Absorption Spectra of the 4f Electron Transitions of the Praseodymium Complex with 1-Cyclopropyl-6-fluoro-1,4-dihydro-7-(4-ethyl-1-piperazinyl)-4-oxo-3-quinoline Carboxylic Acid Hydrochloride and Its Analytical Application

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The absorption spectra of the praseodymium complex with 1-cyclopropyl-6-fluoro-1,4-dihydro-7-(4-ethyl-1-piperazinyl)-4-oxo-3-quinoline carboxylic acid hydrochloride (NNFX) has been studied by normal and derivative spectrophotometry. The complex showed maximum absorption at 350 nm at pH 6.0. The stoichiometry of the Pr-NNFX complex was calculated by the molar ratio and continuous variation methods. The ratio of Pr to NNFX was 1:3. The absorption bands of the 4f electron transitions of the praseodymium complex with NNFX are enhanced markedly, especially the wavelength at 481 nm. Using the third-derivative spectrum, the calibration graph is linear over the range 2.5×10^{-5} – 3.5×10^{-4} mol dm⁻³ for praseodymium. The detection limits (signal-to-noise ratio of 2) is 1.4×10^{-6} mol dm⁻³. The relative standard deviation is 1.2% for 7.0×10^{-5} mol dm⁻³ of praseodymium. A method for the direct determination of praseodymium in rare earth mixtures with good accuracy and selectivity is described.

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A number of metallochromic reagents have been described for the spectrophotometric determination of praseodymium.^{1–5} None of them are specific for praseodymium in the presence of other rare earths because of a considerable overlap between their broad absorption spectra. However, there has long been interest in the determination of individual elements based on the absorption bands of their 4f electron transitions.^{6–11} In recent papers, the third/second derivative spectrophotometric determination of complexes formed by some rare earths with 8-hydroxyquinoline and its derivative,^{12–15} β -diketones^{16,17} and inorganic salts^{18,19} were investigated, which can be utilized for the determination of neodymium, holmium and erbium. However, applications to praseodymium are rare.

1-Cyclopropyl-6-fluoro-1,4-dihydro-7-(4-ethyl-1-piperazinyl)-4-oxo-3-quinoline carboxylic acid hydrochloride (NNFX) is the third representative of antibacterial medicine, namely the quinolone group, used extensively in clinical treatment with higher potential and a broad antibacterial spectrum as well as fewer side effect. However, its utilization as a reagent for the determination of rare earth elements has not been reported. In the present work, the absorption spectra of the praseodymium complex with NNFX was investigated by applying both normal and derivative spectrophotometric methods. On this basis, a method was developed for the direct determination of praseodymium in rare earth mixtures. The analytical results obtained are satisfactory.

Experimental

Apparatus

A Shimadzu UV-3000 double-beam spectrophotometer

(Kyoto, Japan) with 4.0-cm cells was used. The pH-values of the solutions were measured with a pHs-2 meter (Analytical Apparatus Plant, Shanghai, China).

Reagents and chemicals

Stock lanthanide solutions (0.01 M) were prepared by dissolving an appropriate amount of pure oxides (Johnson Matthey, Royston, Hertfordshire, UK) in hydrochloric acid (1+1), and working solutions were prepared by dilution with water. A solution of 1-cyclopropyl-6-fluoro-1,4-dihydro-7-(4-ethyl-1-piperazinyl)-4-oxo-3-quinoline carboxylic acid hydrochloride (NNFX, 0.05 M) was prepared by dissolving 1.797 g of NNFX (Zibo Pharmacy Plant, People's Republic of China) in 100 ml of distilled water in a calibrated flask. A buffer solution of pH 6.0 was prepared by dissolving 200 g of hexamethylene tetramine in 500 ml of distilled water, the pH being adjusted with hydrochloric acid (1+1) and diluting to 1000 ml with distilled water.

Analytical-reagent grade chemicals were used whenever possible.

Procedure

A known volume of a lanthanide solution (containing Pr up to 50 μ g) was transferred into a 10 ml calibrated flask; 3.0 ml of 0.05 M NNFX and 4.0 ml of pH 6.0 buffer solutions were added. The mixture was diluted to the mark with distilled water, and after 30 min the third-derivative spectra were recorded against a reagent blank using 4.0-cm cells with a $\Delta\lambda$ of 2.8 nm, a band pass of 1.0 nm and a scan rate = 50 nm min⁻¹ as instrumental parameters. The amplitudes were measured between the 484.5(+) nm positive peak and the 482.5(–) nm negative peak for praseodymium.

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Fig. 1 Absorption spectra of the reagent, lanthanide complexes, and praseodymium ion. $[\text{Ln}^{3+}] = 2.5 \times 10^{-4} \text{ M}$, $[\text{NNFX}] = 1.5 \times 10^{-2} \text{ M}$. pH = 6.0, 4.0-cm cells. 1, Pr; 2, La; 3, Nd; 4, Gd; 5, Er; 6, Ho; 7, $\text{Pr}^{3+}(\text{PrCl}_3)$; 8, NNFX. Reference: 1 - 6, reagent blank; 7 & 8, water.

