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Luminescence is the emission of nonequilibrium or nonthermal radiation as opposed to incandescence. A number of materials have been observed to luminesce when placed in a flame. This phenomenon, called candoluminescence, must be distinguished from thermoluminescence - in which a material is excited by radioactivity or other means but luminesces only when raised to a higher temperature - and from incandescence and luminescence of the flame itself. The blue luminescence of an aerated methane flame is an example of the latter. Candoluminescence is of interest from two standpoints - that of obtaining a better understanding of flames and flame-solid interactions, and secondly the possibility, though remote, of developing a new method of gaslighting. The work reported here was supported in part by the American Gas Association.

Candoluminescence has been known and studied for many years. It was probably first reported by Balmain in 1842 (3) in his description of the material boron nitride, which he was the first to prepare. Apparently the phenomenon was not recognized with other materials until it was reported by Donau in 1913 (5). The subject was reviewed by L. T. Minchin in 1938 (8) and by E.C.W. Smith in 1941 (11).

The materials that luminesce in flames share the characteristics of phosphors generally; that is, they are comprised of a colorless crystalline host or matrix material into which a small concentration of foreign atoms or ions, called the activator, is incorporated. The radiation is typically continuous and extends over only a small wavelength range, thus having a definite color. The color is usually characteristic of the activating ion and can also be obtained with other means of excitation, such as ultraviolet light or cathode rays.

Excitation by a hydrogen flame has been used in most studies of candoluminescence, although Tiede and Buescher reported that, in addition to hydrogen, flames of ethyl alcohol, hydrogen sulfide, and carbon disulfide excited the luminescence of boron nitride (14). Excitation by the flame of city gas has also been reported (9).

The existence of the phenomenon at relatively low temperatures has not been seriously questioned. The temperature range here is from the temperature attained when a flame impinges on a thin film of phosphor spread on a cool metal support up to a bright red heat. This upper limit is based on the observation of Tiede and Buescher (14) that blue luminescence occurred when a flame touched boron nitride in a carbon boat heated electrically to redness.

E. L. Nichols (10) claimed that at much higher temperatures he had observed light outputs from materials heated in an oxyhydrogen flame that were several times greater than the light output from a blackbody at the same temperature. Apparently this work was inspired by the

limelight which was produced by heating a cylinder of lime with an oxyhydrogen flame. The fact that a fresh portion of the lime had to be brought to the flame from time to time was interpreted to mean that something other than thermal radiation was involved (8). Neunhoeffer (9) reports that the natural chalks from which the lime was prepared contain rare earths. If this were known to Nichols, it would no doubt have suggested to him that the rare earths were activators in a luminescence process. However, the work of later investigators indicated that the limelight was similar to the light of the Welsbach mantle in that both are only excited thermally.

Nichols applied his "phosphors" on ceramic adjacent to a uranium-oxide-coated area and heated both areas evenly with an oxyhydrogen flame. Observations were made of both areas with an optical pyrometer; the uranium oxide was taken to behave essentially as a blackbody and to have the same temperature as the companion material. Many mixtures of colorless oxides with small amounts of rare earths, or with some other elements that were also regarded as activators, had a greater emittance than uranium oxide. E.C.W. Smith (11) repeated some of Nichols's experiments and obtained similar emittance readings. He then proceeded to determine or approximate the actual temperature of the two coatings - a matter of some difficulty. By means of thermocouples made of extremely fine wires, he was able to show large differences in the temperatures of the two coatings - differences sufficient to conclude that at incandescence temperatures there was no emission other than thermal. This conclusion has been confirmed by Sokolov and his co-workers (12), (13).

In hydrogen flames, at least, recombination of hydrogen atoms is generally accepted as the major source of energy for the low-temperature excitation (1), (7); earlier Donau (5) and Nichols (10) considered an oxidation-reduction mechanism, and Neunhoeffer (9) thought that electrons in the flame were responsible. Smith, and Arthur and Townend (1), (2) investigated this question with phosphors composed of calcium oxide activated with manganese, antimony, or bismuth. They found that:

1. Activated oxides that luminesce in hydrogen flames also luminesce when subjected to the action of hydrogen atoms produced in an electrical discharge. When subjected to the latter action and heated electrically, the color of the luminescence approached the color produced in the flame. Presumably, the temperature of the heated oxides approached the temperature of oxides in the flame.
2. The intensity of hydrogen flame luminescence increases when the hydrogen is burned under reduced pressure. This effect was presumed to be caused by a decrease in the number of three-body collisions. These collisions remove hydrogen atoms by recombination.
3. The luminescence is strongest in hydrogen, erratic and very faint in town gas, and absent in carbon monoxide flames. It is also absent in methane and ethylene flames tested at pressures from atmospheric to 10 cm Hg.
4. The luminescence is extinguished when small amounts of hydrocarbon gases or vapors are added to the hydrogen.

