

The Rare Earths As Possible Flame Color Agents

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ABSTRACT

Colors observed when solutions of scandium, yttrium and the lanthanide elements were sprayed into an inductively coupled plasma are reported. It is suggested, but without experimental evidence, that the colors seen in the lower temperature regions of the plasma (and in a pre-mixed air-acetylene flame) might also be produced by appropriate pyrotechnic mixtures. The color-emitting species (metal monoxide molecules) are remarkably stable, as shown by the dissociation energies of the M-O bonds. These monoxides might be able to exist in useful concentrations at the high temperatures of the glitter flash reaction, thus providing colored glitter. The possibility of using yttrium or erbium, or corrosion resistant alloys thereof, to produce red or green sparks is also suggested.

Keywords: rare earth element, colored flame, colored glitter, colored spark

Introduction

Only a very limited number of chemicals have been found to be useful for the production of colored pyrotechnic flames. Those that have found practical application include compounds of calcium, strontium, barium and copper (the emitting species are predominantly the gaseous monochlorides, MCl, where M is the metal) and sodium (the emitting species is predominantly the atomic vapor, Na). Other, much less widely-used, color agents include compounds of boron (the emitting species is predominantly the gaseous dioxide, BO₂), and lithium and potassium (the emitting species are predominantly the atomic vapors, Li and K).

Clive Jennings-White^[1a] surveyed the periodic table for materials potentially useful in pyrotechny and discussed several other possible

color agents including rubidium, cesium, indium and thallium. None of these were expected to be useful.

Of the rare earth elements, Jennings-White remarked "...nor do these elements produce useful flame spectra". The rare earth metals include scandium, yttrium and the lanthanides.^[2a] A review of the flame spectroscopy of these elements is presented in Reference 3. The Italian scientist G. Picardi described the oxyhydrogen flame spectra of most of the rare earth elements in a series of papers published from 1929 to 1941.^[3a] He, and the Swedish spectroscopist H. Lundegardh, discussed the use of the characteristic band emission spectra for the analytical determination of the rare earths by flame photometry.^[3a] Many chemists since then will have observed that some of the rare earths produce beautiful colors when sufficiently concentrated solutions are sprayed into a flame or into an inductively coupled plasma. Despite this, there have been (as far as I am aware) no reports of the use of these elements or their compounds as color agents in pyrotechny.

It is common practice to introduce 0.1% yttrium solution into an inductively coupled plasma spectrometer to check that the plasma is properly adjusted. The atomic (actually predominantly ionic, from Y⁺) emission shows up as blue, and the yttrium monoxide emission as red. That makes it easy to see if the various gas flows, and the power level, are correct.^[4] As indicated by Crawford,^[4] solutions of some of the other rare earths can also be used. I tried all the rare earths (except of course the radioactive lanthanide promethium). The colors I observed are reported in this paper, along with some speculations about the possible applications of these novel color agents in pyrotechny.

Table 1. Colors Observed When Solutions of 1 g/l of Individual Rare Earth Elements Were Introduced into a 1 kW Inductively Coupled Plasma.

Element, Symbol	Monoxide emission	Atomic (ionic) emission
Scandium, Sc	Orange-red	Blue-violet
Yttrium, Y	Red	Blue
Lanthanum, La	Faint, yellowish	Pale blue
Cerium, Ce	Pale yellow-orange	Pale blue
Praseodymium, Pr	Pale yellow	Pale greenish blue
Neodymium, Nd	Faint yellow	Greenish blue
Samarium, Sm	Red	Blue-violet
Europium, Eu	Pale pink	Violet
Gadolinium, Gd	Orange	Blue
Terbium, Tb	Yellow	Blue
Dysprosium, Dy	Greenish yellow	Blue
Holmium, Ho	Yellowish green	Blue
Erbium, Er	Green	Pale blue
Thulium, Tm	Green	Pale blue
Ytterbium, Yb	Green	Green
Lutetium, Lu	Deep bluish green	Yellow-green

Experimental

The inductively coupled plasma system was a Labtest Model 2000 (Labtest Equipment Company, Moorabbin, Victoria, Australia), operated at 1 kW. The pre-mixed air-acetylene burner system was part of a Varian Model AA1275 atomic absorption spectrometer (Varian Techtron Pty Ltd, Mulgrave, Victoria, Australia).

