Characteristics of the Red Colored Flame of Firework Compositions

Dayu Ding,* Daichi Tabata and Tadao Yoshida
Ashikaga Institute of Technology, 268-1 Omae-cho, Ashikaga-shi, Tochigi 326-8558, Japan
* Email: dding@ashitech.ac.jp

Abstract: *Experiments have been conducted varying the oxygen balance of firework compositions and adding a chlorine donor to compositions in order to understand how or why a red flame is affected by the oxygen balance and presence of chlorine in the composition. The results show that with a negative oxygen balance, i.e., a fuel-rich composition, the flame extends longer, so a deep red flame is easily formed. The results also show that strontium containing species SrO, SrOH and SrCl can form a red flame. SrO or SrOH is responsible for a deeper red light, SrCl is responsible for a deepest red color. Emissions due to SrO and SrOH can be diminished by the emissions due to SrCl. For forming a red flame, a favorable chlorine donor is not an oxidant like potassium perchlorate but a fuel like chlorinated gum.*

Keywords: *firework composition, red colored flame, chromaticity diagram, oxygen balance*

Introduction

Light and color from firework flames are important effects in firework displays. It has been an enduring goal of pyrotechnists to produce a deep, saturated colored flame in a firework application.

Firework compositions are powder mixtures of several agents such as fuel, oxidant, and color agent etc. To understand the factors affecting the performance of colored flames, many studies have been conducted by other researchers.[1-4]

When a firework composition burns, the combustion products in the flame emit radiation or light. Some products emit light at or near the hue intended in the flame, and they are called desirable emitters. Other products emit light in the visible spectrum that will hinder the performance of the colored flame and they are called undesirable emitters. The desirable or undesirable emitters are atomic or molecular species in the flame. Also present are some incandescent solid and/or liquid combustion products emitting black body, gray body, or continuous radiation. In colored flames, they emit undesirable broadband radiation across a very large wavelength range, even across the entire visible spectrum when the temperature is high.

Strontium compounds are usually used as color agents in red flame firework compositions. Shimizu[1] qualitatively researched the red flames of firework compositions and concluded that the molecular emitter strontium oxide (SrO) is responsible for the red color, and the red flame will become deeper in colour if some chlorine agent is added to the composition.

Since Shimizu's research, optical measurement technology and computer technology have advanced greatly. Therefore, further studies, which use advanced measurement technology to quantitatively show spectral information and to correlate the data with emitters in the flame, are ongoing.

Some research results show that if a chlorine agent is used in a firework composition, a higher quality red flame can be formed by molecular band emitters such as strontium monochloride (SrCl) and strontium monohydroxide (SrOH).

The purpose of this study is quantitatively to investigate the effects of factors such as the

Article Details	***Article No: - 0079***
Manuscript Received:-23/07/2009	***Final Revisions:-17/10/2009***
Publication Date:-19/10/2009	***Archive Reference:-989***

oxygen balance and chlorine donors in firework compositions on the performance of red flames by acquiring spectra with a spectrometer, and to give insight into the relative importance and roles of those factors.

Experimental

Materials

To investigate the influence of oxygen balance and chlorine (element Cl), the formulas of red flame firework compositions were designed separately as four groups listed in Table 1. The oxygen balance (OB) for each formula was calculated by the method explained in the next section. In each group except group 1 the formulas were designed with a positive, near zero and a negative oxygen balance, respectively. The oxygen balance of one formula in group 1 was near zero and the formula would be difficult to ignite if the oxygen balance was below zero. The amount of hydrogen (element H) contained in the charcoal used in group 1 was lower compared with the rice granules used in group 2. Chlorine was not contained in the materials used in group 1 and group 2, but chlorine was contained in the fuel used in group 3 and the oxidant used in group 4.

Magnesium (Mg metal powder) was used as a high energy agent in this experiment to improve the ignition performance.

For all compositions, chemicals except for strontium nitrate ($Sr(NO_3)_2$) were used as supplied from Sunaga Fireworks Co. Ltd. The compound strontium nitrate ($Sr(NO_3)_2$) (JIS special grade reagent) was purchased from Wako Pure Chemical Industries, Ltd. The samples of compositions were prepared by mixing the dry powders of the chemicals. About 2.5 g of the mixture was poured into a steel tube of 13.0 mm inner diameter, 1.0 mm thick and 20 mm long.