According to recent studies of flame mechanisms, hydrogen atoms are present in the methane-air flame as well as in the hydrogen flame (15). Thus it appeared reasonable to search for phosphors that candoluminesce in the methane-air flame. This search and the study of the characteristics of this phenomenon were the objectives of our investigation.

PROCEDURES

Preparation of Phosphors

Materials

Rare earths were obtained as 99.9% pure oxides from Lindsay Chemical Division of American Potash and Chemical Corporation. Other chemicals were research grade.

Calcium Oxide Phosphors

Calcium and rare earth nitrate solutions were prepared and mixed in the required amounts. The mixed nitrate solution was slowly poured into hot ammonium carbonate solution with stirring. The precipitate was filtered, washed with hot ammonium carbonate solution, dried at 100°C, and ignited at 900°C for 30 minutes. The pure rare earth oxides were prepared by precipitation from the nitrate in the same manner.

Yttrium Europium Tungstate - $(Y_{0.9}Eu_{0.1})_2O_3WO_3$ - and Gadolinium Europium Molybdate - $(Gd_{0.8}Eu_{0.2})_2O_3.MoO_3$

The required amounts of the oxides (tungstic acid in the case of tungsten) were mixed, heated in a platinum crucible at 1000°C for 2 hours, ground with mortar and pestle, and reheated at 1000°C for 2 hours. The X-ray patterns of the two products showed that in both a new phase had been formed.

Screening Tests

Mounting strips about 2 cm wide and 10 cm long were made of insulating fire brick and of copper sheet. Phosphor powder, thick enough to hide the surface of the strip, was pressed on to it with a spatula. The nearly vertical face of the strip was observed as it was passed through a methane-air flame (bunsen burner) and a hydrogen diffusion flame in a dark room.

Spectra

Three different methods of mounting the phosphors were used in obtaining the spectra. When we wished to observe the effect of temperature, the phosphor was applied as a paste to a silicon carbide rod. Pastes made with monomethyl ester of ethylene glycol seemed to adhere after drying somewhat better than those made with other liquids. The silicon carbide rod, about 6 mm in diameter, was held between two water-cooled electrical terminals to allow the electrical current passing between the terminals to heat the silicon carbide rod and the phosphor.

When hydrogen was used as a fuel, the phosphor could be coated dry on the fritted disk of a gas-dispersion tube. The fritted disk was operated as a porous-plate burner (Figure 1) without primary air. Known amounts of other gases could be added to the hydrogen.

The phosphor was coated on a water-cooled copper plate when a methane-air flame was to be used. The plate was 1 in. square x 1/4 in. thick with two 1/4-in. copper tubes soldered to the back for cooling water. Plating the face with silver was found to be necessary to prevent slow poisoning of the phosphor by the copper. The phosphor was settled onto the plate from a water suspension. The plate was mounted facing upwards at about 45° to the horizontal and the flame of a National Welding Equipment Co. Type-3A blowpipe was directed downward onto it.

A Beckman DK-2 spectrophotometer with an IP 28 photomultiplier was used to record spectra. The backplate of the lamp housing was removed to allow direct entrance of the radiation from the excited phosphor into the spectrophotometer. A slit opening of 0.4 mm without an auxiliary light-gathering system gave sufficient energy. Varying light intensity from the flickering of the flame was troublesome and made it necessary to use the highest time constant and the slowest recording rate of the instrument. The porous-plate burner gave the steadiest radiation.

RESULTS

Screening tests to discover phosphors that candoluminesce in methane-air flames or in hydrogen flames were run on a number of commercial phosphors and on others prepared in our laboratories. The latter were principally rare earths - pure and in calcium oxide. The phosphors were spread on fire-brick slabs and on copper strips - the latter to hold down the temperature of the phosphor at least momentarily - and tested by impingement in both hydrogen and methane-air flames. Several phosphors that candoluminesce in both flames were found. Detailed results are shown in Tables 1 and 2. These results should be regarded as tentative rather than conclusive.

