

# Color Purity Measurements of Traditional Pyrotechnic Star Formulas

Brian V. Ingram

Sandia National Laboratories, PO Box 5800 – MS 1452, Albuquerque, NM 87185-1452, USA  
email: bvingra@sandia.gov

## ABSTRACT

*Pyrotechnic formulas designed to produce colored flames are well known, but the trends in color quality due to individual formula components are less well understood. This paper presents spectrometer work done to record spectra and processes them into chromaticity coordinates. Major formulas of the basic additive colors of red, green, and blue were tested and compared. Impact sensitivities were gathered for those major formulas. Then single suitable formulas were chosen for the basic colors, which were then systematically altered and measured for color quality performance. The formulas were altered to investigate the role of oxidizer to fuel ratio, chlorine donor content, colorant content, and colorant source.*

**Keywords:** color purity, chromaticity diagram, chromaticity coordinate, star formula, flame emission

## Introduction

Pyrotechnics are used to create light, heat, sound, smoke, ash, metal, or gas. Within the visible light effects, the creation of colored flames is one of the most commonly recognized. The pyrotechnic compositions of this class are used in fireworks and civilian and military pyrotechnics.<sup>[1]</sup> In any usage, the efficient formation of a desired color is paramount. Depth of color, or saturation, is usually a prerequisite of correct device function. In addition to the pleasing aesthetic effect of a deep, saturated color star in a firework application, high quality colors permit observer discrimination between similar signal flares at extreme distances. Because of the importance placed on function of these compositions, studies have been conducted to understand factors affecting their performance.<sup>[2-5]</sup>

In the formation of a colored flame, some species are desirable to have in the flame, and some species are not desirable. The desirable species are those that emit light at or near the hue intended for that formula. Other atomic or molecular emitters in the flame, which emit at wavelengths that detract from the intended hue, will hinder performance. Also undesirable are certain solid and/or liquid combustion products that can glow in an incandescent fashion. When these materials emit radiation, it is not radiation of a specific electronic transition, but rather a broadband radiation across a very large wavelength range. This is called blackbody, graybody, or continuous radiation. When the temperature of the glowing matter is high enough, it can emit light across the entire visible spectrum.

The desired emitters for most colored flames are well known.<sup>[2,7]</sup> For forming a red flame, the molecular emitter strontium monochloride (SrCl) is responsible for the deepest red color, with emissions at 635, 660, and 673 nm.<sup>[7-9]</sup> Strontium monohydroxide (SrOH) emits at 606 nm, which contributes an undesirable orange-red light.<sup>[7]</sup> For forming a green flame, the molecular emitter barium monochloride (BaCl) is responsible for emissions at 514 and 525 nm.<sup>[7-9]</sup> A contributing barium emitter is the triatomic barium monohydroxide (BaOH), which emits desirable light at 487, 515, and 527 nm.<sup>[3]</sup> For forming blue flames, the molecular emitter copper(I) chloride (CuCl) is responsible for emissions at 430, 436, 484, 489, and 527 nm.<sup>[7-9]</sup> As an aside, copper(II) oxide (CuO) has a weak molecular emission at 609 nm,<sup>[8]</sup> widely recognized as orange-red tips on otherwise blue flames. While there are smaller peaks in the spectra, the overwhelming contribution to the flame hue is from the emitters mentioned. Other detrimental emitters are present as well. As examples, there are the ubiquitous sodium atomic emission at 589 nm<sup>[10]</sup> and the sometimes-present

calcium monochloride (CaCl) at 594, 619, and 621 nm.<sup>[7]</sup> Both are caused by contamination of chemicals used in the formula. The sodium contamination arises because many oxidizer salts are produced by a double displacement reaction with sodium salt. The calcium contamination is typically found in ammonium perchlorate where tricalcium phosphate is used as an anti-caking additive.<sup>[11]</sup> In some orange flame formulas, the CaCl emitter is desired; however this work will not address orange, yellow or other non-primary flames.

## Objective of Present Work

Study of the conditions that give rise to the desirable species is important, because understanding those conditions will allow tuning of a composition at the formulation stage. Past studies that were conducted have used elegant and ingenious techniques to show intensity and wavelength information<sup>[4,12,13]</sup> and to correlate that data to chemical species.<sup>[3]</sup> In fact, work to demonstrate the spectra due to emitters is ongoing.<sup>[14]</sup> Chromaticity coordinates have also been generated for colored flame formulas<sup>[3]</sup> in an effort to show the change in color purity as a function of formula. This study attempts to add to this field, by acquiring spectra with a spectrometer suited for visible range flame emission, and processing the spectra into CIE color coordinates. The 1931 CIE Chromaticity Diagram is shown in Figure 1.<sup>[7,15]</sup> Further, systematic experiments are performed, which follow the flame color quality as a function of formula, to identify trends in performance. These experiments are also designed to give insight into the relative importance and roles of the components of typical color formulas.

## Experimental

Experiments were performed using a PC2000 spectrometer from Ocean Optics, Inc., which was outfitted with a grating optimized for the visible range, and which was especially suited to color measurements. Its blaze wavelength, which is the wavelength of greatest efficiency, was located at 500 nm. The spectrometer could

read from 340 to 860 nm, with relative efficiencies of at least 40% from 380 to 700 nm. A high temperature quartz collimating lens was employed to gather light from the sample, directed into a 400  $\mu$  diameter, 8 m long fiber optic cable, which transmitted the sample light to the spectrometer. The system was calibrated using an Ocean Optics, Inc. 3100 K color temperature tungsten lamp. The Ocean Optics 16-bit OOI-Base V1.5 proprietary software, which was packaged with the spectrometer, was used to control the spectrometer and collect spectra. An Excel spreadsheet program was used to calculate CIE coordinates from wavelength-intensity data exported from the spectrometer.

For all experiments, chemicals were used as supplied straight from the source bottle, without pretreatment. Chemicals were obtained from Skylighter Pyrotechnic Supply, except for the strontium peroxide, barium peroxide, and copper(I) chloride. The strontium and barium peroxides were obtained from Firefox Enterprises, and the copper(I) chloride was obtained from Acros Organics. The compositions were prepared by first passing the components through a 100-mesh sieve, to break up any clumps.<sup>[16,17]</sup> Components that were too coarse to pass a 100-mesh sieve, were reduced with an alumina mortar and pestle, and then passed through the sieve. To achieve homogeneous mixtures, components were shaken in a 500 mL Velostat<sup>™</sup> antistatic container, and then passed through the sieve. This procedure was repeated 3 times. Blended components were stored in airtight high-density polyethylene bottles. The formulas chosen for testing will be described in the Results section.

The samples were compacted into pellets for the data collection procedure. Cylindrical pellets were formed having a diameter of 3/8 inch (9.5 mm), and sufficient composition was used to form cylinders 3/8 inch (9.5 mm) in length. The samples were hydraulically pressed at 1000 psi (145 kPa), with 110 pounds (50 kg) of force applied to the ram. To facilitate consolidation, the compositions were dampened with 2% by weight distilled water. After ejection from the die, the pellets were allowed to dry for at least 48 hours before being used.