Fig. 2 Third-derivative spectra of lanthanide complexes. $\Delta\lambda = 2.8 \text{ nm}$, band pass = 1.0 nm , scan rate = 50 nm min^{-1} . Other conditions were the same as in Fig. 1, curves 1 - 6.

Results and Discussion

Absorption spectra

The absorption spectra of Pr^{3+} , Ln^{3+} -NNFX and NNFX systems are shown in Fig. 1. From Fig. 1, it is evident that the differences between curves 1 and 7 show some changes in the spectral features. The absorption peaks of Pr^{3+} as chloride are at 466.5 nm and 480 nm; those of the complex move to longer wavelengths of 469 nm and 483 nm. The sensitivity is enhanced by factors of 6.5 (at 469 nm) and 8.3 (at 483 nm), respectively. It can be concluded that the absorption bands are changed because the strength of the coordinate field of NNFX surrounding the Pr^{3+} is sufficient to penetrate the shielding by 5s5p shells. A narrow absorption band at 483 nm

Fig. 3 Effect of the pH on the absorbance of the complex. $[\text{Pr}^{3+}] = 1.0 \times 10^{-4} \text{ M}$, $[\text{NNFX}] = 1.5 \times 10^{-2} \text{ M}$. The instrumental parameters were the same as in Fig. 2. The Pr peak-to-valley amplitude measurements were at 484.5(+) nm and 482.5(-) nm.

Fig. 4 Effect of NNFX on the absorbance of the complex. pH = 6.0. Other conditions were the same as in Fig. 3, except for the NNFX concentrations.

corresponding to the $^3\text{H}_4 \rightarrow ^3\text{P}_0$ transition²⁰ of Pr^{3+} , allows its determination by means of the derivative spectra. The other lanthanide complexes in this wavelength range show only pure complex background absorption, except that the 4f electron transitions of the holmium complex at 450 nm was lightly enhanced. The experimental results show that the normal spectrophotometry for praseodymium is subject to interference of the pure complexes background absorption by other lanthanides. Therefore, we investigated the first- to fourth-derivative spectra of different lanthanide complexes and variable measuring parameters of the instrument. The optimum instrumental conditions for praseodymium determination are the use of the third-derivative spectrum with a $\Delta\lambda$ of 2.8 nm, a band pass of 1.0 nm and a scan rate of 50 nm min^{-1} , because they afforded the best sensitivity. Figure 2 shows the third-derivative spectra of the representative lanthanide complexes. It is obvious that the optimal analytical signals are at 484.5(+) nm positive peak and 482.5(-) nm negative peak for the praseodymium complex, where other lanthanide complexes produce only a constant absorption signal, thus causing no interference for praseodymium.

Optimization of reaction conditions

The chemical variable pH and reagent were optimized for praseodymium by varying one of them at a time (see Figs. 3 and 4). On this basis, the optimum conditions for praseodymium thus selected were those given in the procedure. Taking into account the consumption of the reagent by other lanthanides in the mixtures, the NNFX amount recommended in the procedure

Fig. 5 Absorption spectra of the different complexes. $[\text{Pr}^{3+}] = [\text{Nd}^{3+}] = [\text{Ho}^{3+}] = 1.0 \times 10^{-4} \text{ M}$, $[\text{NNFX}] = 3.0 \times 10^{-4} \text{ M}$. pH = 6.0, 1.0-cm cells. 1, Pr; 2, Nd; 3, Ho

Scheme 1

is about 20-times greater than necessary for the sum of the lanthanides present. The complex takes 25 min to form, and the derivative absorption signal is stable for at least 48 h.

Determination of the stoichiometry of the complex

The determination of the composition of the complex by means of the visible absorption spectra based on the 4f electron transitions of the praseodymium complex are not definitive conclusions because the absorption signals vary little with the changes in the NNFX concentration. Therefore, the ultraviolet absorption spectra of the complexes of the praseodymium and other lanthanides at pH 6.0 were studied. Figure 5 shows the absorption spectra of some lanthanide complexes, from which it was found that the complexes have a maximum absorption peak at 350 nm, and that the spectral characteristics of the complexes are similar.

With praseodymium as a representative, the composition of the complex was investigated by means of the molar ratio and continuous-variation methods. The experimental results are shown in Fig. 6. Both methods produced similar results,

Fig. 6 Determination of the stoichiometry of the complex. pH = 6.0, 1.0-cm cells, $\lambda = 350 \text{ nm}$. (a) Molar ratio method, $[\text{Pr}^{3+}] = 1.0 \times 10^{-4} \text{ M}$. (b) Continuous variation method for the Pr to NNFX ratio; total concentration = $5.0 \times 10^{-4} \text{ M}$.

showing that the complex had a praseodymium-to-ligand ratio of 1:3. We therefore guess that the complex $\text{Pr}(\text{NNFX})_3$ is formed under the experimental conditions, the structure of which is probably as shown in Scheme 1. The results for the other elements (Nd, Ho, etc.) are similar to those of Pr.