A few additional phosphors not listed in the tables were tested. Three General Electric silver-activated zinc sulfides (Nos. 118-2-3, 118-2-11, and 118-3-1) showed emission in the blue. Their spectra, obtained with a hydrogen diffusion flame on a fritted glass disk, showed that the emission was the band spectrum of S₂ and that no candoluminescence was present (6). The S₂ was undoubtedly formed by decomposition of the phosphor. Zinc sulfide activated by silver and copper showed both candoluminescence and the band spectrum of S₂ (Figure 2). A boron nitride sample from Carborundum Co., Electronics Division showed weak, green luminescence in hydrogen and methane flames. Two recently developed rare earth phosphors, (Y_{0.9}Eu_{0.1})₂O₃·WO₃ and (Gd_{0.8}Eu_{0.2})₂O₃·MoO₃ were prepared and tested (4). Both luminesced red in hydrogen and methane flames on the fire-brick strip.

Light emission in some of the screening tests may have had a source other than candoluminescence. The emission from magnesium germanate was probably thermal. This is indicated by the color of the emission (white to yellowish white), by the absence of a maximum of emission intensity with increasing temperature of the phosphor, and by equal emission when the phosphor is heated to the same temperature with or without the flame. For this test, the phosphor was mounted on the electrically heated silicon carbide rod, and temperature equivalence was indicated by the emission of the phosphor at 2.25 microns. Light

Table 1. LIGHT EMISSION OF YTTRIUM OXIDE AND RARE EARTHS (Pure and in CaO) IN HYDROGEN AND METHANE-AIR FLAMES

Element	Atomic No.	Symbol	Metal Conc in CaO, wt %	Light Emission				Color
				With H ₂		With CH ₄ -Air		
				On Cu Strip	On Fire Brick	On Cu Strip	On Fire Brick	
Yttrium	39	Y	0.2 1.0 PO*	Trace Trace Weak	Weak Trace Trace	Nil Nil Trace	Nil Nil Nil	Violet Violet Green and Orange
Lanthanum	57	La	0.2 1.0 PO	Trace Trace Weak	Weak Trace Trace	Nil Nil Nil	Nil Nil Nil	Lavender Lavender Green and Orange
Praseodymium	59	Pr	0.2 1.0 PO	Trace Trace Nil	Strong Strong Trace	Nil Trace Nil	Strong Strong Nil	Red Red Red
Neodymium	60	Nd	0.2 1.0 PO	Trace Trace Nil	Trace Weak Trace	Nil Nil Nil	Nil Nil Nil	Violet Lavender Red
Samarium	62	Sm	0.2 1.0 PO	Trace Trace Nil	Trace Trace Nil	Trace Nil Nil	Trace Trace Nil	Orange Orange --
Gadolinium	64	Gd	0.2 1.0 PO	Trace Trace Strong	Trace Weak Strong	Nil Nil Trace	Nil Nil Weak	Violet Violet Red
Dysprosium	66	Dy	0.2 1.0 PO	Trace Trace Nil	Trace Weak Nil	Nil Nil Nil	Nil Nil Nil	Lavender Blue --
Holmium	67	Ho	0.2 1.0 PO	Trace Trace Nil	Trace Weak Trace	Nil Nil Nil	Nil Nil Trace	Aqua to Blue Aqua Red
Erbium	68	Er	0.2 1.0 PO	Trace Trace Nil	Trace Weak Trace	Nil Nil Nil	Nil Nil Nil	Blue White Red
Ytterbium	70	Yb	0.2 1.0 PO	Trace Trace Nil	Trace Trace Nil	Nil Nil Nil	Nil Trace Nil	Lavender Red --

* Pure oxide.

emission in a few cases may be caused by decomposition of the phosphor, as was shown in the case of the silver-activated zinc sulfides.

