

# Determination of Nanogram Amounts of Praseodymium and Terbium by Means of Candoluminescence Emission

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Praseodymium and terbium give rise to intense red and green candoluminescence, respectively, in a calcium oxide - calcium sulphate matrix, placed in a hydrogen - nitrogen - air flame. The emissions are used to determine 0.05-1 ng of praseodymium and 1-25 ng of terbium in 1  $\mu$ l of solution. Most other lanthanoids have little effect on the determination of praseodymium, but cerium, scandium, europium and praseodymium seriously interfere in the determination of terbium.

Recently, a selective and rapid method for the determination of nanogram amounts of bismuth was reported,<sup>1</sup> based on the candoluminescence stimulated by bismuth ions when applied to the surface of a calcium oxide based matrix and the surface introduced into a hydrogen - nitrogen - air flame. Neunhoeffer<sup>2</sup> has shown that trace amounts of certain lanthanoids can be detected by their candoluminescence emission in a calcium oxide matrix. Belcher *et al.*<sup>3</sup> confirmed this finding by co-precipitating a number of lanthanoids with calcium hydroxide, which was used to prepare a matrix for candoluminescence studies. They reported very strong emission from praseodymium, strong emissions from lanthanum, cerium and yttrium, and weak emissions from many other lanthanoids. The spectra of many of the emissions were reported.

This paper describes an investigation of lanthanoid candoluminescence, after injection of the sample solution on to the surface of a calcium oxide based matrix. It includes a detailed study of the two activators that have been found to be most sensitive, *viz.*, praseodymium and terbium.

## Experimental

The flame spectrophotometer, burner, recorder and matrix holder were as described previously.<sup>1</sup> The preparation of the calcium oxide - calcium sulphate matrix was also as described previously, except that it was dried at 105 °C for 5 min, and a 6 + 1 *m/m* mixture of calcium oxide and calcium sulphate was used for the terbium studies. A calcium fluoride matrix was prepared by mixing 5 g of AnalaR calcium fluoride with 30 ml of water, before filtering and inlaying into the cavity as for the other matrix.

## Preparations of Solutions

Water that had been distilled from an all-glass apparatus, and then passed through an ion-exchange column, was used in all instances.

### *Praseodymium nitrate solutions*

A 100  $\mu$ g ml<sup>-1</sup> praseodymium solution was prepared by dissolving 0.1208 g of praseodymium oxide (Pr<sub>6</sub>O<sub>11</sub>, 99.9%, Ventron Corp.) in the minimum volume (3-5 ml) of AnalaR concentrated nitric acid, and diluting to exactly 1 l with water. Calibration solutions were prepared by diluting an aliquot of the above solution to 2  $\mu$ g ml<sup>-1</sup> with water, pipetting 0.25-, 0.5-, 1.2-, 2.5-, 5.0- and 7.5-ml amounts of this solution into 10-ml calibrated flasks and diluting to 10 ml with water.

### *Terbium nitrate solutions*

A 1000  $\mu$ g ml<sup>-1</sup> terbium solution was prepared by dissolving 0.1176 g of terbium oxide (Tb<sub>2</sub>O<sub>3</sub>, Ventron Corp.) in the minimum volume (3-5 ml) of AnalaR concentrated nitric acid by gentle warming and diluting to exactly 100 ml with water. Calibration solutions were prepared by diluting an aliquot of the above solution to 100  $\mu$ g ml<sup>-1</sup> with water, pipetting

0.1-, 0.5-, 1.0-, 1.5-, 2.0- and 3.0-ml amounts of this solution into 10-ml calibrated flasks and diluting to 10 ml with water.

### Determination of Praseodymium (0.05–1 ng) or Terbium (1–25 ng)

A 1- $\mu$ l amount of the test, blank or calibration solution was injected on to the centre of the matrix surface. The matrix holder was positioned with the matrix surface 5° below the vertical, and introduced rapidly into the flame at the pre-determined optimum position. The change in emission intensity with time, at 610 nm (praseodymium) or 550 nm (terbium), was recorded, and the maximum candoluminescence intensity measured. The blank response was subtracted from every other measurement. When the procedure was used for calibration, a graph of peak intensity *versus* amount of praseodymium or terbium was plotted.