Calibration graphs, precision and detection limits

The third derivative spectra (Fig. 7) provide a linear calibration graph over the range $2.5 \times 10^{-5} - 3.5 \times 10^{-4} \text{ M}$ of praseodymium (in the final solution). The equation obtained by the least-squares method is

$$dA = 0.0012 + 7.41[\text{Pr}^{3+}], r = 0.9993 (n = 8),$$

where $[\text{Pr}^{3+}]$ is the concentration in M, and r is the correlation coefficient. The relative standard deviation evaluated from seven independent determinations of $7.0 \times 10^{-5} \text{ M}$ of praseodymium are 1.2% for praseodymium alone and 1.49% in the presence of $7.0 \times 10^{-4} \text{ M}$ lanthanum. The detection limit (signal-to-noise ratio = 2) is $1.4 \times 10^{-6} \text{ M}$.

Effect of diverse ions

The effect of foreign ions and REEs ions was studied by adding a solution of the ions to a sample containing $7.0 \times 10^{-5} \text{ M}$ of praseodymium and subjecting the solution to the above procedure. The highest permissible molar excesses of other ions (*i.e.*, causing a $\pm 5\%$ relative error in the third-derivative absorption signals) were as follows: Mg^{2+} (800); Ca^{2+} (650); Sr^{2+} ,

Fig. 7 Spectral curves for the praseodymium complex. $[\text{NNFX}] = 1.5 \times 10^{-2} \text{ M}$, $\text{pH} = 6.0$. The instrumental parameters were the same as in Fig. 2. Curves from inner to outer, $([\text{Pr}] \times 10^{-4} \text{ M})$: 0, 0.25; 1, 0.50; 2, 1.00; 3, 1.50; 4, 2.00; 5, 2.50; 6, 3.00; 7, 3.50.

Table 1 Compositions of synthetic samples (oxides %m/m) and analytical results

	Present	Found ^a , %	RSD ^b , %
No. 1	La 21.04, Ce(IV) 47.52, Pr 3.70, Nd 14.60, Ho 4.00 Sm 0.80, Eu 0.73, Gd 1.21, Tb 0.20, Er 4.00	3.55	2.0
No. 2	La 1.85, Ce(IV) 3.62, Pr 5.50, Nd 3.25, Sm 1.89, Eu 1.13, Gd 10.27, Tb 5.78, Ho 4.22, Er 6.00, Y 56.49	5.62	1.7

a. Average of five determinations.

b. RSD = relative standard deviation ($n = 5$)

Ni^{2+} , Co^{2+} (280); Cu^{2+} , Cr^{3+} , Zn^{2+} (250); Ga^{3+} , In^{3+} , Mn^{2+} (120); Ln^{3+} (100); Hg^{2+} , Au^{3+} , Ti^{4+} , Th^{4+} , Zr^{4+} , Pb^{2+} , Ce^{3+} , Ce^{4+} (80); Fe^{3+} (20). Larger amounts decreased the absorption signals.

Analytical application

In order to evaluate the applicability of the proposed method, the results obtained for two synthetic samples (prepared based on the relative contents of rare earth oxides in the earth's crust²¹) are given in Table 1.

In addition, two reference materials and a lanthanide base rock sample containing a little Ca, Mg, Sr, Fe, Al, Th, Zr metals were also analyzed for praseodymium. In the procedure, 0.5 g of the reference material was dissolved in 10 ml of hydrochloric acid (1+1) by heating with a few drops of hydrogen peroxide, and then evaporated nearly to dryness on a water-bath. The residue was dissolved in water, filtered if needed and diluted to 100 ml with water in a calibrated flask. An aliquot (0.50 – 1.50 ml) of this solution was diluted and transferred into a 10 ml calibration flask. The praseodymium content was then determined by the above procedure. The obtained results are given in Table 2. These results are in agreement with the

Table 2 Analytical results of praseodymium in three reference materials

	Present (oxides %m/m)	Found ^a	RSD ^b
No.1	La 27.11, Ce(IV) 49.21, Pr 5.18, Nd 16.75, Dy 0.09 Eu 0.23, Sm 1.29, Gd 0.40, Tb 0.03, Tm 0.0095 Ho 0.023, Er 0.027, Y 0.27, Yb 0.013, Lu 0.003	5.15	1.2
No.2	La 13.83, Ce(IV) 62.98, Pr 5.76, Nd 14.43, Eu 0.25 Yb 0.015, Gd 0.42, Tb 0.027, Dy 0.077, Ho 0.019 Er 0.022, Y 0.045, Tm 0.0076, Sm 1.83, Lu 0.001	5.60	1.0
No.3	La 23.10, Ce(IV) 0.90, Pr 7.31, Nd 21.53, Sm 2.21, Tb 0.32, Y 5.25, Ho 0.98, Er 0.30, Yb 0.24, Gd 3.24	7.21	0.88

a. Average of five determinations.

b. RSD = relative standard deviation ($n = 5$).

No.1 and No.2 from Baotou Rare Earths Academy, China.

No.3 from Jiangxi Xiunwu lanthanide base rock samples, China

certified values.

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