The manganese-activated zinc phosphate (Sylvania No. 151) phosphor appeared to give the most intense luminescence emission in methane-air flames of any tested, and, accordingly, its light emission was investigated further. When the phosphor was coated on a fritted disk and the disk used as a porous-plate burner, a steady emission was obtained with a hydrogen diffusion flame. However, no emission could be obtained in this manner when the fritted-disk burner was fed with pure methane or with a methane-air mixture. Only when the phosphor was brought into a Bunsen flame was the light emission observed. We do not know the cause of this effect. A greater concentration of hydrogen atoms in the hydrogen flame may play a role. The high diffusivity and other properties of hydrogen that cause its flame to burn closer to the solid surface may be of equal or greater importance.

Spectra recorded with the Beckman DK-2 spectrophotometer were used to compare the light emission of this phosphor in the hydrogen flame with its emission in the methane-air flame. The phosphor was coated on a silicon carbide rod for this experiment. No significant difference other than that of the emission from the flame itself was observed (Figure 3).

The effect of temperature on the light emission of the phosphor was investigated by electrically heating the silicon carbide rod. With a methane-air flame impinging on the phosphor-coated rod, and with the spectrophotometer focused on the rod near one of its water-cooled ends, the light emission increased to a maximum with an increase in electrical heating, then decreased to near extinction with further heating. This agrees with the observation of Neunhoeffler (9) that the hydrogen flame candoluminescence of calcium oxide impregnated with various activators exhibits temperature maxima.

When the phosphor was heated to a still higher temperature, thermal emission appeared. When the emission of the phosphor was corrected for the emission of the flame, no essential difference in emission at high temperatures with and without the flame was evident. These experiments indicated that the low-temperature light emission experienced with this phosphor is candoluminescence, but that candoluminescence is not involved in the high-temperature emission.

This phosphor was the only one of several tested that luminesced in a carbon monoxide flame. The question of excitation in this flame by high-energy species other than hydrogen atoms was not pursued.

Spectra of the luminescences from several phosphors excited by hydrogen burning on the surface of a sintered glass disk were obtained, and the effect of the addition of small amounts of carbon monoxide and methane to the fuel was observed. The phosphors were calcium silicate activated with lead and manganese (Sylvania No. 290), calcium oxide activated with ytterbium, calcium oxide activated with praseodymium, and calcium oxide activated with samarium. The spectra obtained from the first three of these phosphors when they are excited with pure hydrogen burning on a fritted disk are shown in Figure 4. The Sylvania No. 290 phosphor emits with a broad peak in the green. Praseodymium-activated calcium oxide shows two peaks - one at 595 millimicrons (yellow) and a weaker one at 490 millimicrons (blue-green). Ytterbium-

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activated calcium oxide also shows two peaks - one at 375 millimicrons, which is in the ultraviolet. Samarium-activated calcium oxide also emits with a similar peak in the ultraviolet and another at 570 millimicrons (yellow), as shown in Figure 5.

The effect of the addition of small amounts (1 to 10 volume percent) of carbon monoxide or methane to the hydrogen burning on the fritted disk was different for each of these phosphors. Luminescence of the Sylvania No. 290 phosphor was substantially unchanged with addition of as much as 10% of the carbon monoxide or methane. Luminescence of the praseodymium-activated calcium oxide was not greatly affected by addition of 1% of the carbon monoxide or methane, but decreased rapidly with greater amounts. Only about 10% of the original intensity was obtained with 6% carbon monoxide or 8% methane. The luminescence of the ytterbium-activated calcium oxide was even more strongly quenched by the addition of carbon monoxide or methane. With these phosphors, only the intensity of the luminescence was affected.

With samarium-activated calcium oxide, the spectral distribution of the luminescence was also affected, as shown in Figure 5. Upon the addition of carbon monoxide, emission by this phosphor in both wavelength regions decreased in intensity, and, at about 3% carbon monoxide, emission in the 375-millimicron region had virtually disappeared. The 570-millimicron peak, however, was replaced by two narrower emission bands with peaks at about 560 and 595 millimicrons. With further addition of carbon monoxide the intensity of this emission increased to a maximum several times more intense than the original peak emission, then decreased. These effects were not observed upon the addition of methane to the flame. The variation of the intensity of the luminescence in the two cases is shown in Figure 6.

At a late stage of the work, phosphors were deposited by settling from a water suspension onto a water-cooled copper plate. A few spectra were obtained in this way with methane-air excitation.

Enhancement of the luminescence from the manganese-activated zinc silicate (Sylvania No. 161) by the cooling of the copper plate was very pronounced. (Figure 7).