### Determination of Praseodymium in Didymium

A 1-g sample of didymium was dissolved in 10 ml of AnalaR concentrated nitric acid. The resulting solution was diluted to 1 l with water. This solution was diluted ten times and was used for direct and standard additions procedures for the determination of praseodymium.

#### *Direct method*

The solution was diluted a further ten times and 1  $\mu$ l was analysed for praseodymium as described above.

#### *Standard additions method*

A 1-ml amount of the solution was pipetted into each of three 10-ml calibrated flasks. Standard additions of 1.0 and 2.5 ml of the 2  $\mu$ g ml<sup>-1</sup> praseodymium nitrate solution were made to two of the flasks, all three were made up to 10 ml with water and 1  $\mu$ l of each was analysed for praseodymium as described above.

### Experiments with Other Lanthanoids

Dilute solutions containing approximately 10  $\mu$ g ml<sup>-1</sup> of the nitrates were prepared from the oxides (99.9%, Ventron Corp.) as described for praseodymium; 1- $\mu$ l amounts of the pure solutions, or in admixture with praseodymium and terbium, were injected on to the matrix, which was introduced into the flame as described above.

### Investigation of Experimental Variables

The flame composition and the position of the matrix in the flame greatly influenced the emission intensities of praseodymium and terbium, as had been found for bismuth.<sup>1</sup> Thus, the effects of varying the flame gas flow-rates and the position of the matrix were examined.

Some of the results for praseodymium are shown in Figs. 1 and 2. They show that the optimum hydrogen flow-rate is 2.0 l min<sup>-1</sup> and that of air is 1.5 l min<sup>-1</sup> (a value of 2.0 l min<sup>-1</sup> was used in further experiments to improve flame stability, with little loss of sensitivity). As had been found for bismuth, the nitrogen flow-rate was not of great importance between 6 and 12 l min<sup>-1</sup>; 8 l min<sup>-1</sup> was used in all further experiments. There was no change in emission intensity if the matrix position was changed between 1.0 and 4.5 cm above the burner head; 3 cm was used in all further studies. The effect of the horizontal position of the matrix in the flame, however, was of critical importance. Greatest emission intensity for praseodymium was achieved at the extreme edge of the flame. A change of 1 mm in this position reduced the intensity by 40%, and so exact, reproducible positioning of the matrix is very important. This arises because the concentration of hydrogen radicals, which are presumed to stimulate candoluminescence, is large at the flame edge, and sharply decreases in the immediately adjacent parts of the flame.

The effects of the variables on terbium candoluminescence were similar to those observed for praseodymium. Some of these effects are shown in Figs. 2 and 3. The optimum hydrogen and air flow-rates were 1.75 and 2.0 l min<sup>-1</sup>, respectively. The nitrogen flow-rate was of no importance between 0 and 7.5 l min<sup>-1</sup>, so a value of 7.5 l min<sup>-1</sup> was chosen, to give the stiffest flame. The burner - cavity distance had no effect between 0.5 and 3 cm; 2 cm was

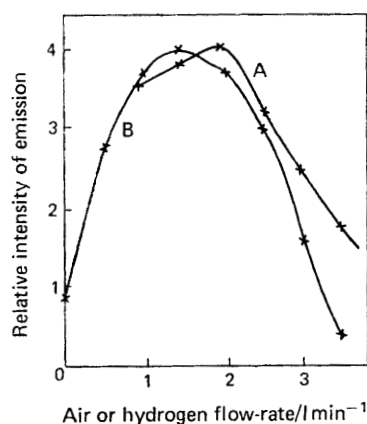


Fig. 1. Effect of A, hydrogen flow-rate (air = 2.1 min<sup>-1</sup>, N<sub>2</sub> = 7.5 l min<sup>-1</sup>), and B, air flow-rate (H<sub>2</sub> = 2.5 l min<sup>-1</sup>, N<sub>2</sub> = 7.5 l min<sup>-1</sup>) on the candoluminescence emission of praseodymium at 610 nm.