Calculation of oxygen balance

The oxygen balance is the amount of oxygen available within an explosive material in grams when 1 g of the material burns or explodes as a result of complete conversion of the explosive material to CO_2, H_2O, KCl, MgO, Al_2O_3, etc. For example, the oxygen balances of magnesium (Mg) and potassium perchlorate ($KClO_4$) are calculated as follows.

	Mg → MgO	$-0.5O_2$
Molecular wt	24.3	−0.5 × 32

OB of Mg = −16/24.3 = −0.658

	$KClO_4$→KCl	$+2O_2$
Molecular wt	138.5	+2 × 32

OB of $KClO_4$ = +64/138.5 = +0.462

Therefore, the oxygen balance of a mixture of Mg and $KClO_4$ (mix ratio = 40 : 60) can be calculated as:

$$\text{OB} = (-0.658) \times 40\% + (+0.462) \times 60\% = +0.014$$

For the calculation of oxygen balance, the chemical formula of charcoal was approximately expressed in carbon (element C) as its main ingredient is carbon. Similarly rice granules are approximately expressed in the chemical formula $(C_6H_{10}O_5)_n$ of starch because the main ingredient is starch. The chemical formula $(C_{10}H_{11}Cl_7)_n$ of chlorinated gum is cited from Sturman.[5] A negative oxygen balance means the oxygen within the material is deficient for complete reaction, and zero or a positive oxygen balance identifies that the material has

Table 1. *Red colored flame firework formulations (wt%).*

Component	Group1	Group 2			Group 3			Group 4		
Strontium nitrate	80%	80%	70%	60%	80%	70%	60%	40%	35%	30%
Potassium perchlorate								40%	35%	30%
Magnesium	10%	10%	10%	10%	10%	10%	10%	10%	10%	10%
Charcoal	10%									
Rice granules		10%	20%	30%				10%	20%	30%
Chlorinated gum					10%	20%	30%			
OB	−0.03	0.12	−0.04	−0.19	0.14	0.01	−0.12	0.18	0.04	−0.09

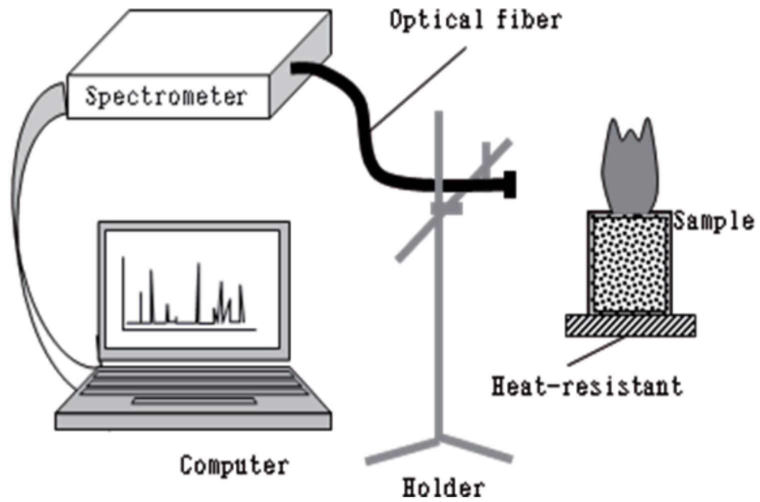

Figure 1. *Schematic diagram of the experimental setup.*

sufficient available oxygen within itself to enable the combustion to go to completion. It is known that an explosive or a firework composition with an oxygen balance close to zero is the most powerful during combustion or explosion.

Methods

A schematic diagram of the experimental setup used in this work is shown in Figure 1. A spectrometer named PMA-11C7473-36 from Hamamatsu Photonics Co. Ltd was used for measuring the spectrum of light from the firework flame. Once the sample at the top, which was vertically placed on a heat-resistant plate, was ignited, the light of the flame was transmitted to the spectrometer through an optical fiber and the spectral data were recorded on a personal computer. The photographs of the flame were taken by a camera with the same conditions for each test. The experiments were conducted in a dark room and the chamber in which samples were burned was painted flat black to avoid reflections. Two samples for each formula were prepared and tested under the same conditions.