The test solutions each contained 1 gram per liter of a single rare earth metal as the chloride or nitrate in dilute nitric acid. Some were commercial spectroscopic calibration solutions, others were prepared in the laboratory by dissolving the equivalent amount of the appropriate rare earth oxide in acid and diluting to volume with distilled water.

Results and Discussion

The colors I observed are shown in Table 1. Some, but not all, were consistent with Crawford's observations, and I have included some elements that were not reported by Crawford. I viewed the colors through green welding glass, and this must have changed the perceived colors to some degree. Given the range of colors seen, it appears that most regions of the visible spectrum were transmitted to some extent.

The atomic/ionic emission colors were seen only in that part of the plasma called the "normal analytical zone".^[5] This is the region of the plasma that is used for spectrochemical measurements, and it has been well characterized. The temperature in this zone in a 1 kW inductively coupled plasma is around 5000 K (4727 °C).^[6] These atomic/ionic emitters are most unlikely to be useful in pyrotechnic flames because the temperatures would be too low to break up the very stable monoxides into atoms.

The colors emitted at temperatures likely to be feasible in pyrotechnic flames are evidently produced by the molecular emission bands of the gaseous metal monoxides, MO. The spectrum of the colored light consists of bands, rather than lines, showing that the emitter is a molecule, not an atom or ion. For Sc, Y, and La the emitter has been identified as the metal monoxide.^[7a] The other rare earth elements are so similar in their electronic structure to these three that it can be presumed that their emission bands also come predominantly from the monoxides. Some of the bands in the flame spectra of Eu and Yb, however, have been attributed to the monohydroxides, MOH.^[7b] Spectra showing the emission bands are published; for example, see references 3b and 8.

There is some analogy between the rare earth monoxides and the monochlorides of calcium, strontium and barium. The latter metals are divalent, having two electrons in their outer shells. Chlorine is monovalent, requiring just one electron to complete its outer shell. In the metal monochloride molecules one of the two outer electrons of the metal atom is tied up in the covalent bond linking the metal atom and the chlorine atom. The other electron readily absorbs energy from molecular collisions by moving into molecular orbitals of higher energy. When it returns to a lower energy orbital, the excess energy is emitted as light of wavelengths characteristic of the energy difference between the orbitals. The molecule thus converts thermal energy (random molecular motion) into light of specific wavelengths. There are discrete energy sublevels associated with the vibration and rotation of the diatomic molecule. Consequently, many slightly different energies are available to the electron, and the spectrum appears as a series of bands.

The rare earth metals are trivalent, and have three electrons in their outer shell. Oxygen is divalent, requiring two electrons to complete its outer shell. When a gaseous monoxide molecule is formed, two of these electrons are tied up in the covalent bond linking the two atoms, and once again a single electron is left in a molecular orbital. In the periodic table, scandium is adjacent to calcium, and yttrium to strontium. It is noteworthy that the colors emitted by the monoxides of scandium and yttrium are rather similar to those emitted by the monochlorides of calcium and strontium, respectively.

The monoxide emission colors were seen in the lower temperature regions of the plasma, located just below the normal analytical zone and just above it. They are also seen when the solutions are introduced into a pre-mixed air-acetylene flame. The maximum temperature of this flame is around 2550 K (2277 °C).^[9] Yttrium solution sprayed into a premixed air-acetylene flame gave a deep red color, while ytterbium solution gave a bright grass green.

