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SIMULTANEOUS DETERMINATION OF SAMARIUM, EUROPIUM AND TERBIUM WITH QUINALDIC ACID AND PHENANTHROLINE BY SYNCHRONOUS DERIVATIVE FLUORIMETRY

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Summary—Synchronous derivative fluorescence of samarium, europium and terbium complexes with quinaldic acid and phenanthroline was examined in aqueous solution. The composition of these complexes was determined. The maximum emission wavelengths are 645 nm, 617 nm and 545 nm for samarium, europium and terbium, respectively. Under the optimal experimental conditions, the fluorescence intensity was a linear function of concentration in the range of 10–250 ppm for samarium, 0.5–50 ppm for europium and 0.5–300 ppm for terbium. Simultaneous determination of samarium, europium and terbium was successfully carried out for samarium oxide and middle rare earth mixture. The precision of the method, expressed as relative standard deviation, is within 1.1–2.5%.

Since its introduction by Lloyd,[1] synchronous fluorimetry has been described as a method to improve the selectivity of conventional fluorimetry by taking full advantage of the ability to vary both excitation and emission wavelengths during analytical determination. In this method, the excitation and emission monochromators are scanned simultaneously, synchronized so that a constant wavelength difference ($\Delta\lambda$) is maintained between two monochromators. The fluorescence signals are characterized by simple spectra, narrow bands and low scattering interferences of excitation radiation relative to conventional ones.[2,3] While $\Delta\lambda$ equals Stokes shift of fluorescent molecules, satisfactory results are obtained. This method is mainly used in the simultaneous determination of multicomponent solutions,[4-8] which have similar properties. Furthermore, it frequently combines with derivative fluorimetry in order to provide high sensitivity at the same time.[9,10] In this work, we want to show that characteristic fluorescence spectra of samarium, europium and terbium ions were resolved simultaneously and clearly by synchronous derivative fluorimetry in the mixture of rare earths when $\Delta\lambda$ equals 5 nm.

EXPERIMENTAL

Apparatus

A Hitachi MPF-4 spectrofluorimeter equipped with a high-pressure xenon lamp and data processor was used for all fluorescence measurements. A response time of 1 sec, slit widths of 5/5 nm and a scanning speed of 120 nm/min was adopted. The amplifier gain was adjusted according to the fluorescence intensity. For the measurement of acidity, a pHS-2 meter was employed.

Reagents

Analytical-grade reagents were used throughout.

Standard solutions of the rare earths and thorium were prepared by dissolving the 99.99% of pure oxides (except for cerium) in dilute perchloric acid, evaporating to near dryness, cooling to room temperature and diluting to the mark with ethanol. A standard cerium solution was obtained by dissolving cerium dioxide in nitric acid containing hydrogen peroxide.

Standard solutions of quinaldic acid and phenanthroline were prepared by dissolving the corresponding reagents in ethanol. They were further diluted to give 1.0×10^{-2} mol/l working solutions. In the experiment, ammonium acetate

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buffer solution was used to control acidity of aqueous solution.

Procedure

An aliquot of solution containing europium of 5–100 μg (100–500 μg for samarium and 5–500 μg for terbium) was transferred into a 10-ml calibrated tube, then 5 ml of 1.0×10^{-2} mol/l quinaldic acid, 2 ml of 1.0×10^{-2} mol/l phenanthroline and 1 ml of ammonium acetate buffer solution were added. After adjusting pH to about 6.5–7.5 with dilute hydrochloric acid or sodium hydroxide solutions, the solution was made up to the mark with distilled water. After 5 min, second synchronous derivative fluorescence intensity was measured in a 1-cm quartz cell keeping 5 nm for constant wavelength difference between excitation and emission monochromators.

RESULTS AND DISCUSSION

Synchronous derivative fluorescence spectra

The complexes of samarium, europium and terbium with quinaldic acid in aqueous solution show their ion characteristic fluorescence. In the presence of phenanthroline, significant enhancement of the fluorescence of these complexes was observed. The maximum excitation and emission wavelengths are 325 and 645 nm for samarium, 319 and 617 nm for europium and 320 and 545 nm for terbium. Figure 1 shows the apparent and the corresponding synchronous, fluorescence spectra of samarium, europium and terbium complexes with quinaldic acid and phenanthroline when constant wavelength difference is 5 nm between excitation and emission monochromators. As compared with conventional fluorescence, synchronous fluorescence possesses simpler spectra, higher fluorescence intensity and lower background signals (except for europium).