Results and discussion

Experimental data reduction

The CIE1931 Chromaticity Diagram, which is a two-dimensional diagram with x and y coordinate axes shown in Figure 2, is used for quantifying colored firework flames in this work. The outside boundary of the tongue-shape is called the monochromatic light line, which defines perfect purity and complete saturation at a given wavelength. ICI illuminant “C” locates at $x = 0.33$, $y = 0.33$ and defines perfectly balanced white light.

The color coordinates (x, y) were calculated from measured spectra and were plotted on the chromaticity diagram. For example, color point A is plotted with calculated coordinates (x, y) in Figure 2. The straight line that connects point A with C extends to a point B on the monochromatic light line. The wavelength of monochromatic light point B is called the dominant wavelength of color point A. The percentage of the distance along the straight line CB from point C is called excitation purity or purity, with white light point C having 0% purity and monochromatic light point B having 100% purity.

In our experiments, the change of the spectrum with time was measured using a spectrometer with a repeat measurement function. After ignition, the sample began to burn and light radiated from the flame. The light intensity changed noisily with time because of the flickering of the flame, and it decreased with time due to the presence of smoke. To eliminate the effects of flame flickering and smoke, and to correctly evaluate colored firework flames, the time-average intensity within one second after ignition, before the smoke had spread widely, for each wavelength was used to calculate