The fact that a material can color a laboratory flame does not mean that it is automatically a suitable color agent for pyrotechnics. Lithium compounds color the pre-mixed air-

acetylene flame a vivid red, but as Jennings-White noted, they are not particularly effective for making a red pyrotechnic flame.^[1b] In the experiments reported in this article, the materials were introduced into the flame (or plasma) as an aerosol by passing the solutions through an appropriate nebulizer and spray chamber system to produce a mist of very fine droplets. On entering the flame or plasma the aerosol droplets evaporate, leaving the dissolved solids as sub-micron sized particles. This provides almost ideal conditions for the volatilization and decomposition processes needed to form the emitting species. These processes might not be so efficient in a burning pyrotechnic mixture.

It might be thought pointless even to consider the use of the rare earths as color agents, because their practical application in fireworks is ruled out by their high cost. The cost might decrease in the future, however, as commercial applications for the rare earths increase. These elements occur together in nature and only some of them are useful in industry. The others, being essentially by-products, might become less costly. If it should turn out that unique effects are indeed possible with these materials, it would do no harm to know. It would be a shame to have to find out by analyzing some Chinese product in years to come. China, by the way, is a major producer of rare earths.

Some values of relevant properties of the rare earth metals and their oxides are listed in Table 2. The values sometimes differed from one reference to another; in such cases, the tabulated value is from the most recent reference.

The gaseous rare earth monoxides are extremely stable, as indicated by the bond dissociation energies. They are the last materials to disappear when solutions of these elements are atomized in the inductively coupled plasma; indeed, the ratio of CeO^+ to Ce^+ is widely used to assess the performance of inductively coupled plasmas when they are used as ion sources for elemental mass spectrometry. The stability of rare earth monoxides suggests that they might be effective color agents for glitter. Most color emitting species cannot survive the high temperatures of the glitter flash reaction, but these may very well be able to do so. Of course, any color produced might be swamped by white

Table 2. Properties of the Rare Earth Metals and their Oxides. Aluminum, Magnesium and Titanium Are Included for Comparison.^[2b,10,11,12]

Element, Symbol	Melting Point of Metal (°C)	Boiling Point of Metal (°C)	Melting Point of Oxide (M ₂ O ₃ , unless otherwise indicated) (°C)	Boiling Point of Oxide (°C)	Bond Strength of M-O bond (kJ mol ⁻¹)
Scandium, Sc	1540	2832	~2500	unknown	670
Yttrium, Y	1525	3337	2430	unknown	720
Lanthanum, La	920	3464	2305	4200	800
Cerium, Ce	798	3433	~2500 (CeO ₂)	unknown	800
Praseodymium, Pr	931	3520	~2200 (Pr ₆ O ₁₁)	unknown	750
Neodymium, Nd	1021	3074	2320	unknown	700
Samarium, Sm	1074	1794	2335	unknown	620
Europium, Eu	822	1429	2350	unknown	560
Gadolinium, Gd	1313	3273	2420	unknown	720
Terbium, Tb	1365	3230	~2410 (Tb ₄ O ₇)	unknown	710
Dysprosium, Dy	1412	2567	2408	unknown	610
Holmium, Ho	1474	2700	2415	unknown	620
Erbium, Er	1529	2868	2418	unknown	610
Thulium, Tm	1545	1950	2425	unknown	560
Ytterbium, Yb	819	1196	2435	unknown	400
Lutetium, Lu	1663	3402	2490	unknown	700
Aluminum, Al	660.37	2467	2072	2980	510
Magnesium, Mg	648.8	1107	2852 (MgO)	3600 (MgO)	400
Titanium, Ti	1660	3287	1830–1850 (TiO ₂)	2500–3000 (TiO ₂)	660

light emission from Al₂O₃. It would be worth investigating, none the less.