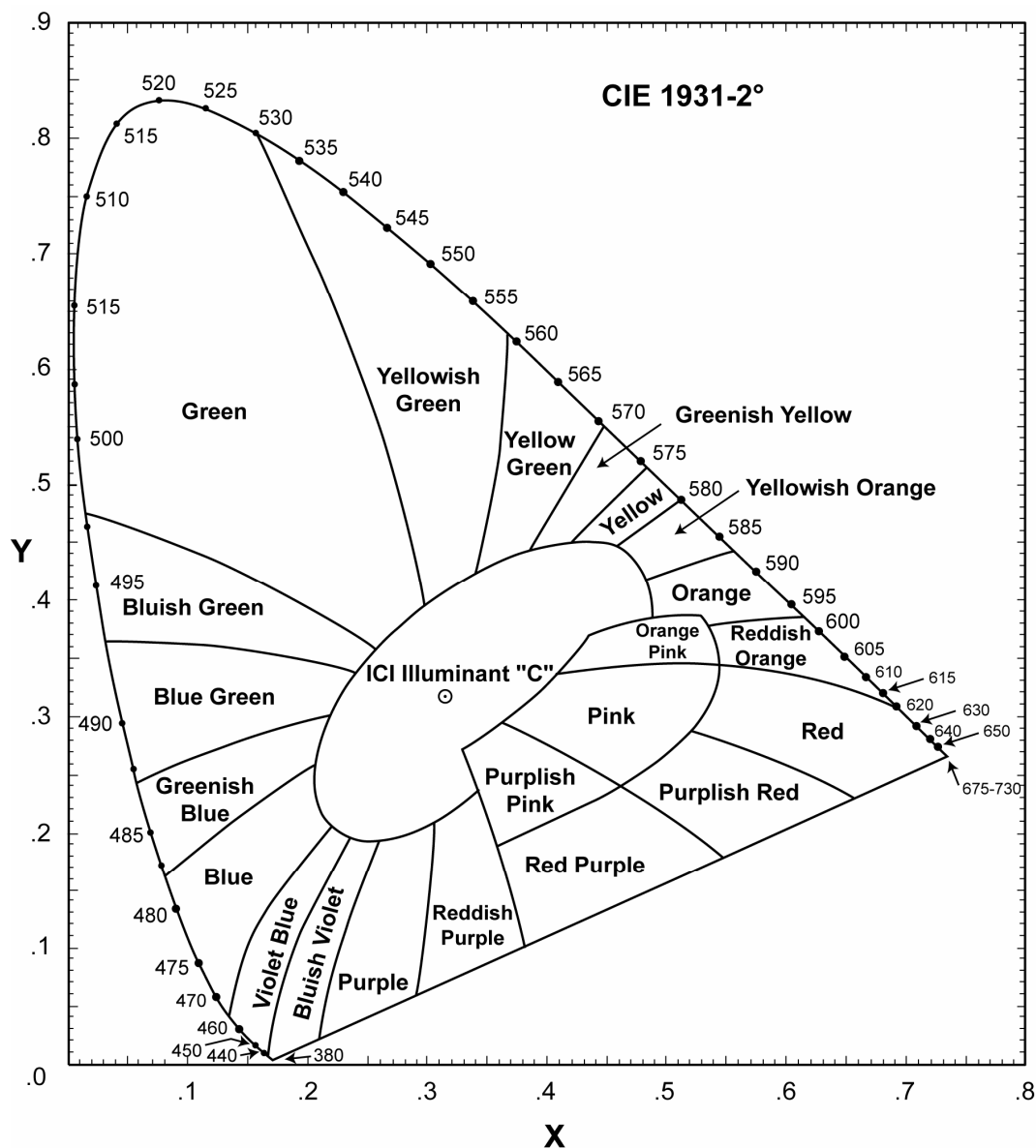


Figure 1. 1931 CIE Chromaticity Diagram. The sail-shaped area encompasses all colors visible to the human eye. The outside edge of the area defines perfect purity and complete saturation at a given wavelength. The straight line between the 700 nm right corner and the 380 nm left corner is the “nonspectral line” where purples, magentas, and other artificial red-blue blends are located. The “equal energy” (ICI Illuminant “C”) point is located at  $x = 0.33$ ,  $y = 0.33$  and defines perfectly balanced white light.

The pellets tested were held above rather than set on a surface so that ash could fall away. They were ignited with a nichrome hotwire, so that remote ignition and collection were possible. Once a stable burn was achieved, the sample spectra were frozen and recorded. The chamber they were burned in was painted flat black to avoid reflections, as was the tunnel

between the sampling lens and the chamber. Also, a cross-flow ducting system was constructed that carried the smoke away to avoid attenuation by the particulate matter. It was also hoped that the moving air would further simulate an operational condition. The airflow velocity was not measured, though a rough estimate would be 3 to 5 feet (1–2 m) per second.

## Sensitivity Testing

Drop hammer impact sensitivity tests were performed on the 17 standard color formulas. The samples for impact sensitivity testing were taken from the larger samples blended for spectral acquisition. Samples were not desiccated prior to testing, which would certainly have caused them to be more sensitive. Also, to consolidate the sample and then granulate the material before testing would give an interesting comparison with the values reported here. The impact tester employed complied with the Modified Type 12 Impact Tool description.<sup>[18]</sup> The drop height results are reported as an  $H_{50}$ , which gives the height at which a 2.5 kg mass dropped on the sample has a 50% chance of initiating the sample. The Bruceton Up-Down calculation method was used to obtain the  $H_{50}$  values.<sup>[18]</sup>

## Results and Discussion

### Standard Formulas Tested

Compositions tested were in two series: a series of known traditional formulas, and a series of experimental color formulas. For the known traditional formulas, some of the literature central in the field<sup>[1,6,7,16,19-23]</sup> was surveyed to identify classes of formulas for the primary additive colors of red, green, and blue. For example, there are numerous formulas for red fire both accepted and proposed, but a majority of those formulas belong to 6 major types or classes. Six classes of green and five classes of blue were identified. There are indeed some color formulas that do not fit perfectly in any of these classes, but they are a minority and are reserved for future treatment.

The major red classes identified are:

- 1)  $\text{SrCO}_3$  and  $\text{KClO}_4$ , with no metal fuel
- 2)  $\text{SrCO}_3$  and  $\text{KClO}_4$ , with metal fuel
- 3)  $\text{SrCO}_3$  and  $\text{KClO}_3$ , with no metal fuel
- 4)  $\text{SrCO}_3$  and  $\text{KClO}_3$ , with metal fuel
- 5)  $\text{Sr}(\text{NO}_3)_2$ , with metal fuel
- 6)  $\text{SrCO}_3$  and  $\text{NH}_4\text{ClO}_4$

Note: a table of chemical formulas and chemical names is included at the end of this article.

Symbol →	Red Flame Formulas					
	●	○	▼	▽	■	□
Chemical ↓	1	2	3	4	5	6
$\text{KClO}_4$	66	54				
$\text{KClO}_3$			70	58.5		
$\text{NH}_4\text{ClO}_4$						41
$\text{K}_2\text{Cr}_2\text{O}_7$						1.9
$\text{Sr}(\text{NO}_3)_2$					55	
$\text{SrCO}_3$	12	10	15	9.8		9.5
Al				19.5		
Mg					28	
Mg/Al		14				
Mg(coated)						33.3
PVC	2				17	
Parlon™		13				
Red Gum	13	4	10			9.5
Lampblack	2					
Airfloat C				2.4		
Dextrin	5	5	4	4.9		4.8
Shellac				4.9		
Reference	6	16	16	19	16	6

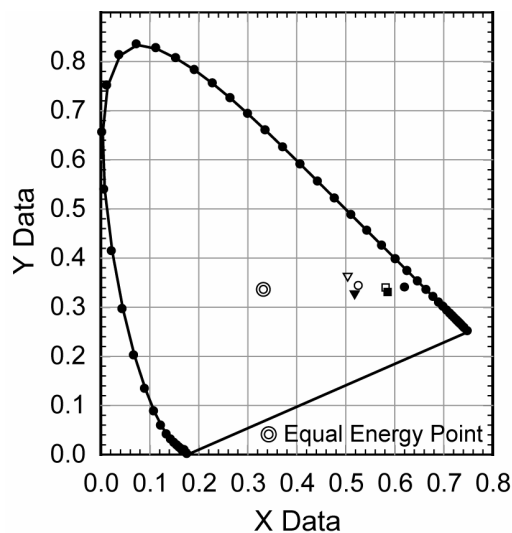


Figure 2. Red flame formula performances.

