Determination of Neodymium with 1-(2-Pyridylazo)-2-naphthol in Micelles of Triton X-100 by Derivative Spectrophotometry*

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There are few methods for the spectrophotometric determination of neodymium [1] and, except those that employ arsenazo(III) [2, 3], their low sensitivity makes them unsuitable. Derivative spectrophotometry [4–6] has opened excellent possibilities for increasing the sensitivity and selectivity of analytical methods.

1-(2-Pyridylazo)-2-naphthol has been used in the separation and determination of rare earths [7, 8]; however, the low solubility of the chromophore and of the chelates requires the use of non-aqueous media.

The use of micellar media can be one of the best ways of avoiding the extraction processes [9–11] and in many cases increasing the sensitivity and selectivity of the analytical methods.

Experimental

Reagents

Solutions of neodymium were prepared by dissolving a suitable amount of the oxide (Nd_2O_3, 99.9% pure) in the smallest volume possible of HCl and then dilution with water. Ethanolic solution of 1-(2-pyridylazo)-2-naphthol (Merck) and aqueous solutions of Triton X-100 (Merck) were used. Buffer solution was $HBO_2/NaBO_2$. All reagents used were of analytical grade.

Apparatus

A Shimadzu UV 160 spectrophotometer and cells of 10 mm optical pathway were used. A radiometer PHM 51 pH meter was used with a combined Metrohm AG-1800 glass electrode. Statistical parameters were obtained using the 'Statworks' program on an Apple Macintosh computer.

Procedures

Conventional spectrophotometry

Successive additions were made to the 1-(2-pyridylazo)-2-naphthol solution in the following order: a suitable amount of Triton X-100 such that the Triton X-100/PAN ratio expressed in g/mg was 0.10, the solution of neodymium and the buffer solution ($[HBO_2 + NaBO_2] = 0.04$ M, pH = 9.2), then dilution with water up to the desired volume. Absorbance was measured at 535 nm against a blank after at least 10 min.

Derivative spectrophotometry

Having obtained the corresponding absorption spectrum (375–1025 nm), the fourth-order derivative was obtained for a $\Delta\lambda$ value of 54 nm. The analytical signal was obtained by measuring the peak–valley signal at 550 nm and 612 nm, respectively.

Results and Discussion

Absorption Spectra

The Nd–PAN–TX-100 system shows an absorption band with a maximum at 535 nm and a shoulder at 560 nm (Fig. 1). The fourth-order derivative has a peak at 550 nm and a valley at 612 nm (Fig. 1, dotted line).

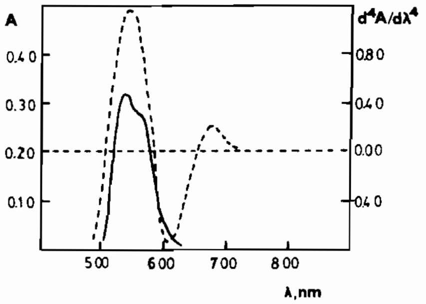

Fig. 1. Absorption spectrum and fourth-order derivative spectrum of the Nd–PAN–TX-100 system: $[Nd] = 8.0 \times 10^{-6}$ M, $[PAN] = 1.6 \times 10^{-4}$ M, TX-100/PAN = 0.10 g/mg, pH = 9.2, $[HBO_2 + BO_2^-] = 0.04$ M).

Influence of the Order of Addition of the Reagents

The order of addition of the reagents does not affect the spectrum but does affect the time necessary to reach stable values of absorbance. The most suitable order of addition proved to be: PAN, TX-100, neodymium and then buffer solution.

Influence of the Concentration of Triton X-100 (TX-100)

The results obtained (Fig. 2) show that for the same reaction time, absorbance decreases as the

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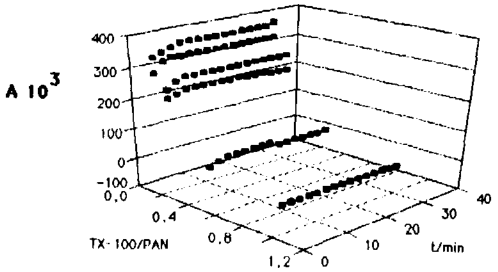

Fig. 2. Influence of the TX-100/PAN ratio and reaction time on the absorbance of the system Nd–PAN–TX-100: [Nd] = 8.0×10^{-6} M, [PAN] = 8.0×10^{-5} M, pH = 9.2, [HBO_2 + BO_2^-] = 0.04 M.

TX-100/PAN ratio increases; as the concentration of tensoactive agent increases a rise appears only in the number of micelles in solution; this causes a decrease in the concentration of chromophore per micelle and hence greater difficulty in the formation of the complex.

A TX-100/PAN ratio of 0.10 g/mg was chosen as the most suitable; at lower values the system forms turbid solutions.

Effect of pH

The variation in absorbance of the Nd–PAN–TX-100 system with pH fits an inverted bell-shaped curve with the flat zone for values ranging between 8.5 and 10 (Fig. 3). From among the different buffers employed the $HBO_2/NaBO_2$ (0.04 M) was found to be the most suitable.

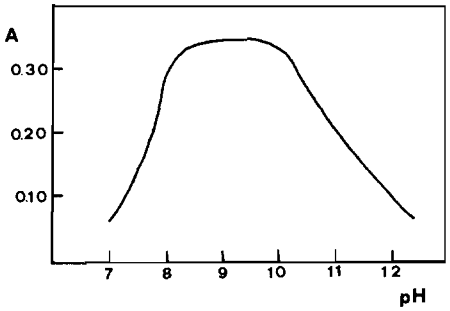

Fig. 3. Effect of pH on the absorbance of the system Nd–PAN–TX-100: [Nd] = 8.0×10^{-6} M, [PAN] = 8.0×10^{-5} M, TX-100/PAN = 0.10 g/mg.