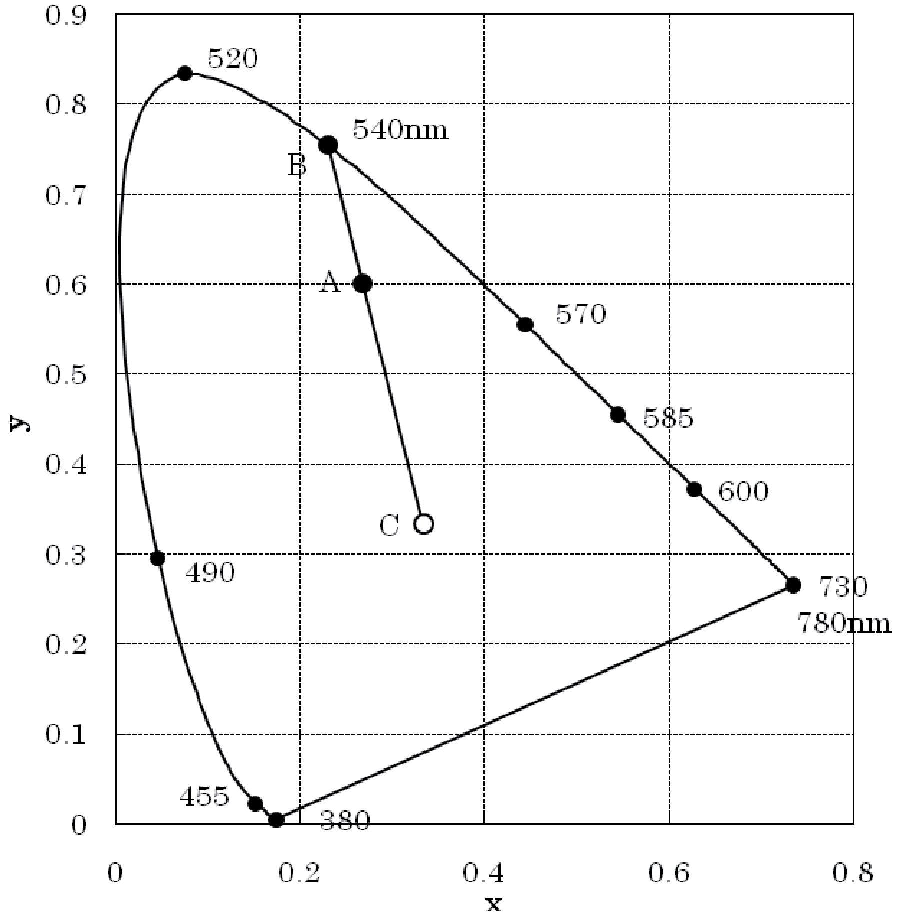

Figure 2. *Chromaticity diagram.*

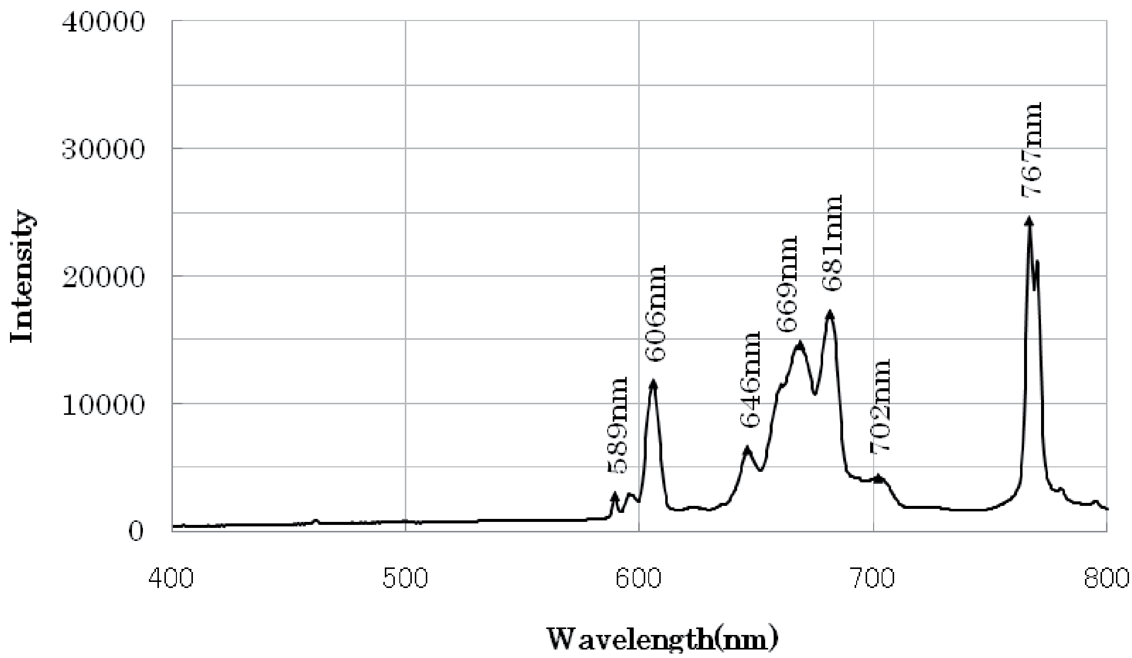

Figure 3. *Spectrum of group 1.*

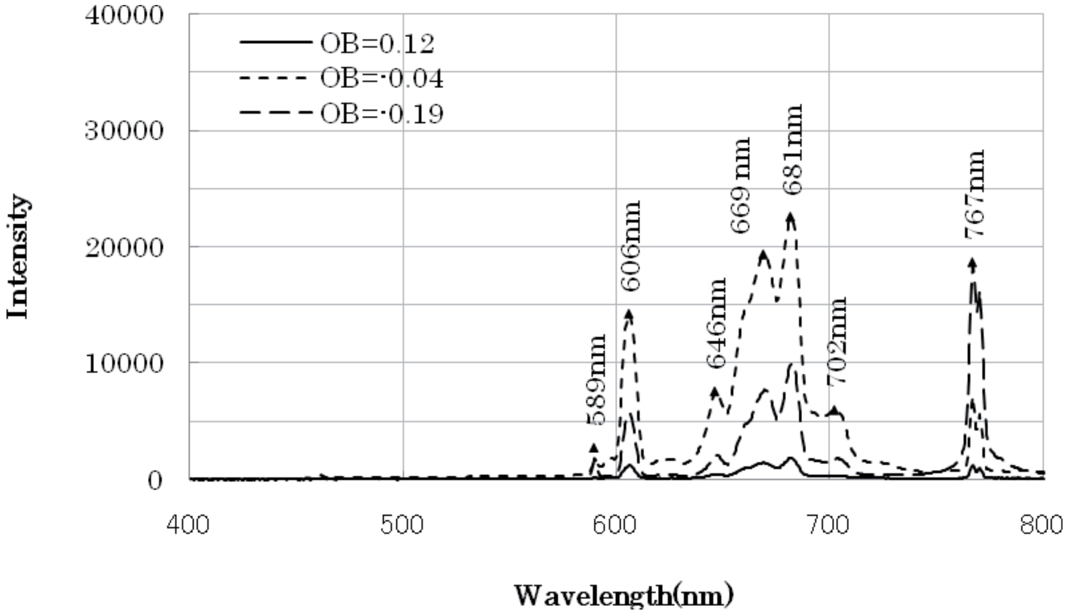

Figure 4. *Spectrum of group 2.*

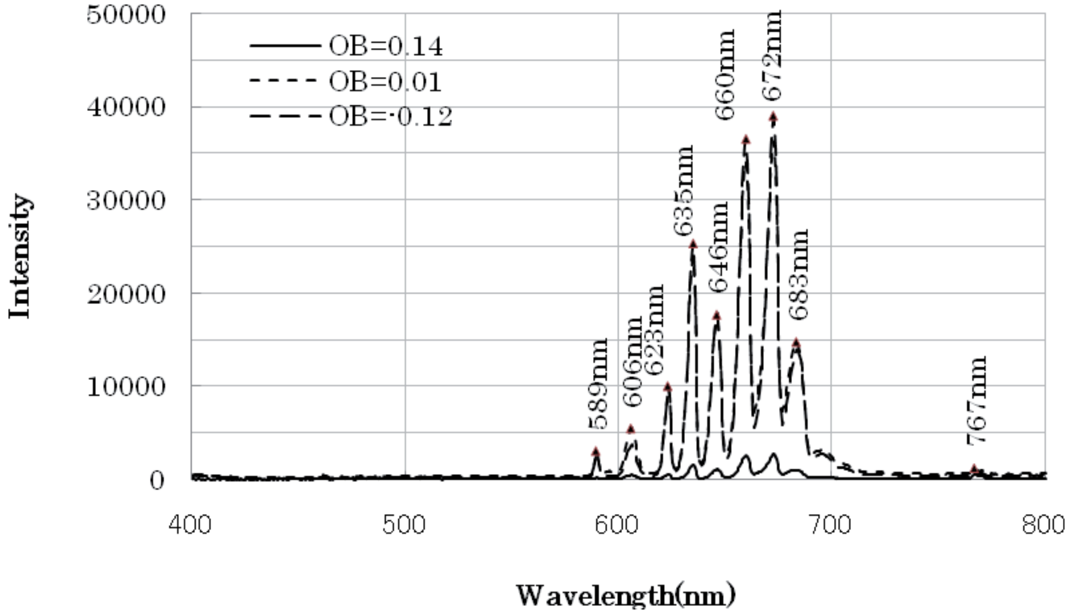

Figure 5. *Spectrum of group 3.*

CIE coordinates.

Characteristics of red flame spectra

The experiments were performed varying the oxygen balance of the compositions and adding a chlorine donor to the compositions for the four groups listed in Table 1. The measured spectra are shown in Figures 3 through 6.

As can be seen from the measured spectra shown in Figures 3 through 6, the flame of each composition shows some band emissions in the wavelength range 600–700 nm. The quality of the red color is mainly responsible for the performance of those band emissions such as their position, width, and intensity.

The patterns of band emissions of compositions of group 1 are similar to those of group 2. The patterns of band emissions of group 3 are also similar to those of group 4. But the patterns of band emissions of group 1 and group 2 are very

