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DETERMINATION OF TRACES OF TERBIUM AND INDIUM BY CANDOLUMINESCENCE IN VARIOUS MATRICES BY USING A ROD TECHNIQUE

ZUHAIR M. KASSIR*, ALA-DIN M. AL-MUAIBED and ALI H. A. KAREEM
Department of Chemistry, College of Science, University of Basrah, Basrah (Iraq)
TARIK A. K. NASSER
Department of Chemistry, College of Education, University of Basrah, Basrah (Iraq)

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SUMMARY

The candoluminescence of terbium and indium was studied in various matrices coated on $CaO/CaSO_4$ rods. Terbium was studied in Y_2O_3, Gd_2O_3, ThO_2 and La_2O_3. Calibration graphs were linear over different ranges, up to 90 ng in some cases, with 0.2—0.3 ng μl^{-1} detection limits and 2.8—3.2% relative standard deviations (r.s.d.). The candoluminescence of indium in Y_2O_3, Gd_2O_3 and Al_2O_3 was also examined. Calibration graphs were linear over different ranges, up to 20 ng in some cases, with detection limits of 0.08 ng μl^{-1} for Y_2O_3 and Al_2O_3 and 0.2 ng μl^{-1} for Gd_2O_3, with r.s.d. of 2.5—2.9%. There are many interferences.

Candoluminescence is the emission stimulated from certain metal oxides when activated by traces of metal ions and exposed to a cool hydrogen flame. The applicability of candoluminescence for the determination of selected trace elements has been demonstrated by Belcher et al. [1, 2] who used several matrices including calcium oxide/calcium sulphate, aluminium oxide and calcium fluoride. The matrix was inlaid in the aperture of a hexagonal steel cavity. Dhaher and Kassir [3] described a technique in which the matrix, usually calcium oxide/calcium sulphate, was shaped into a rod and the activator was introduced onto the end of the rod which was inserted into a hydrogen flame. The technique was used for the determination of nanogram amounts of bismuth, manganese and antimony. Only a few elements have been used as activators in different matrices [2]. To extend the number of matrices used to produce candoluminescence for a wide range of activators, and because of the difficulties and expense of producing rods from certain metal oxides, especially those of the lanthanides, rods were prepared by coating the metal oxide matrix onto the tip of calcium oxide/calcium sulphate rods in the work described here.

The candoluminescence of terbium in Y_2O_3, Gd_2O_3 and La_2O_3 was studied by Sweet and White [4], who identified the spectra and reported a concentration dependence of the intensity between 27 and 11 200 mg l^{-1} terbium.

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Belcher et al. [5] determined 1—25 ng of terbium in a $CaO/CaSO_4$ matrix. Nasser continued the study, using $Mg(OH)_2$, $Sr(OH)_2$ and CaF_2 matrices [6]. Indium was also studied by Nasser [6] in $CaO/CaSO_4$ and $Mg(OH)_2$. The blue-green emission obtained was measured at 500 nm and a linear calibration graph for 0.1—10 ng of indium was obtained.

This paper describes the candoluminescence emission of terbium and indium in a number of matrices coated on $CaO/CaSO_4$ rods. Such a study is important at this stage of development in order to identify matrices that give selective and sensitive emissions.

EXPERIMENTAL

Reagents and chemicals

Deionized, glass-distilled water and analytical-reagent chemicals were used for the preparation of solutions and rods. Hydrogen and argon (99% purity) were used to produce the cool flame.

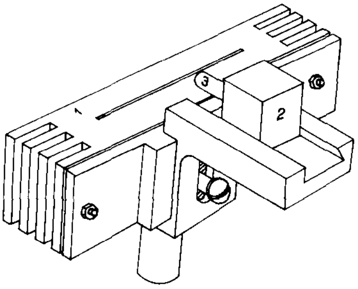
Preparation of coated rods. The rods of calcium oxide and calcium sulphate were prepared as described previously [3]. A few hundred rods were usually prepared in each batch. The tips of the rods were smoothed, and the rods were stored in a desiccator. A suspension of the metal oxide to be used for coating was prepared by adding 3 ml of water to 1 g of metal oxide in a small beaker; the suspension was stirred continuously to keep it homogeneous. The tip of each rod was immersed in water for 5 s, dipped in the suspension to a fixed depth (usually 1 mm) for 15 s, withdrawn and placed in a rod support. The coated rods were heated in an oven at 110°C for 30 min and stored in a desiccator. Dipping the rods in water before coating was essential for obtaining a uniform coating of the oxide matrix on the tip and sides of the rod. If dry rods were directly dipped in the suspension they very quickly absorbed water from the suspension, leaving the solid metal oxide in a bead form with a depression in the centre.