Stoichiometry of the Compound Formed

The stoichiometry of the compound, determined by the slope–ratio method, proved to be 3:1 (PAN/Nd) in the presence of an amount of tensoactive agent such that the TX-100/PAN ratio was 0.10 g/mg.

Optimization of Variables

The chemical variables pH, TX-100/PAN ratio and reaction time were optimized by the modified Simplex method [12], considering as the function to be maximized the value of absorbance at 535 nm; these proved to be as follows: pH = 9.2; TX-100/PAN = 0.10 g/mg and t = 10 min.

The variables measuring wavelength range, Δλ and the order of the derivative were also optimized by the modified Simplex method, considering as the function to be optimized the values of the peak–valley distance corresponding to the derivative of the spectrum; these proved to be as follows: measuring wavelength range 650 nm (1025–375); Δλ = 54 nm and order of derivative = 4.

Calibration Graph, Precision and Detection Limit

In the conventional spectrophotometric method the Nd–PAN–TX-100 system fulfills Beer's law at 535 nm, the data fitting the equation: $A = 4.43 \times 10^4\ [\mathrm{Nd}] + 0.008$ ($r = 0.9996$) with a relative standard deviation ($n = 10$, [Nd] = 4.0×10^{-6}) of 0.95% and a detection limit ($3S_B/\epsilon$) of 1.8×10^{-7} M (25 ppb).

In derivative spectrophotometry the results obtained fit the equation $d^4A/d\lambda^4 = 2.48 \times 10^5\ [\mathrm{Nd}] - 0.002$ ($r = 0.9998$) with $s_r = 0.89\%$ and a detection limit of 9.8×10^{-8} M (11 ppb) under the same conditions as above.

Selectivity of the Method

The reagent PAN forms chelates with many cations [4], among which are those that are present in certain glasses and which thus interfere in the determination. However, their separation is easy by extracting them as diethyldithiocarbamates with a 1:1 chloroform/ethyl acetate mixture. Ce(IV) is not extracted under these conditions and small amounts of this element produce a marked decrease in the neodymium signal. The interference of Ce(IV) can be avoided by previously precipitating the corresponding basic salt in the presence of $KBrO_3$.

The divalent and monovalent cations do not interfere even at concentrations close to 0.01 M.

Of the anions studied, the following do not produce interference ($E \leqslant 3\%$) for 100 anion/Nd ratios ([Nd] = 8.0×10^{-6} M): Cl^-, Br^-, I^-, NO^{3-}, $S_2O_3^{2-}$, CO_3^{2-}, ClO_4^- and $C_2O_4^{2-}$. The ions F^- and tartrate interfere at ratios close to 10. Citrate and PO_4^{3-} are serious interferences and must be absent.

Since the lanthanides must be present, under the experimental conditions, in the form of hydroxocomplexes and the reagent must be present in the undissociated form, the complexing reaction may be expressed as:

$$\mathrm{Nd(OH)}_n^{3-n} + 3\mathrm{PANH} \rightleftharpoons \mathrm{Nd(PAN)}_3 + 3\mathrm{H_2O} + (n-3)\mathrm{OH}^-$$

Determination of Neodymium in Commercial Glasses

Glasses are essentially a solution of oxides; the presence of Fe(II) in the raw materials gives a green tone to the glass which in most cases is undesirable. When the glass to be made must be colourless, a first addition of Ce(IV) is made to oxidize the Fe(II) to Fe(III); this gives the final manufactured product a yellow colouring. The yellow tone can then be optically compensated by adding neodymium (light violet tone).

Procedure

Approximately 0.25 g of mortar (agate)-ground glass were treated with 2.0 ml of HNO_3, 10 ml of $HClO_4$ and 20 ml of HF in a Teflon or platinum crucible, heating the mixture to 150 °C and bringing it to dryness. Following this, a further 10 ml of $HClO_4$ were added and the mixture was brought to dryness again. The residue was dissolved in dilute HCl and the volume was brought up to 10.0 ml. Five ml of this solution were treated with 3 ml of 1 M diethyldithiocarbamate, extracting with 20 ml of the chloroform–ethyl acetate mixture (1:1). The aqueous phase was neutralized to pH = 6 and treated with 2.0 ml of 0.1 M $KBrO_3$. The precipitate obtained (the basic salt of cerium) was filtered off and washed with 0.01 M $KBrO_3$. To the solution obtained, together with the washing liquids, were added 5.0 ml of PAN (4.0×10^{-3} M), Triton X-100 and buffer solution, and the volume was made up to 50.0 ml. Absorbance was measured at 535 against a blank after at least 10 min have elapsed.

Derivative spectrophotometry was used, scanning from 375 nm to 1025 nm and measuring as indicated in the general procedure.

The results obtained with both the conventional spectrophotometric method and the derivative method were contrasted with those obtained with the X-ray fluorescence method (Table I). This method can be used for other lanthanides.

TABLE I. Determination of Neodymium in Commercial Glass

Sample	Nd_2O_3 (%)		
	Conventional spectrophotometry	Derivative spectrophotometry	X-ray fluorescence
1	0.03(7)	0.03(7)	0.05
2	0.03(6)	0.03(7)	0.05
3	0.03(7)	0.03(6)	0.05

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