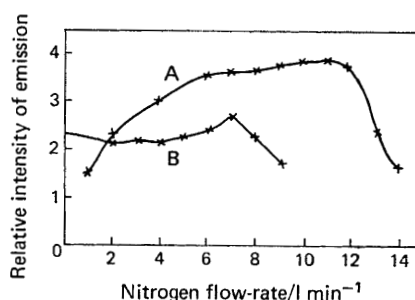


Fig. 2. Effect of nitrogen flow-rate on the emission of A, praseodymium (H<sub>2</sub> = 2.0 l min<sup>-1</sup>, air = 2.0 l min<sup>-1</sup>) at 610 nm, and B, terbium (H<sub>2</sub> = 1.75 l min<sup>-1</sup>, air = 2.0 l min<sup>-1</sup>) at 550 nm.

used in all further studies. Again, the horizontal position of the matrix was very important. Maximum emission intensity was achieved near the edge of the flame, approximately 1.5 mm inside the optimum position for praseodymium. A 1 mm change in position decreased the intensity by 25%.

### Results and Discussion

Praseodymium, terbium and europium gave the most intense emissions, of the lanthanoids studied, in the calcium oxide-calcium sulphate matrix. Cerium(III) gave a weak, green emission, but lanthanum, lutetium, gadolinium, neodymium, dysprosium, erbium, holmium, ytterbium, samarium and thulium gave no observable emission under the conditions used, at the 10 µg ml<sup>-1</sup> level. The candoluminescence of praseodymium, terbium, europium and cerium was therefore investigated in more detail.

The emissions obtained were red (praseodymium), green (terbium), yellow (europium) and green (cerium). The spectra of the praseodymium and terbium emissions are given in Figs. 4 and 5. They were obtained under conditions where the candoluminescence intensity

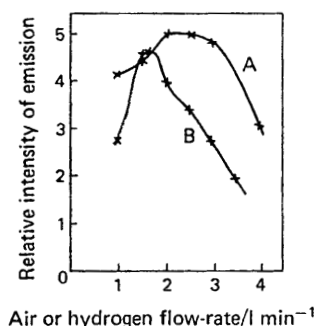


Fig. 3. Effect of A, air flow-rate (H<sub>2</sub> = 1.75 l min<sup>-1</sup>, N<sub>2</sub> = 7 l min<sup>-1</sup>), and B, hydrogen flow-rate (air = 2 l min<sup>-1</sup>, N<sub>2</sub> = 7 l min<sup>-1</sup>) on the candoluminescence emission of terbium at 550 nm.

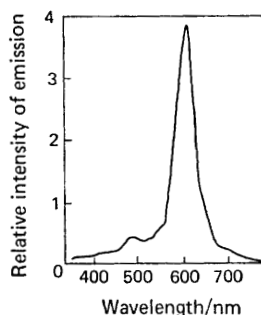


Fig. 4. Candoluminescence spectrum of praseodymium.

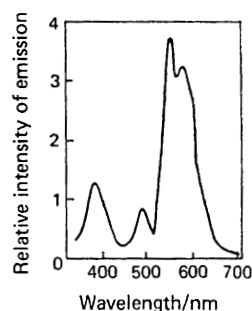


Fig. 5. Candoluminescence spectrum of terbium.

remains constant for at least 10 min, as described previously for bismuth.<sup>1</sup> The peak wavelengths for the four activators are given in Table I. The spectral slit width varied from 2 nm at 250 nm to 14 nm at 450 nm and 38 nm at 650 nm.

TABLE I  
PEAK CANDOLUMINESCENCE WAVELENGTHS FOR SOME ACTIVATORS

Activator	Peak wavelengths/nm
Pr .. .. .	490, 540 (sh),* 610,† 650 (sh)*
Tb .. .. .	390, 490, 550,† 580–590 (Na?)
Eu .. .. .	585
Ce .. .. .	395,† 500, 570

\* (sh) = shoulder.

† Most intense peak.

Emission from terbium, under the optimum conditions, is rapid. It begins 5 s after introduction of the matrix into the flame, rapidly reaches a maximum and disappears after 25 s. Emission from praseodymium does not begin until approximately 15 s (very similar to bismuth) and disappears after 45–50 s. These times are those during which the surface temperature is within the range over which candoluminescence can be stimulated, which is characteristic of each matrix-activator combination.<sup>1</sup> By measuring the peak height, linear calibration graphs were determined for 0.05–1 ng of praseodymium and 1–25 ng of terbium (Fig. 6). Above the upper limits, the calibration graphs levelled off, and eventually fell back. The coefficients of variation for the determination of 0.5 and 0.2 ng of praseodymium and 5 ng of terbium were 3, 7 and 6.5%, respectively, for measurement on ten matrices for each element. The smallest amounts that could be detected were 0.016 ng of praseodymium and 0.1 ng of terbium (in a 0.4- $\mu$ l sample). After removal of matrices from the flame, and allowing them to cool, candoluminescence responses identical with those previously obtained were given when they were re-introduced into the flame. This process could be repeated numerous times, and could be used to optimise the flame and matrix position parameters.