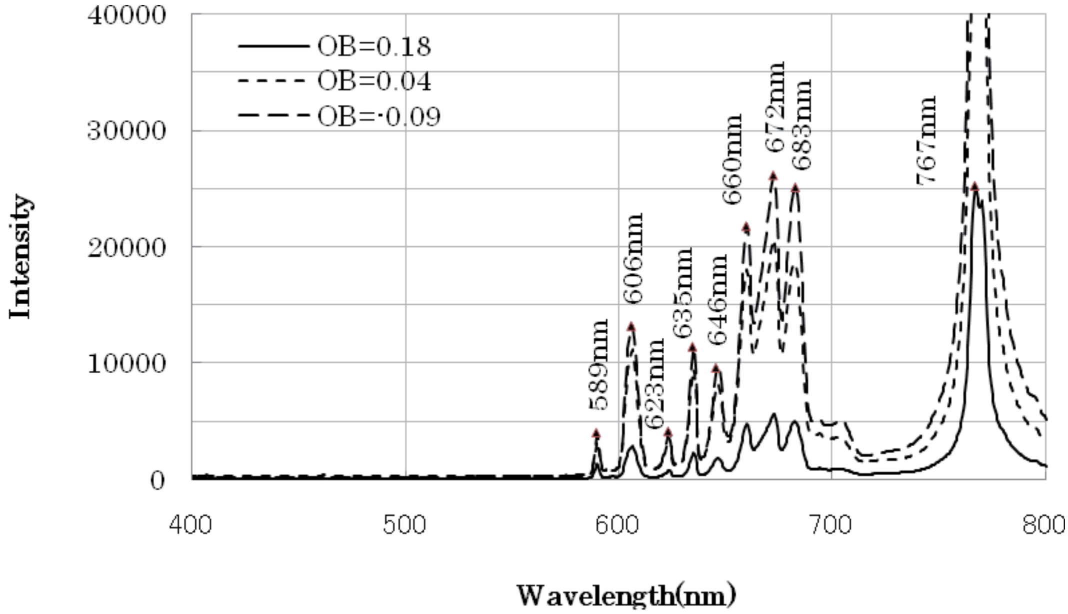

Figure 6. *Spectrum of group 4.*

different from those of group 3 and group 4.

For the compositions of groups 1 and 2, in which no chlorine (Cl element) is contained, the spectra displayed in Figure 3 and Figure 4 show that there is one narrow band emission with a peak at 606 nm and another wide band emission in the wavelength range 630–700 nm with some peaks at 646 nm, 669 nm and 681 nm.

According to Pearse and Gaydon,[6] strontium salts give bright red banded radiation in a flame, but the flame bands are mostly due to strontium monohydroxide (SrOH). Also, strontium oxide emits light with strong bands near 595 nm and 605 nm and a stronger complex structure between 640 nm and 685 nm. The strong band due to SrOH is centered at 605 nm.

Also according to the spectrum graphs provided by Meyerriecks and Kosanke,[3] strontium oxide (SrO) emits light near 600 nm, and strontium monohydroxide (SrOH) displays a similar spectrum in the wavelength range 630–700 nm like that shown in Figure 3 or 4.

For the compositions in groups 3 and 4, in which chlorine (Cl element) is contained, the spectra in Figure 5 and Figure 6 show that the structure of the spectrum between 600 nm and 700 nm is very different from that of non-chlorine compositions and displays several separated narrow band emissions.

The narrow band emissions with peaks at 635 nm, 660 nm and 672 nm are stronger than that of other band emissions. According to Ingram,[3] those band emissions are due to strontium monochloride (SrCl).

For each composition, there are a sodium atomic emission at 589 nm and a potassium atomic emission at 767 nm in the flame. The sodium atomic emission contributes an undesirable yellow or orange-yellow light to the red flame. The potassium atomic emission is also an undesired

Table 2. *Identification of spectra shown in Figures 3–6.*

Wavelength/nm	Emitter	Wavelength/nm	Emitter
589	Na	660	SrCl
606	SrO, SrOH	672	SrCl
623	SrCl	681	SrOH
635	SrCl	683	SrOH
646	SrOH	767	K