The identification of suitable compounds for introducing rare earth elements into pyrotechnic compositions will require some research. The oxides are the most readily available compounds of these elements, but they may not be particularly useful. Some of them can be quite reactive, and this might lead to problems with spontaneous heating of mixtures containing them. Additionally, the oxides are so refractory that they may not volatilize to any useful extent in the flame. Many of the salts of the rare earths are deliquescent. Rare earth salts of organic acids would perhaps be useful. Ideally, the compound should vaporize at a relatively low temperature so that it would be in the gaseous state before it decomposed to the oxide. If the decomposition occurred in the solid or liquid state, it might be difficult to get sufficient material into the flame, because the oxides are ex-

tremely stable and have very high melting and boiling points (Table 2).

A highly desirable, yet elusive, firework effect is the colored spark. Some of the rare earth metals might produce colored sparks if they could be included in appropriate compositions as filings or coarse powders. The melting points of yttrium, erbium, thulium and lutetium are similar to that of titanium. This suggests that these metals would behave similarly to titanium in a spark-producing composition. If the monoxide emission colors were sufficiently intense to be visible above white light from hot oxide particles, yttrium would be expected to produce red sparks, and the other three metals, green. As noted by Jennings-White, however, the rare earth metals themselves are almost certainly too reactive to be used in pyrotechny.^[1c] Alloys of appropriate rare earths with metals that form protective oxide films (aluminum or titanium, for example), might be more stable, and would be worth investigating.

References

- 1) C. Jennings-White, "Some Esoteric Firework Materials", *Pyrotechnica* XIII, 1990; [a] pp 26–32; [b] p 27; and [c] p 32.
- 2) B. Elvers, S. Hawkins, W. Russey and G. Schulz, Eds., *Ullmann's Encyclopedia of Industrial Chemistry*, VCH Verlagsgesellschaft mbH, Weinheim, Vol. A22, 1993; [a] p 607; [b] p 616.
- 3) R. N. Knisely, V. A. Fassel, C. C. Butler, "Atomic Emission and Absorption Spectrometry of the Rare Earth Elements", in R. Mavrodineanu, Ed., *Analytical Flame Spectroscopy*, Macmillan and Co. Ltd, London and Basingstoke, Ch. 6, 1970; [a] pp 379–380, [b] pp 393–409.
- 4) R.L. Crawford, "Plasma Colors", *ICP Information Newsletter*, Vol. 3, No. 6, 1977, p 262.
- 5) S.R. Koityohann, J. S. Jones and D. A. Yates, "Nomenclature System for the Low-power Argon Inductively Coupled Plasma", *Analytical Chemistry*, Vol. 52, 1980, pp 1965–1966.
- 6) T. Hasegawa and H. Haraguchi, "Fundamental Properties of the Inductively Coupled Plasma", in A. Montaser and D. W. Golightly, Eds., *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, VCH, New York and Weinham, Chapter 8, 1987.
- 7) R. Mavrodineanu and H. Boiteux, *Flame Spectroscopy*, John Wiley & Sons, Inc., New York, London and Sydney, 1965: [a] p 392; [b] pp 405–407.
- 8) R. Herrmann and C. T. J. Alkemade, *Chemical Analysis by Flame Photometry*, 2nd ed., trans. P. T. Gilbert, Wiley Interscience, New York and London, 1963, p 220.
- 9) W. Snelleman, "A Flame as a Standard of Temperature", thesis, University of Utrecht, Bronder – Offsett, Rotterdam, 1965, p 113.
- 10) R. C. Weast, Ed., *CRC Handbook of Chemistry and Physics*, 63rd ed., CRC Press, Inc., Boca Raton, Florida, 1982–83.
- 11) J. I. Kroschwitz, Exec. Ed., M. Howe, Ed., Kirk Othmer *Encyclopedia of Chemical Technology*, Wiley Interscience, John Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore, Vol. 14, 1995, p 1091.
- 12) B. T. Kilbourne, *A Lanthanide Lanthology*, Molycorp, Inc., White Plains, NY, Part II, M–Z, 1994, p 17.