Generally speaking, the fluorescent complexes of samarium, europium and terbium was sharp-line fluorescence emission. The maximum emission wavelength of their complexes only exhibit slight changes even though they coordinate with different organic ligands[11] at room temperature. From Fig. 1, synchronous techniques cannot eliminate overlapping of fluorescence spectra of samarium, europium and terbium completely. However, since it offers

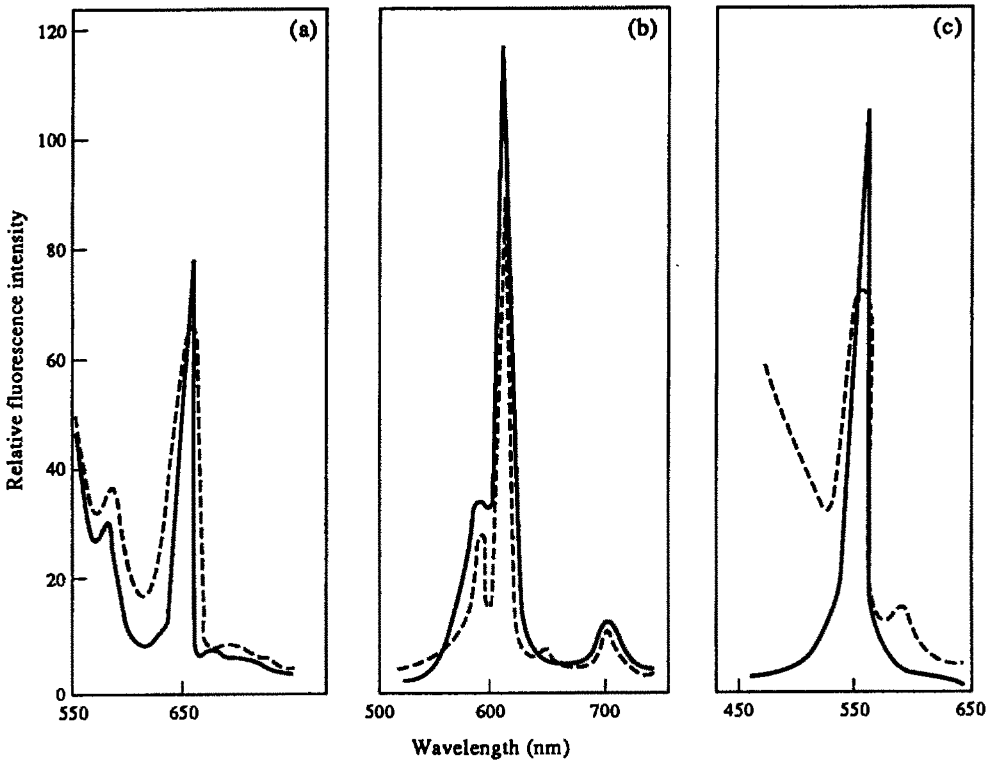

Fig. 1. Fluorescence spectra of complexes of Sm, Eu and Tb (a) Sm^{3+}, 50 ppm (b) Eu^{3+}, 2.5 ppm (c) Tb^{3+}, 2.5 ppm. QU, 5.0×10^{-3} mol/l, Phen 2.0×10^{-3} mol/l, pH 7.0, response 1 sec, slit width 5 nm, scanning speed 120 nm/min, --- conventional fluorescence, —— synchronous fluorescence.

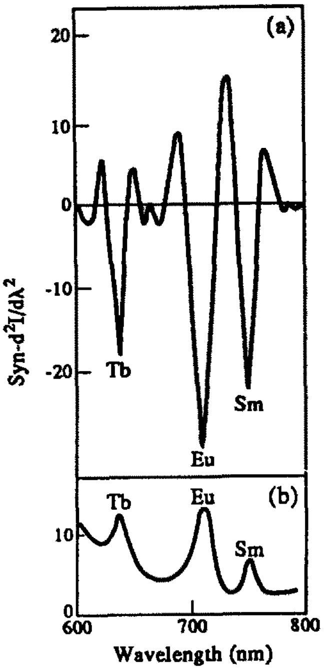

Fig. 2. Synchronous derivative fluorescence spectra (a) and conventional fluorescence spectra at fixed excitation wavelength 319 nm (b) of the mixture. Sm^{3+} 100 ppm, Eu^{3+} 20 ppm, Tb^{3+} 20 ppm, QU 5.0×10^{-3} mol/l, Phen 2.0×10^{-3} mol/l, response 1 sec, scanning speed 120 nm/min, slit widths 5/5 nm.

narrowing of spectrum bands, the synchronous technique gives a prerequisite for application of derivative technique. Derivative technique can further improve the selectivity of synchronous fluorimetry. At the same time, it can also premote the sensitivity of fluorescence measurements.[5,6] As shown in Fig. 2, quite good resolution of fluorescence spectra of samarium, europium and terbium was obtained. Therefore, the combination of synchronous technique with derivative one can eliminate background signals.