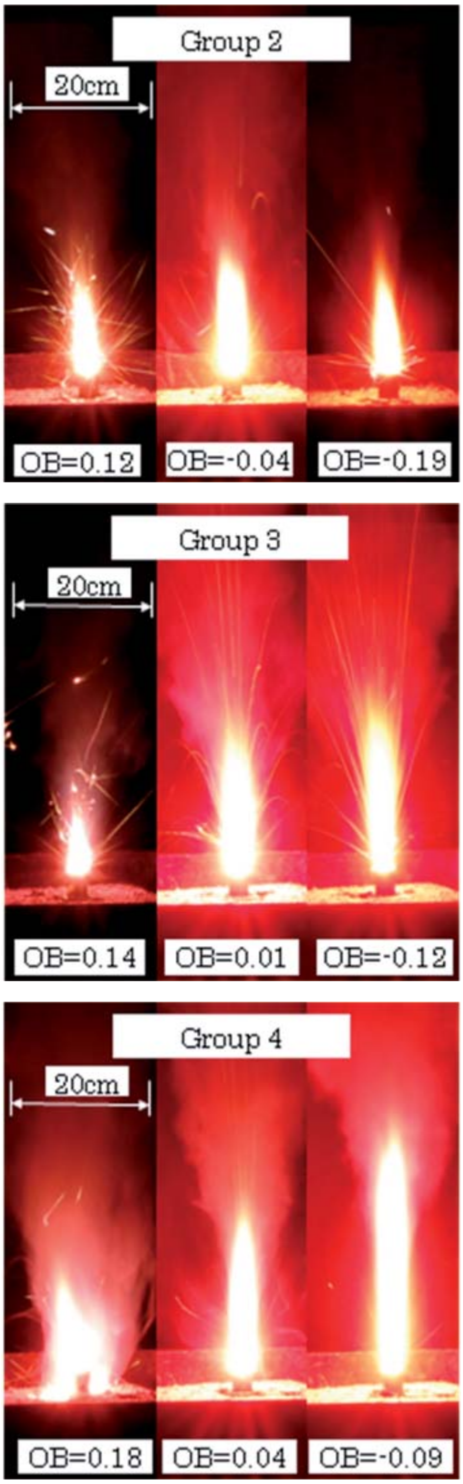

Figure 7. *Pictures of the combustion flames.*

emitter, but there is little effect on the red color because the emission is near the infrared range.

Sodium and potassium probably existed in the strontium nitrate as impurities because neither sodium nor sodium compounds were used in any composition. Potassium or potassium compounds were also not used in the compositions except for the compositions in group 4.

By referring to some spectral data in references 2–4, the emitters with emissions at wavelengths in the spectra indicated in Figures 3–6 can be determined and the information is listed in Table 2.

Effects of oxygen balance

The measured spectra of compositions with varying oxygen balance show that the emissions are weak for compositions with a positive (oxidant-poor) oxygen balance and the emissions become stronger with a negative (fuel-rich) or near zero oxygen balance.

Photographs of the combustion flames taken by a camera are shown in Figure 7. The same distance between sample and camera is kept for all the pictures and the pictures show the same area. As can be seen, there is a tendency for the height of flames to become greater as the oxygen balance decreases from positive to negative, possibly indicating that there is a strong dependence of color performance on the oxygen balance. It suggests that the combustion zone and flame structure are largely influenced by the oxygen balance.

The chromaticity coordinates of the tested compositions were calculated with the measured spectra, and their color performance plotted on a chromaticity diagram is shown in Figure 8. Meanwhile, dominant wavelength (corresponding to hue) and purity (corresponding to color quality) were calculated with the chromaticity coordinates. The results are listed in Table 3.

As the oxygen balance changes from positive to negative, the chromaticity coordinates of the compositions in each group move towards the red region in the chromaticity diagram. It can be seen that the tendency of the change in the height of the flames corresponds to the change in the chromaticity coordinates with the change of the oxygen balance for compositions of groups 3 and 4.

If the oxygen balance varies from positive to negative, the combustion zone of the flame extends longer and the emissions become stronger, because the emitters SrO, SrOH and SrCl emit light only while they exist in a gas or vapor