Instrumentation

A Beckman DU2 spectrophotometer was used in conjunction with the flame compartment of an EEL (Evans Electroselenium) Model 140 atomic absorption spectrometer. The slit width was 0.3 mm. The setup was as illustrated previously [3]. Measurements were made in the dark to prevent stray light from interfering with the measurements. An argon-diluted hydrogen flame was used with a 5-cm slot type burner fitted with a rod holder, as illustrated in Fig. 1. The rod holder was made by shaping a piece of brass drilled along its axis to hold the rod firmly. It was attached to a brass block which slides on a rail to allow smooth movement of the rod. Vertical adjustment was also possible in order to align the rod with the detector.

Procedures

Terbium. A 3-μl portion of terbium solution was introduced onto the tip of the coated rod and exposed to the flame for 30 s. The rod was with-



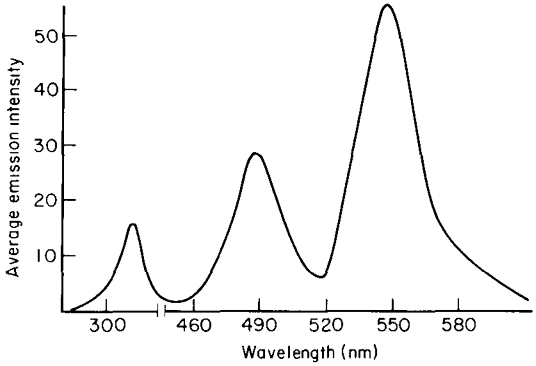


Fig. 1. Slot-type burner (1) fitted with rod holder (2) shown with the rod (3) in position.

Fig. 2. Candoluminescence spectrum of terbium in Y_2O_3.

drawn and allowed to cool for 15 s, during which period the surface was activated. The rod was returned into the flame at the position of greatest intensity, and the emission was recorded at 550 nm. The average emission from 5 rods was measured for each concentration.

Indium. A set of 5 coated rods was used for each concentration. The optimum volume of indium (see below) was introduced onto the tip of the coated rod and the appropriate volume of water (see below) was applied to the body of the rod 5 mm from the tip. The end of the rod was positioned at the edge of the flame until the first emission developed, and the rod was withdrawn and allowed to cool for 30 s. Water was added again to the rod 5 mm from the tip, and the rod was introduced into the flame at the optimum position. The emission was measured at 470 nm (Y_2O_3, Gd_2O_3) or 440 nm (Al_2O_3).

RESULTS AND DISCUSSION

Spectra

The spectra of terbium in Y_2O_3, Gd_2O_3, ThO_2 or La_2O_3 were recorded by injecting 3 μl of 10 mg l^{-1} terbium onto the tip of a coated rod and scanning the emission from the rod in the flame. Two broad bands, with peaks at 490 and 550 nm were obtained (Fig. 2). The same spectrum was obtained from each matrix, and it was identical with those reported in the literature [4, 5]. The band at 550 nm was more intense than that at 490 nm, and this wavelength was therefore chosen for further study.

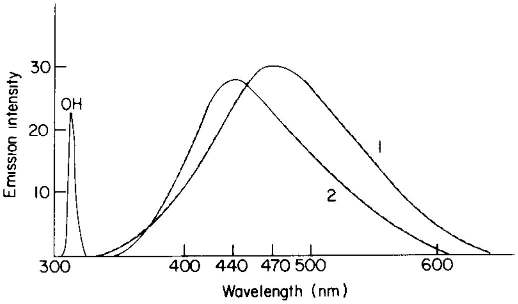
The spectra of indium in Y_2O_3, Gd_2O_3 and Al_2O_3 were recorded by the point-to-point method, because the emission of indium does not last long enough to allow for the spectrum to be scanned. Indium is classified as a low-temperature activator, therefore the body of the rod was cooled by adding water to the rod at a fixed distance from the tip; this produced a more sustained emission, the spectrum of which could be recorded by scanning. The spectra showed one band centred at 470 nm in Y_2O_3 and Gd_2O_3, but at 440 nm in Al_2O_3. Such shifts in wavelength from a change of matrix have been noted by other investigators for other activators [2]. The shift can be caused by the presence of impurities in the matrix. The spectra of indium in the three matrices are shown in Fig. 3.

Effect of experimental variables

In order to obtain the best flame conditions for producing candoluminescence from these activators, the effect of the argon/hydrogen ratio was studied. The most intense emission for terbium in the above matrices and in $CaO/CaSO_4$ was obtained with a ratio of 10:1 ($Ar:H_2$); for indium, the ratios were 14:1 for Y_2O_3, 8:1 for Gd_2O_3, and 15:1 for Al_2O_3.