ACKNOWLEDGMENT

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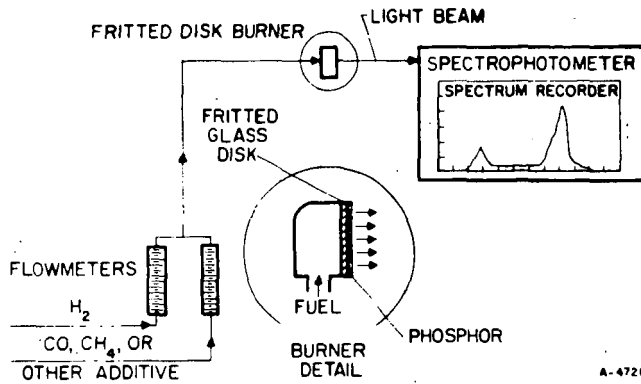


Figure 1. SCHEMATIC REPRESENTATION OF THE POROUS BURNER APPARATUS FOR LIGHT EMISSION STUDIES

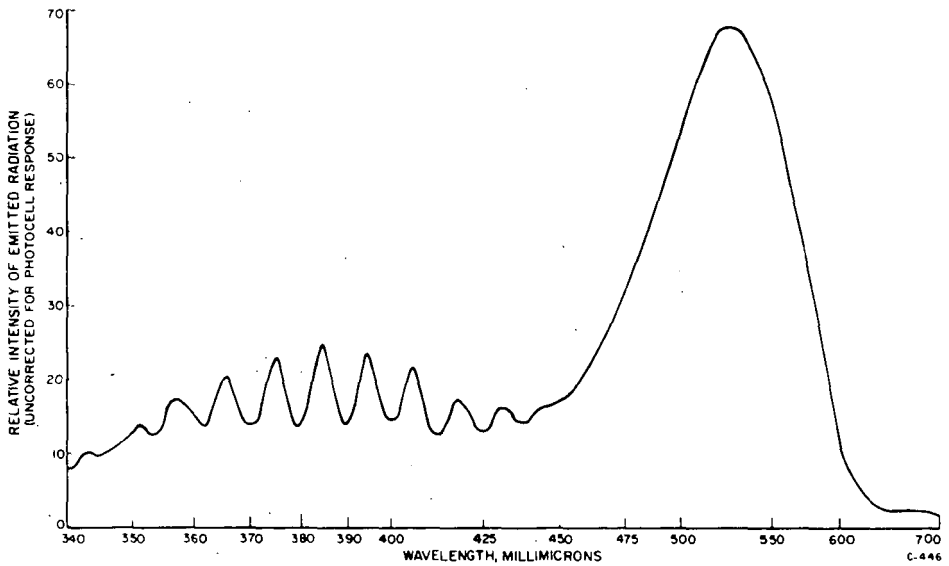
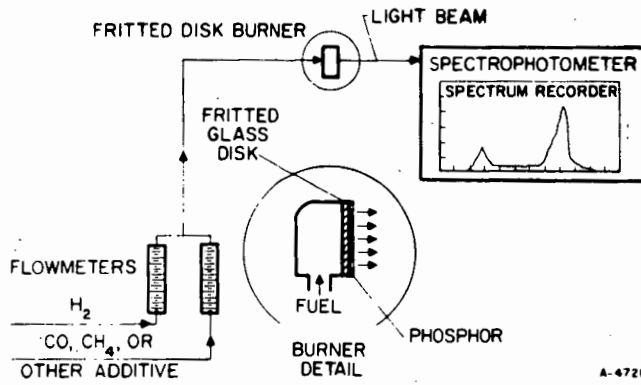