Table 1a. Chromaticity Coordinates of Standard Red Compositions.

Formula	Symbol	x-Coordinate	y-Coordinate
1	●	0.622	0.339
2	○	0.528	0.342
3	▼	0.518	0.328
4	▽	0.504	0.364
5	■	0.585	0.331
6	□	0.581	0.340

The red flame formulas were processed and tested, and their performance plotted on a chromaticity diagram shown in Figure 2. Their chromaticity coordinates are given in Table 1a. The equal energy point at  $(x,y) = (0.33,0.33)$  shows the location of perfect white on the diagram. The outside boundary of the diagram defines perfect saturation at that color. Thus, it can be seen that the best performing composition in terms of color purity is red formula 1, denoted by the solid circle, while the worst is red formula 4, which is denoted by the open triangle.

The major green classes identified are:

- 7)  $Ba(NO_3)_2$ , with metal fuel
- 8)  $Ba(NO_3)_2$  and  $KClO_4$ , with no metal fuel
- 9)  $Ba(NO_3)_2$  and  $KClO_4$ , with metal fuel
- 10)  $Ba(ClO_3)_2$  and  $BaCO_3$ , with no metal fuel
- 11)  $BaCO_3$  and  $NH_4ClO_4$
- 12)  $Ba(ClO_3)_2$ , with no metal fuel

Symbol →	Green Flame Formulas					
	●	○	▼	▽	■	□
Chemical ↴	7	8	9	10	11	12
$KClO_4$		47.2	10			
$Ba(ClO_3)_2$				72		87.8
$NH_4ClO_4$					41	
$K_2Cr_2O_7$					1.9	
$Ba(NO_3)_2$	55	28.3	50			
$BaCO_3$				4	9.5	
Mg	16					
Mg/Al			13			
Mg(coated)					33.3	
PVC	29					
Parlon™		4.7	15			
Red Gum		14.2	7	12	9.5	
Airfloat C				8		
Dextrin		5.6	5	4	4.8	2.45
Shellac						9.75
Reference	16	6	16	16	6	20

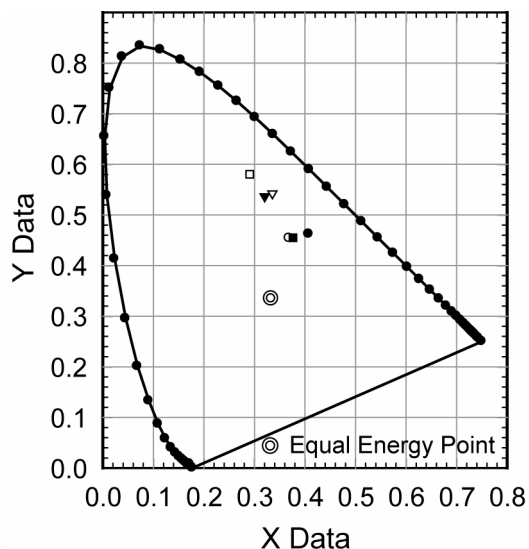


Figure 3. Green flame formula performances.

Table 1b. Chromaticity Coordinates of Standard Green Compositions.

Formula	Symbol	x-Coordinate	y-Coordinate
7	●	0.408	0.462
8	○	0.369	0.454
9	▼	0.320	0.537
10	▽	0.336	0.542
11	■	0.376	0.455
12	□	0.291	0.580

The green flame formulas were tested, and their chromaticity coordinates are shown in Figure 3 and listed in Table 1b. Formula 12 displayed the best color purity followed closely by green formula 10. Formulas 10 and 12 were both of the same type; that is, a barium chlorate formula having no metal fuel. The poorest performing green flame composition was green formula 7.

The major blue classes identified are:

- 13)  $\text{KClO}_4$  based, with no metal fuel
- 14)  $\text{KClO}_4$  based, with metal fuel
- 15)  $\text{KClO}_3$  based, with no metal fuel
- 16)  $\text{KClO}_3$  based, with metal fuel
- 17)  $\text{NH}_4\text{ClO}_4$  based

The performances of the blue flame formulas are shown in Figure 4, and their chromaticity coordinates are given in Table 1c. The two best formulas tested were 14 and 17. Formula 14 is the blue primary from the Veline color system, while 17 is a formula including ammonium perchlorate. The lowest performance for a blue formula was recorded for blue formula 15.

### Impact Sensitivities

The results of the standard formula impact sensitivity testing are shown in Table 2. For points of reference, on impact machines with the same tooling and falling mass, trinitrotoluene (TNT) has an  $H_{50}$  of 100 cm, and pentaerythritol tetranitrate (PETN) has an  $H_{50}$  of 17 cm.<sup>[24]</sup> TNT is widely regarded as a relatively safe secondary explosive in terms of handling, while PETN is deemed the most sensitive secondary explosive, bordering on classification as a primary explosive. From the results, it is not obvious that potassium chlorate or barium chlorate based formulas are more sensitive than formulas with other oxidizers. In fact, the most sensitive formulas appear to be those with ammonium perchlorate. The least sensitive seem to be based on metal nitrates such as barium and strontium nitrate. It is highly likely that friction sensitivity would show potassium chlorate and barium chlorate formulas are the most sensitive, but that will be left for future work.

### Experimental Formulas Tested

To show the change in color quality as a function of composition, suitable formulas were chosen for further study. Formula 2 was chosen for experiments with the color red, formula 8 for the color green, and formula 13 for the color blue. With these formulas, the fuel to oxidizer ratio, chlorine donor percentage, colorant percentage and colorant source were varied and spectral and chromatic performance data were collected.

Symbol→	Blue Flame Formulas				
	●	○	▼	▽	■
Chemical↴	13	14	15	16	17
$\text{KClO}_4$	66.5	55			39
$\text{KClO}_3$			54.2	68	
$\text{NH}_4\text{ClO}_4$					29
CuO	13.4	15			
Shellac			1.7		
$\text{CuCO}_3$					14
Mg/Al		6			
Al			13.6		
Paris Green			27.1	22	
Colophony Resin				6	
Parlon™	5.4	15			
Red Gum	9.9	9			14
Dextrin	4.8	4	3.4	4	4
Reference	6	22	19	16	16

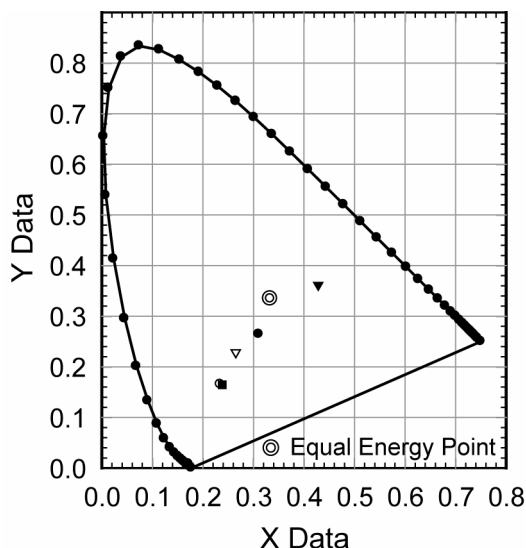


Figure 4. Blue flame formula performances.

Table 1c. Chromaticity Coordinates of Standard Blue Compositions.