The distribution of the activator on the surface of the matrix material was found to affect the emission intensity. This effect was studied by applying various volumes of solution containing 10 ng of the activator. The results for indium are shown in Fig. 4. The optimal volume was 4 μl for Y_2O_3 and Al_2O_3, and 2 μl for Gd_2O_3. Similar results were obtained for terbium; the optimal volume was 3 μl for all matrices.

A preliminary study showed that the candoluminescence of indium was weak. It was found that addition of water to the body of the rod 5 mm from the coated tip enhanced the emission and improved its repeatability. Maximum intensity was achieved by addition of 0.04 ml water for Y_2O_3 and Al_2O_3 and 0.06 ml for Gd_2O_3.



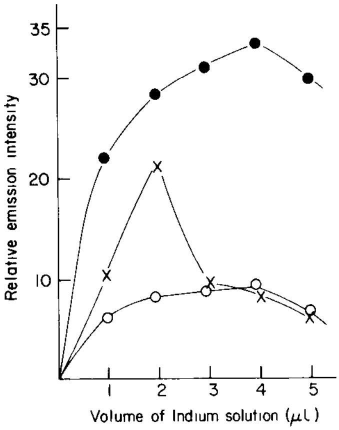


Fig. 3. Candoluminescence spectra of indium: (1) in Y_2O_3 or Gd_2O_3; (2) in Al_2O_3.

Fig. 4. Effect of volume of activator solution on the emission intensity of 10 ng of indium: (●) in Y_2O_3; (×) in Gd_2O_3, (○) in Al_2O_3.

Some activators require a high temperature to produce candoluminescence while others need lower temperatures. Terbium is considered to belong to the first category; therefore, it can produce emission which lasts for >6 min without becoming overheated. Figure 5 illustrates the duration of emission in various matrices. In contrast, indium is a low temperature activator; its emission reaches a maximum after 30 s, and disappears within 30 s. However, on cooling the rod and then re-inserting it into the flame, the emission has a similar duration but the intensity is enhanced by 60%.

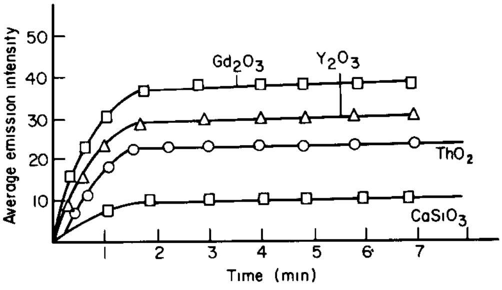
Calibration

When the optimal conditions were used, linear calibration graphs were obtained over the following ranges: 0—15 ng of terbium and 0—5 ng of indium in Y_2O_3, 0—30 ng of terbium and 0—14 ng of indium in Gd_2O_3, 0—90 ng of terbium in La_2O_3, 0—20 ng of indium in Al_2O_3 and 0—150 ng of terbium in $CaSiO_3$. Figure 6 shows a calibration graph for indium in Y_2O_3.

Interferences

The interferences of a number of species, especially lanthanides, on terbium were studied by measuring the emission from 15 ng of terbium in the presence of the interfering species. The results are shown in Table 1. Most cations enhanced the emission at very low concentrations of the cation, but decreased it at high levels. Choice of matrix helps in avoiding some interferences. Similarly, the effects of some cations on indium emission are shown in Table 2. Most cations depressed the signal from the three matrices. Terbium showed some enhancing effect on indium in Gd_2O_3 and Al_2O_3.

Nitric, hydrochloric and sulphuric acids depressed the emission from terbium and indium when used at 0.01 and 0.05 M, except for indium in Y_2O_3, which showed slight enhancement with nitric acid. The results for indium are shown in Table 3.



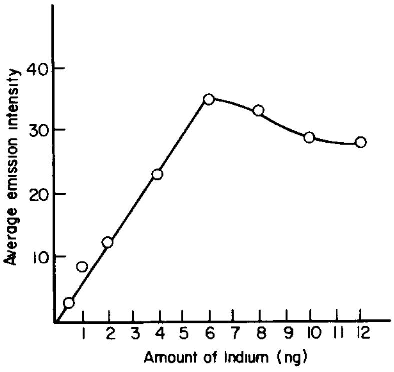


Fig. 5. Emission-time relation of terbium in various matrices (optimal flame conditions).

Fig. 6. Calibration graph for indium in Y_2O_3.