Effect of pH on fluorescence intensity

The fluorescence of samarium, europium and terbium appears in the pH range of 5.0–9.0. A little increase in pH causes remarkable enhancement of fluorescence of samarium, europium and terbium with quinaldic acid and phenanthroline in aqueous solution. In the presence of sufficient quinaldic acid and phenanthroline, the fluorescence intensity is practically constant for pH between 6.5 and 7.5. Under these conditions, the fluorescence remains stable for at least 24 hr.

Selection of instrumental parameters

For the selection of the optimum constant difference in wavelength ($\Delta\lambda$) between two monochromators, the synchronous spectra at various wavelength differences near the Stokes shift of the complexes were recorded, 5 nm between synchronous peaks corresponding to samarium, europium and terbium gives best selectivity and sensitivity.

In general, the wavelength scanning speed, the response time and the derivative order affect the shape of derivative spectrum. A rapid scanning speed gives peaks with high amplitude but small resolution, whereas a long response time contributes low amplitude but high signal to noise ratio.

In addition, slit width is closely related to the sensitivity. It has been found that scattering interferences are not negligible for slit width more than 5 nm, whereas the sensitivity decreases for slit width less than 5 nm. For this reason, slit widths of 5/5 nm were employed in the experiment.

Comparison of the complexes

The continuous variations method was employed in order to determine the composition of complexes. The results showed that the composition of Eu–QU binary complex and Eu–QU–Phen ternary complex is $Eu(QU)_2$ and $Eu(QU)_2(Phen)_2$, respectively. This conclusion is also suitable for complexes of samarium and terbium.

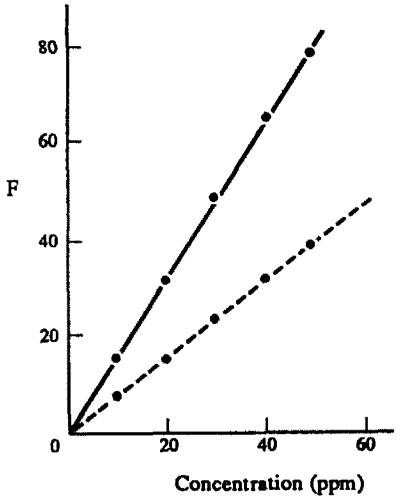

Fig. 3. Calibration curves of Eu. ---- conventional fluorimetry, —— synchronous derivative fluorimetry.

Table 1. Analytical results of synthetic samples

Sample	Element	Added (*ppm*)	Found (*ppm*)	Recovery (%)	Average relative error
1	Eu	15	14.5	96.7	−3.3
	Tb	10	9.5	95	−5.0
2	Sm	200	192	96	−4.0
	Eu	5	5.5	110	+10.0
3	Sm	300	291	97	−3.0
	Tb	10	11	110	+10.0
4	Sm	100	98	98	−2.0
	Eu	15	15.5	103	+3.0
	Tb	15	15.5	103	+3.0
5	Sm	100	97	97	−3.0
	Eu	15	15.2	100.1	+0.1
	Gd	150			
	Tb	15	15	100	0.0
	Dy	150			

Calibration curves

Figure 3 shows the characteristics of calibration curves obtained for representative europium under the same experimental conditions. Synchronous derivative fluorimetric measurements give higher selectivity and sensitivity relative to conventional ones. For samarium and terbium, similar phenomena were observed. There is a linear function of concentration in the range 10–250 ppm for samarium, 0.5–50 ppm for europium and 0.5–300 ppm for terbium, respectively.

Interferences of diverse ions

Influence of various ions on synchronous derivative fluorescence of samarium, europium and terbium under the optimum conditions were investigated. If sufficient quinaldic acid and phenanthroline were present and the precipitation of complexes did not appear, 25-fold amounts of scandium, 50-fold amounts of lanthanum, gadolinium, dysprosium, lutetium and 20-fold amounts of thorium did not interfere with the determination of europium and terbium. For samarium, 10-fold amounts of scandium and thorium, 25-fold amounts of lanthanum, gadolinium, dysprosium and lutetium did not interfere. However, more and more serious interferences were observed with the progressive increase of prasedymium, neodymium, holium and erbium. A large amount of four ions quenched the fluorescence of samarium, europium and terbium.

Analysis of synthetic samples

Table 1 gives the analytical results of synchronous derivative fluorimetric determination of several synthetic samples. The relative standard deviation with 10 replicate samples for various mixtures is within 1.1–2.5% and the average relative error is less than 10%. The results found are quite satisfactory and further demonstrate the advantages of synchronous derivative fluorimetry. Therefore, this method can be recommended for simultaneous determination of samarium, europium and terbium in samarium oxide and middle rare earth mixture without treatment in advance.

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