
	2.5:1	10.00	9.57 ± 0.17	−4.3			
	1:1				4.00	3.90 ± 0.12	−2.5
	1:1.3				8.00	8.11 ± 0.10	+1.5
	1:2.5				10.00	9.69 ± 0.17	−3.0
	1.3:1				6.00	5.75 ± 0.27	−4.1
	2:1				4.00	3.90 ± 0.11	−2.5
	2.5:1				4.00	3.90 ± 0.15	−2.5

[a]Standard deviation (three separate determinations) was calculated from the range 0.59 × (highest value − lowest value).

$dA = 0.00507$ [Tm] $- 0.00915$

$r = 0.993$ (in mixtures)

$dA = 0.00556$ [Nd] $- 0.00969$

$r = 0.990$ (in mixtures)

The results obtained in the determination of each ion in binary mixtures for different metal/metal ratios are shown in Table I. It can be seen that the reported method gives satisfactory results for analysing the binary mixtures outlined.

Acknowledgement

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