TABLE 1

The effect of cations (ratio by weight) on the candoluminescence of terbium

Interfering cation	Change in intensity (%)							
	Y_2O_3		Gd_2O_3		ThO_2		La_2O_3	
	1-fold	6-fold	1-fold	6-fold	1-fold	6-fold	1-fold	6-fold
La	+54.3	+1.75	−23.6	−7.0	+61.0	—	—	—
Pr	−84.2	−98.2	−88.4	−97.7	−85.4	−87.8	−61.5	−69.2
Nd	−78.9	−93.0	—	—	−70.7	−83.3	−60.5	−64.6
Sm	+19.3	−56.2	−4.6	−53.5	−61.0	−82.9	—	—
Eu	−15.8	−77.2	−14.0	−55.8	+41.5	−63.4	−19.2	−34.6
Dy	0.0	−28.0	+20.9	−28.0	—	—	—	—
Er	−40.35	−82.5	0.0	−74.5	−34.2	−85.4	−57.7	−61.5
Rb	−22.8	−3.5	+2.3	+48.8	+31.1	+7.3	−9.6	+9.5
Cd	+42.1	+28.0	—	—	+34.1	+17.0	+19.2	—
In	0.0	+35.0	+23.3	+9.3	+63.5	+34.1	+40.4	+25.0
Al	+5.3	+8.8	−16.3	+41.6	+80.5	+73.2	—	—

TABLE 2

The effect of cations (ratio by weight) on the candoluminescence of indium

Cation added	Change in intensity (%)					
	Y_2O_3		Gd_2O_3		Al_2O_3	
	1-fold	5-fold	1-fold	5-fold	1-fold	5-fold
Al	−39.1	−10.2	−21.2	−14.3	—	—
Tb	−13.5	−15.1	+22.9	+8.3	+7.9	−25.5
Cd	−20.0	−22.4	−53.7	−50.0	−32.4	−36.7
Pb	−43.1	−79.3	−46.0	−77.1	−33.3	−41.5
Cu	−90.1	−65.1	−78.0	−90.1	−74.8	−90.0
Ca	−12.5	−15.8	−48.8	−58.7	−6.1	−7.3
Dy	−22.4	−19.4	−12.9	−15.7	−29.1	−25.5
La	−47.4	−19.5	−46.0	−38.5	−15.5	−23.5
Y	—	—	−6.3	−32.5	0.0	+19.0
Tl	−25.8	−27.6	−53.2	−30.5	+20.0	+22.0
Er	−19.0	−25.7	−44.5	−50.5	−12.0	−28.5

Comparison of the candoluminescence intensity of terbium and indium in various matrices

The emission of terbium in the lanthanide oxides under investigation was compared with its emission in calcium-based matrices under the respective optimum conditions. The results showed that the emission intensity of terbium in the oxides studied was almost the same (60 in Y_2O_3 and Gd_2O_3, 56 in ThO_2 and 58 in La_2O_3, using a slit width of 0.3 mm). These intensities are very much greater than those obtained in calcium-based matrices (10 in CaO, 5 in $CaSiO_3$, at 2.0-mm slit width). Indium had the following intensities under the optimum conditions: 28 in Y_2O_3 and Gd_2O_3,

TABLE 3

Effect of acids on indium candoluminescence

Acid (M)	Relative emission intensity					
	Y_2O_3		Gd_2O_3		Al_2O_3	
	0.01	0.05	0.01	0.05	0.01	0.05
—	25.6		22.2		39.3	
HCl	27.8	21.3	14.6	6.5	27.0	11.0
HNO_3	30.0	28.2	22.6	15.0	17.8	11.2
H_2SO_4	24.2	17.5	7.6	4.5	28.4	22.3

25 in Al_2O_3 and 10 in La_2O_3 compared with 7.5 in CaO and 15 in MgO (all at 1-mm slit width). Thus the introduction of these new matrices has appreciably increased the sensitivity of the determination for both elements, especially terbium.

Precision and detection limits

The precision was measured for both elements by using ten coated rods for each matrix, with the optimum volume of activator and conditions. The relative standard deviation for terbium in the various matrices ranged from 2.7 to 3.2%, for indium from 2.5 to 2.9%.

Detection limits were defined as the concentration of activator which gave an emission signal twice that of the background. The values (ng μl^{-1}) obtained for terbium were 0.2 in Y_2O_3, Gd_2O_3 and ThO_2 and 0.3 in La_2O_3. Those for indium were 0.08 in Y_2O_3 and Al_2O_3 and 0.2 in Gd_2O_3.

CONCLUSIONS

This study has shown that the coating technique widens the number of matrices that can be used to produce candoluminescence, through the introduction of lanthanide and similar oxides. Increasing the number of matrices in which an activator can give candoluminescence increases the probability of finding a more selective matrix with prolonged emission period. Indium and terbium showed stronger emission from a number of matrices, with low detection limits and good precision, which encourages the application of candoluminescence in trace analysis.

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