Formula	Symbol	x-Coordinate	y-Coordinate
13	●	0.311	0.264
14	○	0.235	0.165
15	▼	0.428	0.362
16	▽	0.265	0.229
17	■	0.238	0.165

**Table 2. Impact Sensitivity of Compositions.**

Formula	Color Effect	Oxidizer, Fuel	H <sub>50</sub> (cm)
1	Red	KClO <sub>4</sub> , Red Gum	49
2	Red	KClO <sub>4</sub> , Mg/Al	30
3	Red	KClO <sub>3</sub> , Red Gum	83
4	Red	KClO <sub>3</sub> , flake Al	58
5	Red	Sr(NO <sub>3</sub> ) <sub>2</sub> , Mg	229
6	Red	NH <sub>4</sub> ClO <sub>4</sub> , Mg	23
7	Green	Ba(NO <sub>3</sub> ) <sub>2</sub> , Mg	> 300
8	Green	KClO <sub>4</sub> , Ba(NO <sub>3</sub> ) <sub>2</sub> , Red Gum	86
9	Green	KClO <sub>4</sub> , Ba(NO <sub>3</sub> ) <sub>2</sub> , Mg/Al	42
10	Green	Ba(ClO <sub>3</sub> ) <sub>2</sub> , Red Gum	37
11	Green	NH <sub>4</sub> ClO <sub>4</sub> , Mg	26
12	Green	Ba(ClO <sub>3</sub> ) <sub>2</sub> , Shellac	34
13	Blue	KClO <sub>4</sub> , Red Gum	32
14	Blue	KClO <sub>4</sub> , Mg/Al	34
15	Blue	KClO <sub>3</sub> , flake Al	180
16	Blue	KClO <sub>3</sub> , Colophony Resin	57
17	Blue	NH <sub>4</sub> ClO <sub>4</sub> , Red Gum	34

### Red Formula Experiments

The experimental formula variations begin with the fuel to oxidizer ratio experiments, starting with red formula 2. The fuel to oxidizer ratio experiments were undertaken to assess the effect of excess oxygen in a formula, as well as excess fuel. The chromaticity coordinates of the experimental mixtures are shown in Figure 5. One would expect the coordinates to lie on a straight line connecting the equal energy point and the point on the saturated border corresponding to the overall hue. This would be because color quality mainly depends on the balance between desirable emitters and undesirable broadband radiators. While there is some semblance of a linear positioning, the formula with the lowest oxidizer content moved towards the yellow region. This is likely because organics released from the fuel-rich pellet were burning in the air with a typical yellow hydrocarbon flame caused by incandescent soot.

### Variation of Oxidizer to Fuel Ratio Based on Red Formula 2.

Symbol→	Red Oxidizer to Fuel Ratio - ROFX				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
KClO <sub>4</sub>	37.0	46.8	54.0	59.5	63.8
Mg/Al	19.2	16.2	14.0	12.3	11.0
Parlon™	17.8	15.1	13.0	11.5	10.2
SrCO <sub>3</sub>	13.7	11.5	10.0	8.8	7.9
Dextrin	6.9	5.8	5.0	4.4	3.9
Red Gum	5.5	4.6	4.0	3.5	3.1

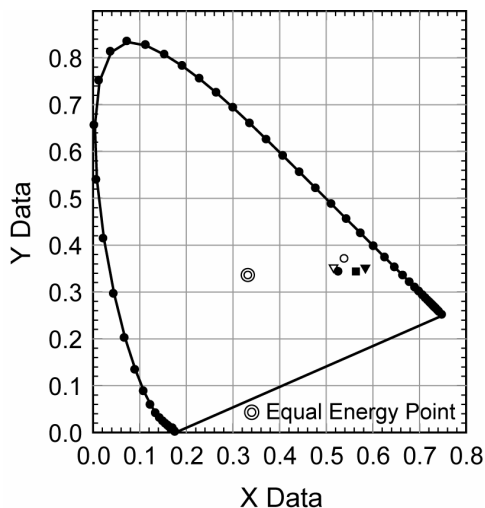


Figure 5. Red oxidizer to fuel ratio experimental composition performances.

Table 3. Chromaticity Coordinates for Oxidizer to Fuel Ratio Experimental Red Compositions. [ROFX-#]

Oxidizer (%)	Symbol	x-coordinate	y-coordinate
37.0	○	0.539	0.371
40.8	▼	0.584	0.352
54.0	●	0.528	0.342
59.5	▽	0.516	0.352
63.8	■	0.564	0.344

The next experiments performed were variations of the chlorine donor content. Those spectra are shown in Figure 6, and the chromaticity results are shown in Figure 7. Note that the peak at 606 nm is due to SrOH emissions. As the amount of chlorine in the flame increases, the SrOH is converted to SrCl. However, it seems that as long as some chlorine is present, the performance seems to be about the same.

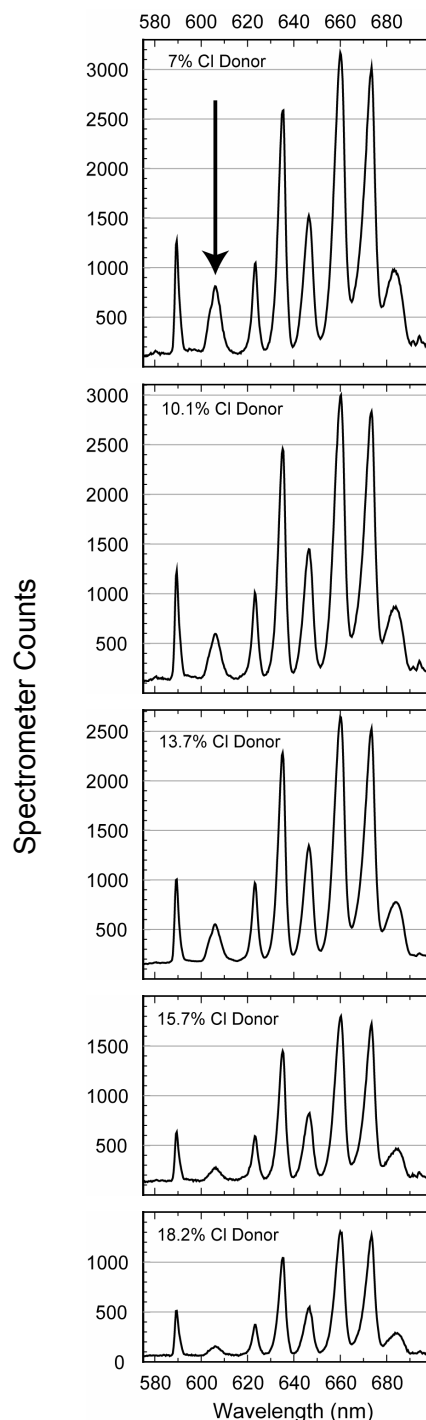


Figure 6. Spectra of red chlorine donor ratio experiments. The top spectrum, number 1, is of the mixture RCDX1, with the least chlorine donor. Spectrum 5, at the bottom, is of RCDX4, with the highest fraction of chlorine donor. Note the gradual suppression of the SrOH peak at 606 nm as more chlorine is present in the flame. The chromaticity points computed from these spectra are shown in Figure 7.



**Variation of Chlorine Donor Percentage Based on Red Formula 2.**

Symbol→	Red Chlorine Donor % - RCDX-				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
Parlon™	7.0	10.1	13.0	15.7	18.2
KClO <sub>4</sub>	57.8	55.8	54.0	52.4	50.8
Mg/Al	15.0	14.5	14.0	13.6	13.2
SrCO <sub>3</sub>	10.7	10.3	10.0	9.7	9.4
Dextrin	5.3	5.1	5.0	4.8	4.7
Red Gum	4.3	4.1	4.0	3.9	3.8

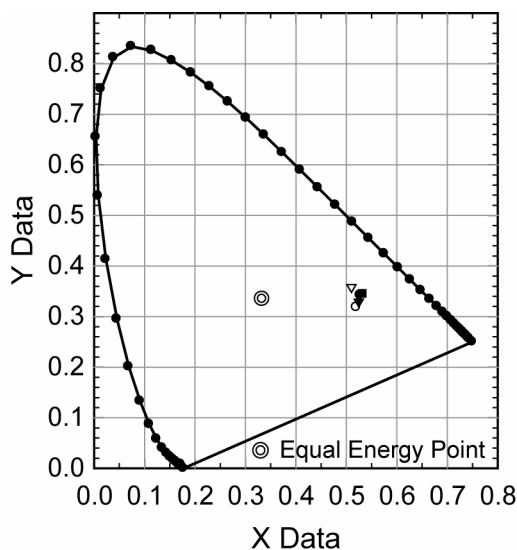


Figure 7. Red chlorine donor percentage experimental composition performances.