Figure 2. EMISSION SPECTRUM OF ZnS:Cu:Ag EXCITED BY A HYDROGEN DIFFUSION FLAME

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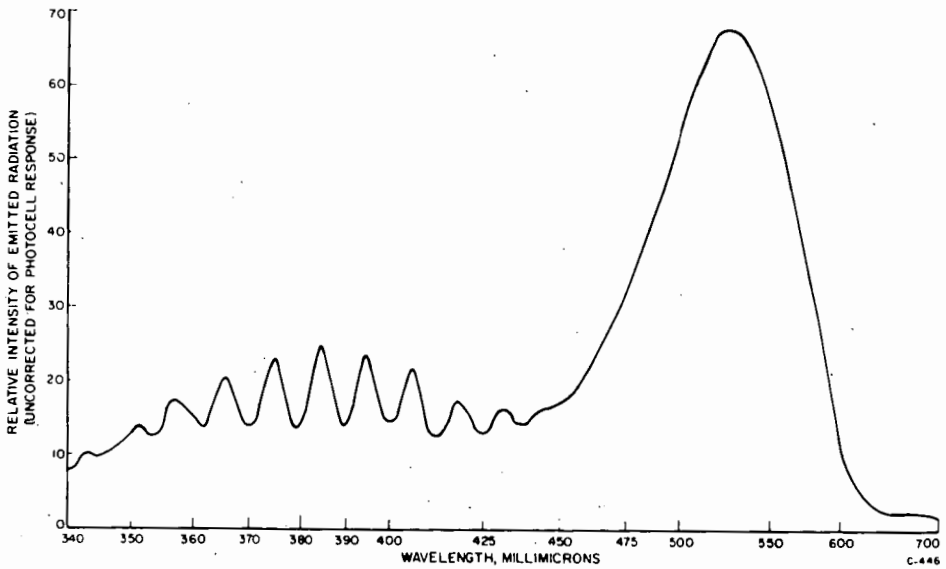


Figure 2. EMISSION SPECTRUM OF ZnS:Cu:Ag EXCITED BY A HYDROGEN DIFFUSION FLAME

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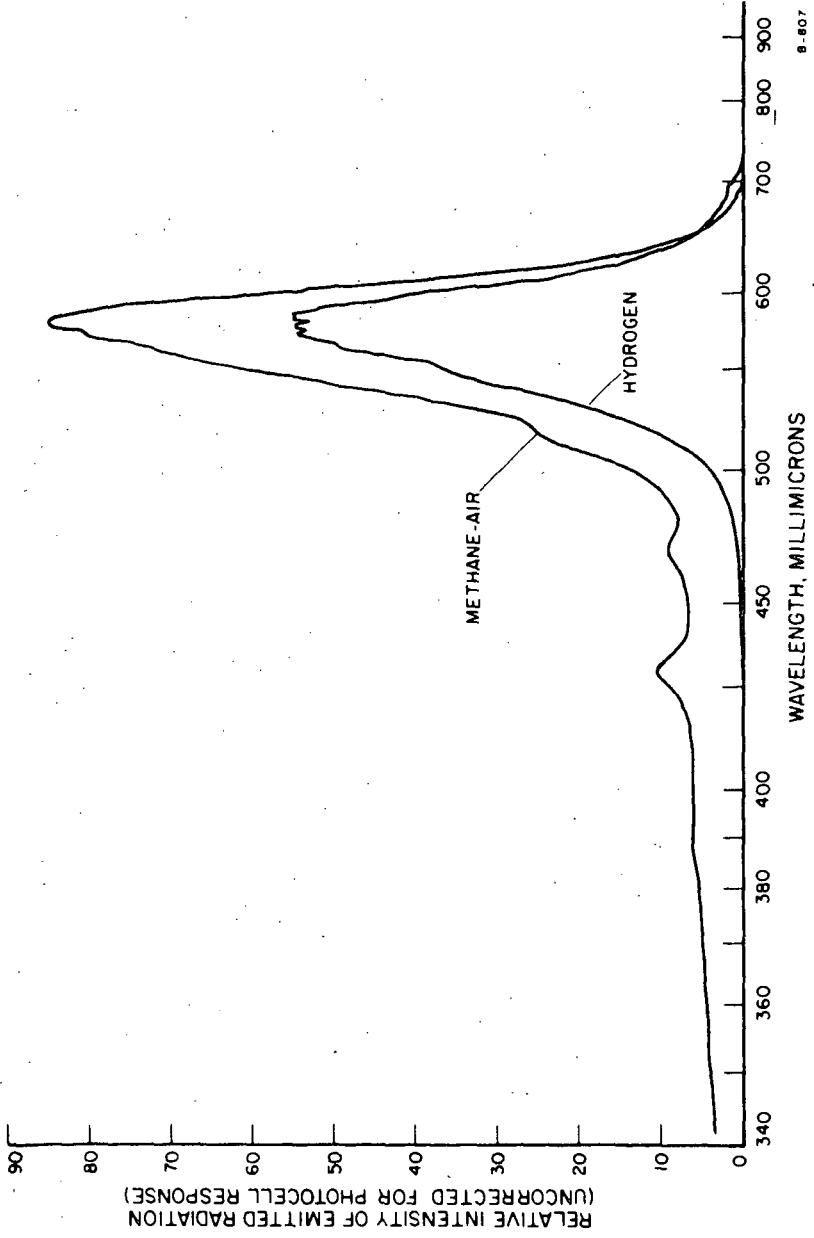