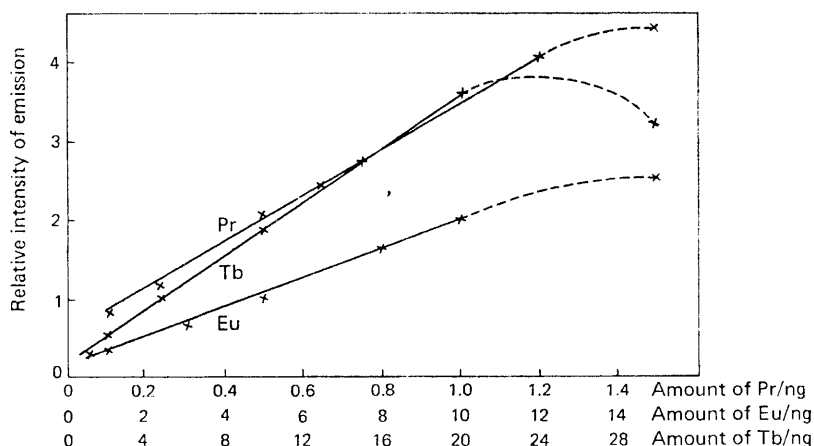


Fig. 6. Calibration graphs for praseodymium, terbium and europium. The dotted portions of the lines are extrapolations.

Terbium also gave an intense green candoluminescence on a calcium fluoride matrix. The luminescence lasted longer (approximately 40 s) than on the calcium oxide based matrix, and the optimum location was slightly further inside the flame. It was not investigated further at this stage.

Europium emission appears at a similar time after introduction of the matrix into the flame as praseodymium emission. The optimum position in the flame, however, is the same as that

for terbium candoluminescence. Using optimum flame gas flow-rates of  $1.75 \text{ l min}^{-1}$  (hydrogen),  $2.0 \text{ l min}^{-1}$  (air) and  $8.0 \text{ l min}^{-1}$  (nitrogen), with the matrix 2.5 cm above the burner top, a linear calibration graph was obtained for 1–10 ng of europium (Fig. 6). The coefficient of variation for 5 ng was 10% (10 determinations). The reproducibility was considered to be unsatisfactory, but could not be improved. The emission from cerium(III) was too weak to be analytically useful.

Studies of europium and cerium were not carried further, except on one important aspect. Addition of sulphuric acid gave a 10-fold enhancement to europium and cerium(III) emission intensity. No other lanthanoids appeared to give enhanced emissions in the presence of sulphuric acid. The acid was therefore considered to be a co-activator. A detailed investigation of this phenomenon is being undertaken, and the results will be reported later.

### Interference Studies

The effects of other lanthanoids, and of bismuth, scandium and yttrium, which are known candoluminescing elements, on the candoluminescence of 0.2 ng of praseodymium, were investigated. Few spectral interferences were expected because the praseodymium luminescence was stimulated at the extreme edge of the flame, where other activators were much less active. This expectation was borne out by the results. The following mass ratios of elements to praseodymium did not interfere:  $75 \times$  (La, Lu, Gd),  $50 \times$  (Y, Nd, Eu),  $25 \times$  (Sm, Tm),  $10 \times$  (Sc, Dy, Ho, Er, Yb, Bi),  $5 \times$  (Tb). Larger amounts of lanthanum, europium, scandium and bismuth enhanced the emission, whereas larger amounts of the other elements depressed it. The luminescence therefore provides a selective means of determining praseodymium in the presence of most other lanthanoids. In order to test the efficacy of such a procedure, it was applied to the determination of praseodymium in didymium oxide, composed mainly (approximately 95%) of neodymium oxide, but containing small percentages of samarium and praseodymium oxides, and less than 1% each of lanthanum and europium oxides. The interference study indicated that these levels of lanthanoids should not interfere. The direct measurement method and a standard addition method were compared, as exact analytical figures for the didymium oxide obtained by other methods were not available. The result obtained for triplicate analyses of the sample were: direct method 3.0, 2.8, 3.0% and standard addition method 3.2, 3.1, 3.1%, which are in good agreement and within the expected range.