**Table 4. Chromaticity Coordinates for Percentage Chlorine Donor for Experimental Red Compositions. [RCDX-#]**

Chlorine Donor (%)	Symbol	x-coordinate	y-coordinate
7.0	○	0.520	0.520
10.1	▼	0.525	0.525
13.0	●	0.528	0.528
15.7	▽	0.510	0.510
18.2	■	0.531	0.531

The amount of colorant in the formula was then varied, and the results of those experiments are shown in Figure 8. Interpreting these results, the amount of colorant in a formula is indeed

**Variation of Colorant Percentage Based on Red Formula 2.**

Symbol→	Red Colorant % – RCPX-				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
SrCO <sub>3</sub>	5.3	7.7	10.0	12.2	14.3
KClO <sub>4</sub>	56.8	55.4	54.0	52.7	51.4
Mg/Al	14.8	14.4	14.0	13.7	13.4
Parlon™	13.6	13.3	13.0	12.6	12.3
Dextrin	5.3	5.2	5.0	4.9	4.8
Red Gum	4.2	4.1	4.0	3.9	3.8

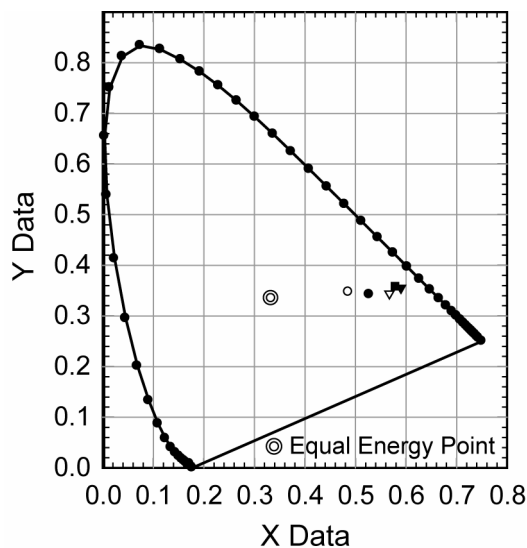


Figure 8. Red colorant percentage experimental composition performances.

**Table 5. Chromaticity Coordinates for Percentage Colorant for Experimental Red Compositions. [RCPX-#]**

Colorant (%)	Symbol	x-coordinate	y-coordinate
5.3	○	0.486	0.347
7.7	▼	0.590	0.355
10.0	●	0.528	0.342
12.2	▽	0.567	0.344
14.3	■	0.578	0.359

important; however, once a certain amount is attained, adding more does not improve performance. Once the amount of colorant in the formula was at or above the level in the original formula, the color performance changes were very slight. A likely reason for this is that as more colorant is added, the heat generated by the fuel and oxidizer is lost in melting and vaporizing excess colorant, cooling the flame below the optimum temperature for the emitting species excitation.

Finally, the effect of changing the source of colorant was explored, and the results of those experiments are shown in Figure 9. The mass percentage of each colorant source was determined by calculating the mass required to offer the same number of moles of colorant atoms as the number that the reference colorant supplied. Strontium chloride and strontium peroxide appear to act as very good strontium donors. Strontium carbonate and strontium nitrate both had similar performance.

#### Variation of Colorant Source Based on Red Formula 2.

Symbol→	Red Colorant Source – RCSX-				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
KClO <sub>4</sub>	50.0	52.8	54.0	51.9	55.0
Mg/Al	13.0	13.7	14.0	13.5	14.3
Parlon™	12.0	12.7	13.0	12.5	13.2
Dextrin	4.7	4.9	5.0	4.8	5.1
Red Gum	3.7	3.9	4.0	3.8	4.0
SrCl <sub>2</sub>	16.6				
SrSO <sub>4</sub>		12.0			
SrCO <sub>3</sub>			10.0		
Sr(NO <sub>3</sub> ) <sub>2</sub>				13.5	
SrO <sub>2</sub>					8.3

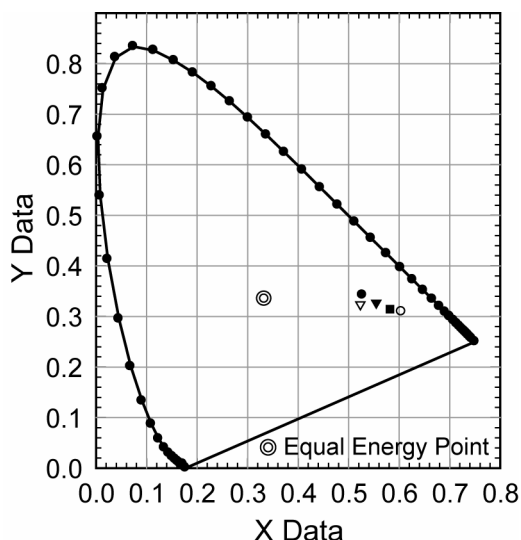


Figure 9. Red colorant source experimental composition performance.

Table 6. Chromaticity Coordinates for Colorant Source for Experimental Red Compositions. [RCSX-#]

Colorant	(%)	Symbol	x-coordinate	y-coordinate
SrCl <sub>2</sub>	7.0	○	0.605	0.309
SrSO <sub>4</sub>	10.1	▼	0.555	0.327
SrCO <sub>3</sub>	13.0	●	0.528	0.342
Sr(NO <sub>3</sub> ) <sub>2</sub>	15.7	▽	0.523	0.323
SrO <sub>2</sub>	18.2	■	0.582	0.314

#### Green Formula Experiments

Green formula 8 was treated in the same way, and results of the oxidizer experiments are shown in Figure 10. As with the red experiments, the excess fuel burning in the air drove the lowest oxidizer mixture towards the yellow region. The rest of the formulas formed a line, between a point in the pale yellow, stretching towards the green region.

**Variation of Oxidizer to Fuel Ratio Based on Green Formula 8.**

Symbol→	Green Oxidizer to Fuel Ratio - GOFX				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
KClO <sub>4</sub>	30.9	40.1	47.2	52.8	57.3
Ba(NO <sub>3</sub> ) <sub>2</sub>	37.0	32.1	28.3	25.3	22.9
Red Gum	18.6	16.1	14.2	12.7	11.5
Dextrin	7.3	6.3	5.6	5.0	4.5
Parlon™	6.1	5.3	4.7	4.2	3.8

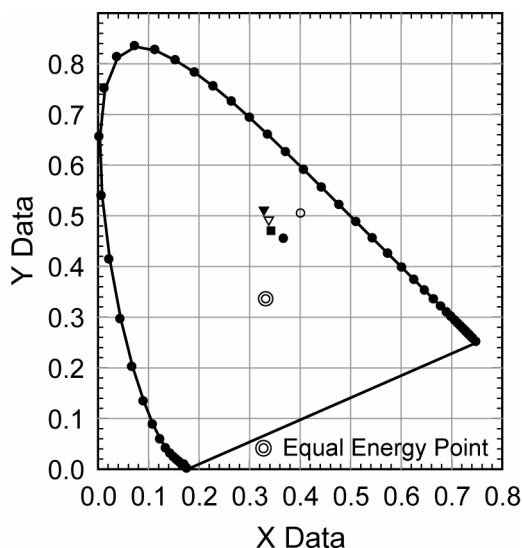


Figure 10. Green oxidizer to fuel ratio experimental composition performances.