Figure 3. EMISSION SPECTRA OF SYLVANIA NO. 151 PHOSPHOR EXCITED BY HYDROGEN AND METHANE-AIR FLAMES

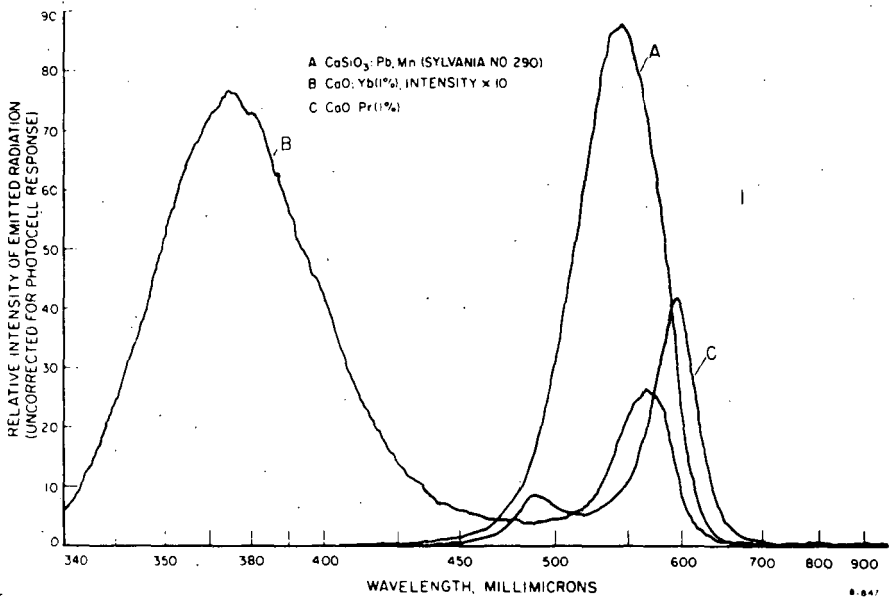


Figure 4. EMISSION SPECTRA OF PHOSPHORS EXCITED BY A HYDROGEN DIFFUSION FLAME

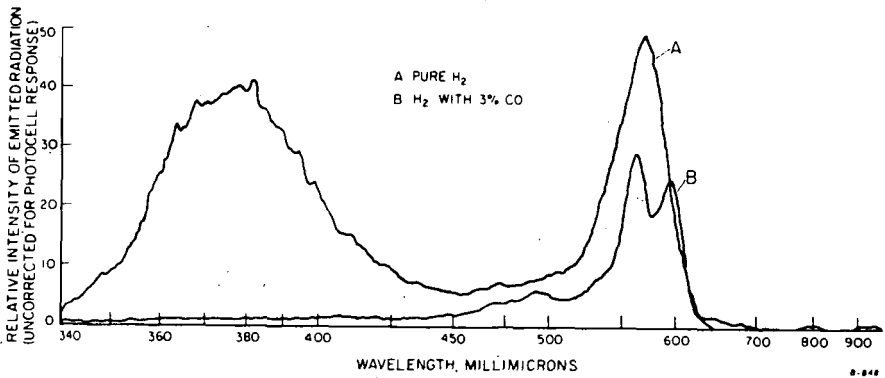


Figure 5. EFFECT OF CARBON MONOXIDE ON THE EMISSION SPECTRUM OF SAMARIUM-ACTIVATED CALCIUM OXIDE