The effects of other lanthanoids, scandium and yttrium on the luminescence of 2 ng of terbium are shown in Table II. It shows that 5 ng of cerium(III) and scandium interfere seriously, cerium by depressing the emission, scandium by increasing it. Europium and praseodymium (10 ng) also depress the emission, as do larger amounts of other lanthanoids, except for lanthanum, lutetium and gadolinium, which enhance the luminescence.

TABLE II

EFFECT OF OTHER LANTHANIDS ON TERBIUM CANDOLUMINESCENCE INTENSITY

Each reading is the mean of five determinations.										
Ion added .. ..			—	La <sup>3+</sup>	Y <sup>3+</sup>	Lu <sup>3+</sup>	Gd <sup>3+</sup>	Nd <sup>3+</sup>	Dy <sup>3+</sup>	Er <sup>3+</sup>
Amount added to 2 ng of terbium/ng .. ..			—	50 75	50 75	20 30	20 30	10 20	10 20	10 20
Intensity (arbitrary units) .. ..			70	70 95	68 60	73 80	76 100	65 48	67 45	69 55
Ion added .. ..			Ho <sup>3+</sup>	Yb <sup>3+</sup>	Sm <sup>3+</sup>	Tm <sup>3+</sup>	Pr <sup>3+</sup>	Eu <sup>3+</sup>	Ce <sup>3+</sup>	Sc <sup>3+</sup>
Amount added to 2 ng of terbium/ng .. ..			10 20	10 20	10 20	10 20	5 10	5 10	5	5
Intensity (arbitrary units) .. ..			64 48	63 42	65 49	62 40	67 52	66 50	40	120

The matrix for terbium was slightly modified. Less calcium sulphate binder was added, because calcium sulphate itself gives a slight green emission at low temperatures in the hydrogen flame used. The 6% matrix gave virtually no green emission.



### Simultaneous Determination of Lanthanoids

It was shown in a previous paper<sup>1</sup> that mixtures of lead and bismuth could be resolved because the blue candoluminescence of lead occurred at a lower temperature than the blue candoluminescence of bismuth, and thus the emission *versus* time graph at 400 nm shows two peaks. Such an effect had earlier been observed by Neunhoeffer.<sup>2</sup> Terbium and praseodymium, which also have similar candoluminescence spectra, can be resolved in the same way, because the emission of terbium occurs more quickly than that of praseodymium. The resolved peaks obtained under optimum conditions for terbium are shown in Fig. 7. If the matrix is removed from the flame after emission has ceased, allowed to cool for 45 s and then replaced in the flame at the optimum position for praseodymium (approximately 1 mm further out than for terbium), little terbium emission is observed, but that of praseodymium is much enhanced (Fig. 7). This improved resolution of praseodymium results from the changed matrix position, and from the temperature of the matrix surface, which has not cooled sufficiently to stimulate maximum terbium emission. Resolution was also obtained between terbium and europium, the optimum matrix position being the same for both activators.

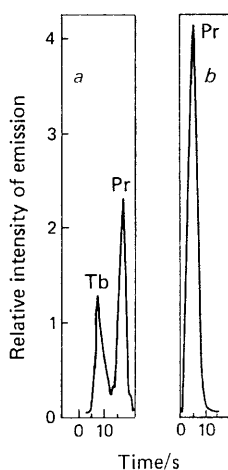


Fig. 7. (a) Sequential luminescence peaks from terbium and praseodymium under optimum conditions for terbium; (b) luminescence peak for praseodymium after allowing the matrix to cool for 45 s and replacing the matrix in the flame at the optimum position for praseodymium.

### Conclusions

The determinations of praseodymium and terbium are achieved very simply. The solution is injected on to the surface of the matrix, which is immediately introduced into the flame. No special applicator or thermal pre-treatment of the matrix-activator combination is required. High sensitivity is achieved for praseodymium, and lower sensitivity for terbium (and europium). Similarly, selectivity for praseodymium is greater than that for terbium. The technique described should therefore provide a useful method for the determination of praseodymium in the presence of other lanthanoid elements.

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### References

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