**Table 7. Chromaticity Coordinates for Oxidizer to Fuel Ratio Experimental Green Compositions. [GOFX-#]**

Oxidizer (%)	Symbol	x-coordinate	y-coordinate
30.9	○	0.404	0.503
40.1	▼	0.328	0.512
47.2	●	0.369	0.454
52.8	▽	0.338	0.492
57.3	■	0.342	0.470

When the chlorine donor amount was varied, the cluster showed a very slight trend with the greatest color quality corresponding to the mixture containing the most chlorine donor. These results are shown in Figure 11.

**Variation of Chlorine Donor Percentage Based on Green Formula 8.**

Symbol→	Green Chlorine Donor Ratio - GCDX				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
Parlon™	2.4	3.6	4.7	5.8	6.9
KClO <sub>4</sub>	52.1	47.7	47.2	46.6	46.1
Ba(NO <sub>3</sub> ) <sub>2</sub>	29.0	28.6	28.3	28.0	27.7
Red Gum	14.5	14.4	14.2	14.0	13.9
Dextrin	5.8	5.7	5.6	5.6	5.5

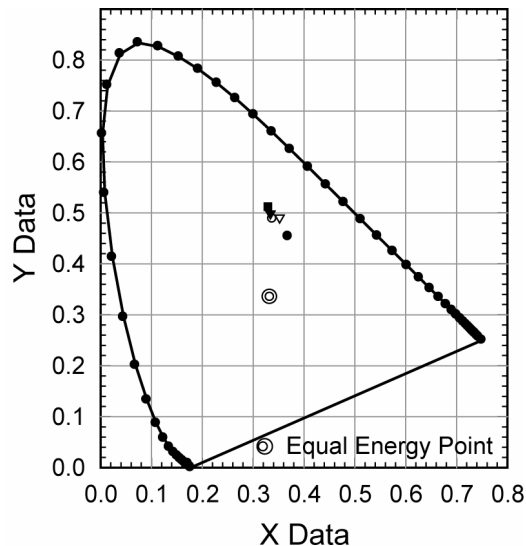


Figure 11. Green chlorine donor percentage experimental composition performances.

**Table 8. Chromaticity Coordinates for Chlorine Donor Percentage Experimental Green Compositions. [GCDX-#]**

Chlorine Donor (%)	Symbol	x-coordinate	y-coordinate
2.4	○	0.339	0.488
3.6	▼	0.334	0.498
4.7	●	0.369	0.454
5.8	▽	0.352	0.490
6.9	■	0.329	0.512

The amount of colorant was varied, and the results from these experiments are shown in Figure 12. As can be seen, there is not a great deal of order to the results, possibly indicating that there is not a great dependence of color performance on the amount of colorant.

**Variation of Colorant Percentage Based on Green Formula 8.**

Symbol→	Green Colorant Ratio - GCPX				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
Ba(NO <sub>3</sub> ) <sub>2</sub>	16.5	22.8	28.3	33.0	37.2
KClO <sub>4</sub>	54.9	50.8	47.2	44.1	41.3
Red Gum	16.5	15.3	14.2	13.3	12.4
Dextrin	6.5	6.0	5.6	5.2	4.9
Parlon™	5.5	5.1	4.7	4.4	4.1

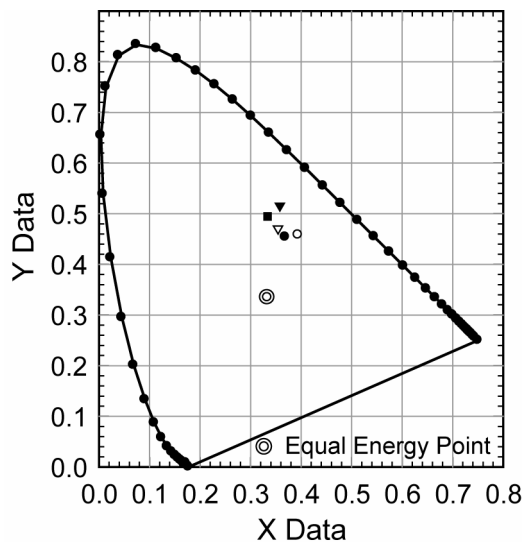


Figure 12. Green colorant percentage experimental composition performances.

**Table 9. Chromaticity Coordinates for Colorant Percentage Experimental Green Compositions. [GCPX-#]**

Colorant (%)	Symbol	x-coordinate	y-coordinate
16.5	○	0.394	0.458
22.8	▼	0.358	0.516
28.3	●	0.369	0.454
33.0	▽	0.354	0.471
37.2	■	0.334	0.494

The source of colorant was varied, and spectra collected and analyzed. The results of these experiments are shown in Figure 13. As in the

**Variation of Colorant Source Based on Green Formula 8.**

Symbol→	Green Colorant Source - GCSX				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
KClO <sub>4</sub>	48.1	50.7	47.2	48.6	52.4
Red Gum	14.5	15.3	14.2	14.6	15.8
Dextrin	5.7	6.0	5.6	5.8	6.2
Parlon™	4.8	5.1	4.7	4.9	5.3
BaCl <sub>2</sub>	26.9				
BaCO <sub>3</sub>		22.9			
Ba(NO <sub>3</sub> ) <sub>2</sub>			28.3		
BaSO <sub>4</sub>				26.1	
BaO <sub>2</sub>					20.4

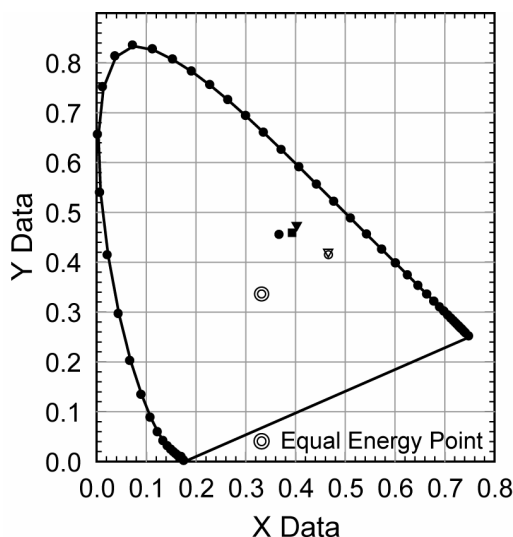


Figure 13. Green colorant source experimental composition performances.

**Table 10. Chromaticity Coordinates for Colorant Source Green Compositions. [GCPX-#]**

Colorant (%)	Symbol	x-coordinate	y-coordinate
BaCl <sub>2</sub>	○	0.369	0.454
BaCO <sub>3</sub>	▼	0.469	0.413
Ba(NO <sub>3</sub> ) <sub>2</sub>	●	0.403	0.474
BaSO <sub>4</sub>	▽	0.466	0.421
BaO <sub>2</sub>	■	0.393	0.459

experiments with the red flame formulas, there is obviously a large dependence for performance on the source of colorant used. The barium nitrate, carbonate, and peroxide performed well, while the barium sulfate and chloride were poor. This is in contrast to the experiments with red, where the strontium chloride offered good performance. The reason for this may lie in the fact that the melting and boiling points of the barium chloride are both 100 °C or more higher than the same physical state changes for the strontium salt. Barium chlorate was shown to be an excellent source of colorant, as its decomposition creates BaCl<sub>2</sub>. This is a different case than introducing solid crystalline BaCl<sub>2</sub> because the decomposition product is already at high temperature and needs little additional energy to decompose into the barium monochloride emitting molecule.

### Blue Formula Experiments

Starting with formula 13 for blue, the oxidizer experiments were repeated, and those results are shown in Figure 14. The results indicate a very definite trend in color quality, increasing as the amount of oxidizer is increased. This may, however, have more to do with the poor oxygen balance generating a cooler flame, than the effect of excess oxygen in the flame envelope.