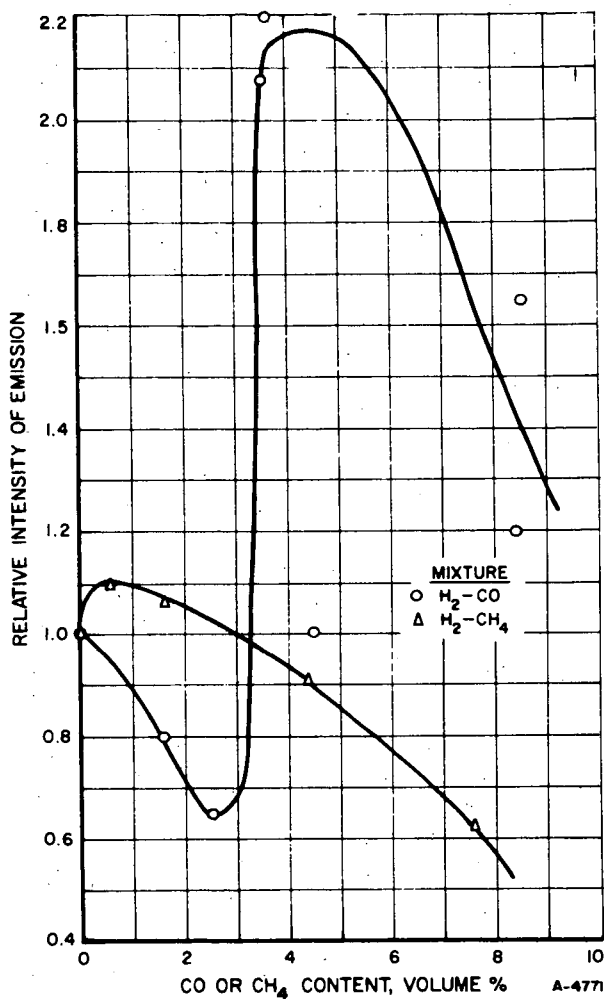


Figure 6. EFFECT OF FUEL COMPOSITION ON THE CANDOLUMINESCENCE OF SAMARIUM-ACTIVATED CALCIUM OXIDE

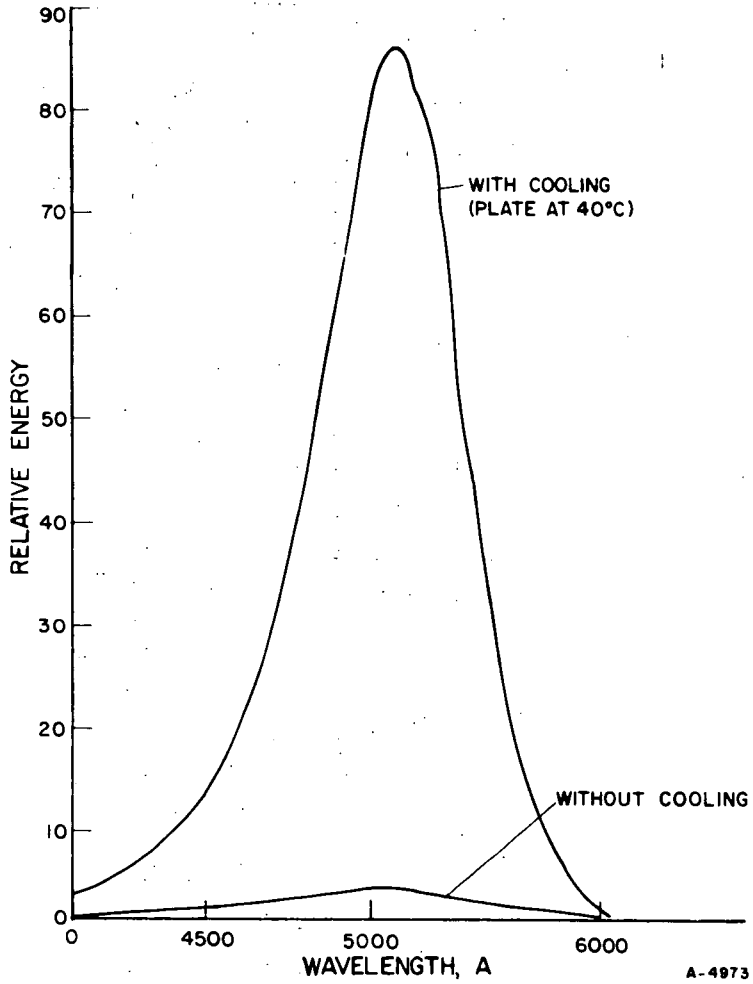


Figure 7. THE EFFECT OF TEMPERATURE ON THE EMISSION SPECTRUM OF SYLVANIA NO. 161 PHOSPHOR EXCITED BY A METHANE-AIR FLAME

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