### Variation of Oxidizer to Fuel Ratio Based on Blue Formula 13.

Symbol→	Blue Oxidizer to Fuel Ratio - BOFX				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
KClO <sub>4</sub>	49.9	59.8	66.5	71.3	74.9
CuO	20.0	16.1	13.4	11.5	10.0
Red Gum	14.8	11.9	9.9	8.5	7.4
Parlon	8.1	6.5	5.4	4.6	4.0
Dextrin	7.2	5.7	4.8	4.1	3.6

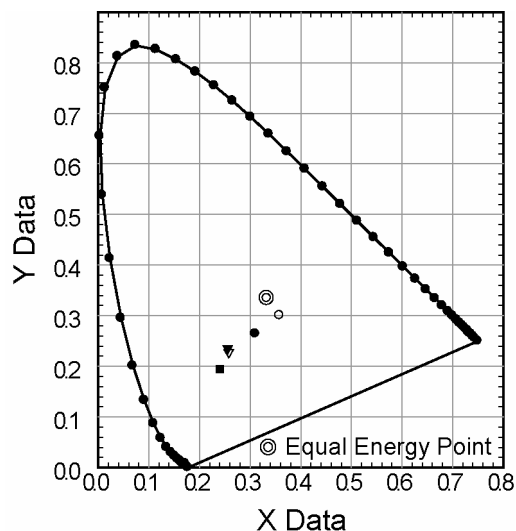


Figure 14. Blue oxidizer to fuel ratio experimental composition performances.

Table 11. Chromaticity Coordinates for Oxidizer to Fuel Ratio for Experimental Blue Compositions. [BOFX-#]

Oxidizer (%)	Symbol	x-coordinate	y-coordinate
49.9	○	0.359	0.300
59.8	▼	0.256	0.235
66.5	●	0.311	0.264
71.3	▽	0.258	0.228
74.9	■	0.240	0.194

When the chlorine donor experiments were conducted, they gave results that did not show a change in performance until the highest increment of chlorine donor, which gave a very much better flame than the other four mixtures, see Figure 15. This may be enough extra material in the mixture to cool the flame, or it may simply show the importance of chlorine availability to the formation of CuCl.

**Variation of Chlorine Donor Percentage Based on Blue Formula 13.**

Symbol→	Blue Chlorine Donor % - BCDX				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
Parlon	2.8	4.1	5.4	6.7	7.9
KClO <sub>4</sub>	68.3	67.4	66.5	65.6	64.7
CuO	13.8	13.6	13.4	13.2	13.0
Red Gum	10.2	9.8	9.9	9.8	9.6
Dextrin	4.9	4.7	4.8	4.7	4.7

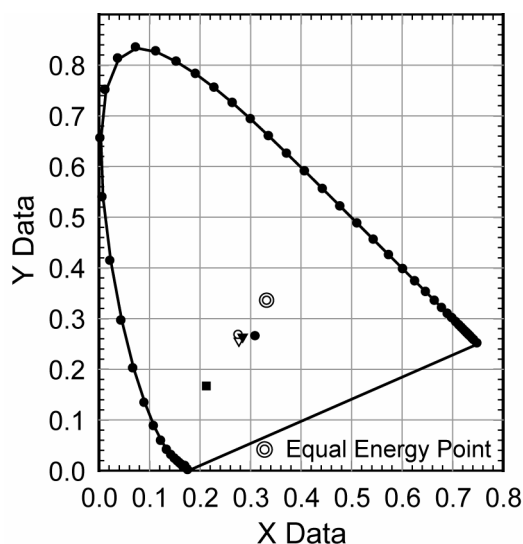


Figure 15. Blue chlorine donor ratio experimental composition performances.

**Table 12. Chromaticity Coordinates for Chlorine Donor Percentage for Experimental Blue Compositions. [BCDX#]**

Chlorine Donor (%)	Symbol	x-coordinate	y-coordinate
2.8	○	0.277	0.267
4.1	▼	0.284	0.264
5.4	●	0.311	0.264
6.7	▽	0.277	0.256
7.9	■	0.213	0.167

When the amount of colorant was varied, as shown in Figure 16, the results were again curious. The data indicates, in general, that a smaller amount of colorant may allow slightly better performance than more colorant would allow. If cooling the flame to limit CuCl dissociation were

**Variation of Colorant Percentage Based on Blue Formula 13.**

Symbol→	Blue Colorant % - BOFX				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
CuO	7.2	10.4	13.4	16.2	18.8
KClO <sub>4</sub>	71.1	68.6	66.5	64.2	62.2
Red Gum	10.6	10.2	9.9	10.2	9.3
Parlon	5.8	5.6	5.4	5.6	5.1
Dextrin	5.1	5.0	4.8	5.0	4.5

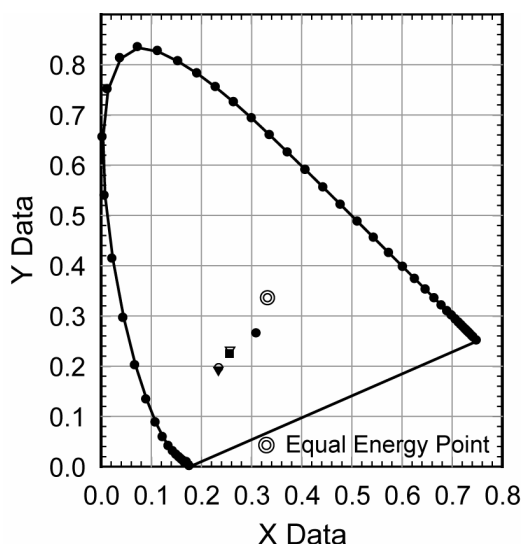


Figure 16. Blue colorant ratio experimental composition performances.

**Table 13. Chromaticity Coordinates for Colorant Percentage for Experimental Blue Compositions. [BCPX-#]**

Colorant (%)	Symbol	x-coordinate	y-coordinate
7.2	○	0.237	0.195
10.4	▼	0.234	0.192
13.4	●	0.311	0.264
16.2	▽	0.257	0.232
18.8	■	0.256	0.225

important, it seems as though the larger amounts of colorant would also serve that purpose.

Experiments were carried out where the colorant source was changed, and those results are plotted in Figure 17. In these experiments, the copper oxychloride served as the best chlorine

donor, followed by the copper sulfate. Interestingly, copper oxide and copper carbonate, both commonly used donors, were not among the best performers. These results may not be observed for other formulas, however.

### Variation of Colorant Source Based on Blue Formula 13.

Symbol→	Blue Colorant Source - BCSX				
	○	▼	●	▽	■
Chemical↴	1	2	Orig.	3	4
KClO <sub>4</sub>	53.6	63.2	66.5	51.6	64.2
Red Gum	8.0	9.4	9.9	7.7	9.6
Parlon	4.3	5.1	5.4	4.2	5.2
Dextrin	3.9	3.9	4.8	3.7	4.6
Cu <sub>2</sub> CO <sub>3</sub>	30.1				
CuOCl		17.5			
CuO			13.4		
CuSO <sub>4</sub>				32.7	
CuCl					16.2

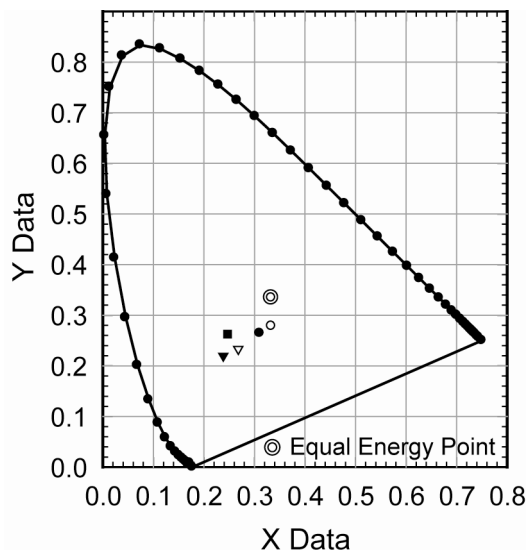


Figure 17. Blue colorant source experimental composition performances.

Colorant	(%)	Symbol	x-coordinate	y-coordinate
Cu <sub>2</sub> CO <sub>3</sub>	16.5	○	0.334	0.278
CuOCl	22.8	▼	0.238	0.219
CuO	28.3	●	0.311	0.264
CuSO <sub>4</sub>	33.0	▽	0.268	0.233
CuCl	37.2	■	0.247	0.263

## Conclusions

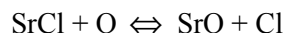
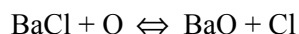
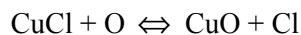
Experiments such as these, varying mixture components and attempting to draw conclusions based on the results, are difficult. In pyrotechnic formulas, many components serve two roles, as most chlorine donors are also fuels. Almost all binders serve as fuels, and some colorants serve as oxidizers. Some oxidizers bring with them chlorine. In these cases, to attempt to vary only the oxidizer and fuel balance, while keeping the chlorine and colorant content constant, is very difficult, and impossible in most cases.

Even more difficult, is the collection of spectra that fairly represent the mixture performance. When burned in a static fashion, pellets shed virtually none of the ash generated. The resultant effect is that the ash is heated to incandescence, diluting the color of the flame. This would not be an issue were the pellet functioning as an aerial shell star—moving at high velocity and tumbling while moving through air. In this case, the ash and smoke would be stripped away to a much larger extent than in static testing. Another difference between static testing and true performance lies in the chemistry of the flame envelope. As a burning pellet moves through the air, oxygen diffuses into the flame envelope much more effectively than in static testing. Also, the flame envelope will be at a somewhat lower temperature in true performance because of the cooling effect on the flame envelope of the high velocity air moving past the pellet and flame envelope. Even with these test conditions built into a testing rig, good data collection was difficult, as the flame envelope tended to dance and move, giving a spectrum with relative peak intensities that were constantly changing with time.

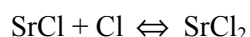
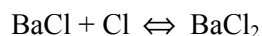
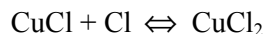
With these shortcomings recognized, there are conclusions that can be drawn from the experiments conducted:

- The most important single component contributing to good spectral performance was the selection of colorant source.
- The oxidizer content of the mixture, amount of colorant, and amount of chlorine donor are secondary in determination of color quality.

- With some exceptions, as long as the mixture will support combustion, it also seems to be able to generate colored light.
- There are chemical equations that illustrate equilibria important in color flame chemistry, for example:



These show the effect of oxygen in the flame on the desired emitters. When excess oxygen (radical or molecular) is present, it is possible that a collision with a metal monochloride emitter will destroy the emitter and form an oxide, which may emit as an undesirable molecular emitter, or condense and emit as an even less desired broadband radiator. Analogous reactions can be represented as:



In these examples, chlorine in the flame envelope may interact destructively with the emitting species. However, for strontium, barium and copper, the boiling points of the chloride salts are many hundreds of degrees lower than the boiling points for the oxides. This would indicate that the chloride salts may stay as a vapor and decompose again to produce the monochlorides. However, once an oxide is formed, it is likely to condense into ash, which not only is *not* an effective color emitter but also *is* a destructive broadband emitter. Thus, the reasoning of the argument for maintaining a reducing flame, as well as a flame with a high level of available chlorine, seems obvious. While the experiments performed may not have clearly shown the dependence of color quality on these elements, it remains a logical goal in composition formulation.

Adjusting a mixture only to give the best quality of light has other pitfalls. Unrelated properties that a composition may possess, such as critical wind velocity, ease of ignition, ease of processing, safety, and cost are also important issues. A blue star that gives a pure blue color on the ground is useless, if it cannot be reliably ignited or does not support a robust

combustion. In fact, some of the mixtures generated in this work were barely combustible. An interesting note: it was often possible to discern differences in color performance with the naked eye that were relatively close together on the chromaticity diagram. In fact, it was usually possible to determine with the eye approximately where the coordinates were going to fall. However, the ultimate usefulness of the spectrometer and the coordinates thus generated lie in the fact that they are definite and objective values, which can be recorded and archived for future reference. While the eye can typically tell one formula as being better than the next, the memory of those observations is subjective and will be suspect. Unless a candidate color formula is burned alongside a sample pellet of a previous formula, the observer's perception of the purity differences in those two formulas may be erroneous.

## Outlook

Future work in this area may be done along several lines. First, constructing a test fixture to address some of the pitfalls of collecting this type of data would be a top priority. For instance, pressing core-burning pellets of color composition may provide a flame that is geometrically fixed and giving a spectrum that is easier to capture. Second, other chlorine donors could be evaluated by directly replacing the chlorine donor in a well-characterized formula. Presumably there would be an increase in flame color purity as a more efficient donor is introduced. Third, the development of a formula designed specifically for formula adjustments would be an interesting approach. As an example, chlorine donors such as PVC (polyvinylchloride), saran, and Parlon™ would not be used, but instead a chlorine donor such as ammonium chloride (NH<sub>4</sub>Cl) could be used, which has less fuel value per chlorine atom. And finally, there are more colorant sources to sample and more types of formulas to investigate. Including the high nitrogen colors<sup>[25,26]</sup> or composite formula colors<sup>[27]</sup> would be worthwhile. It would also be interesting to obtain the chromaticity coordinates of a larger selection of well-established formulas.



## Acknowledgement

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### List of Chemicals Used in Formulations in Text.

Chemical Name	Formula	Familiar Name/Formula
Abietic acid	$C_{20}H_{30}O_2$	Colophony Rosin
Aluminum	Al	
Ammonium perchlorate	$NH_4ClO_4$	AP
Amorphous carbon (pure)	C	Lamp Black
Barium carbonate	$BaCO_3$	
Barium chlorate	$Ba(ClO_3)_2 \cdot H_2O$	
Barium chloride	$BaCl_2$	
Barium nitrate	$Ba(NO_3)_2$	
Barium peroxide	$BaO_2$	
Barium sulfate	$BaSO_4$	Barite
Carbon (with impurities)	C	Air Float Charcoal
Chlorinated isoprene rubber		Parlon™
Copper(II) acetoarsenite	$Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$	Paris Green
Copper(II) carbonate	$Cu_2(OH)_2CO_3$	Basic copper carbonate
Copper(I) chloride	$CuCl$	
Copper(II) oxide	$CuO$	
Copper(II) oxychloride	$Cu_2(OH)_3Cl$	Dicopper(II) chloride trihydroxide
Copper(II) sulfate	$CuSO_4$	Hydrocyanite
Cupric acetoarsenite	$Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$	Paris Green
Dextrin	$(C_6H_{10}O_5)_n \cdot xH_2O$	Dextrin
Magnesium	Mg	
Magnesium with $K_2Cr_2O_7$	Mg (coated)	
Magnesium/aluminum alloy	Mg/Al	Magnalium
Polyvinyl chloride	$(C_2H_3Cl)_n$	PVC
Potassium chlorate	$KClO_3$	KC
Potassium dichromate	$K_2Cr_2O_7$	
Potassium perchlorate	$KClO_4$	KP
Shellac	$C_6H_9.6O_{1.6}$	Lac, Lacca
Strontium carbonate	$SrCO_3$	
Strontium chloride	$SrCl_2$	
Strontium nitrate	$Sr(NO_3)_2$	
Strontium peroxide	$SrO_2$	
Strontium sulfate	$SrSO_4$	
Xanthorrhoea resin	$C_6H_{5.95}O_{2.63}N_{0.01}$	Red Gum, Accroides Resin