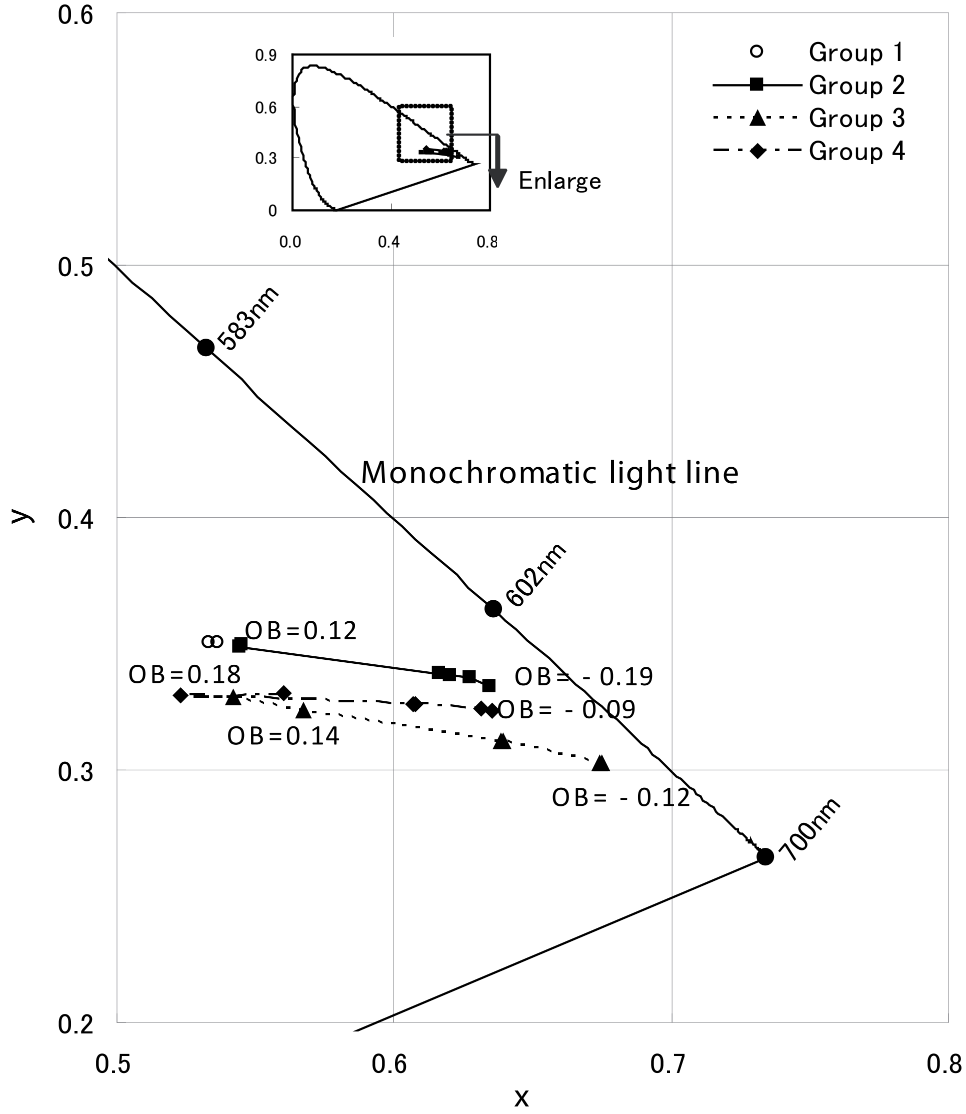

Figure 8. *Chromaticity of red colored flame for tested compositions.*

Table 3. *Dominant wavelength and purity of red colored flame.*

	OB	Dominant wavelength/nm	Purity (%)
Group 1	−0.03	603	66
	0.12	604	68
Group 2	−0.04	609	87
	−0.19	610	90
	0.14	614	64
Group 3	0.01	620	85
	−0.12	624	93
	0.18	612	61
Group 4	0.04	613	80
	−0.09	614	87

state. The experiments suggest that if the oxygen balance of the composition is negative, SrO, SrOH and SrCl are easily formed in the vapor states as the combustion zone is longer. Conversely, if the oxygen balance is positive, SrO, SrOH and SrCl will be difficult to form in the vapor state, and many combustion products concerning strontium maybe do not exist in the gas or vapor states as the combustion zone of the flame is narrow.

Therefore, the experimental results suggest that the color saturation of a red flame is possibly improved with a negative oxygen balance.

Effects of chlorine

For non-chlorine containing compositions, the red color of the flame is mainly due to emissions from emitters SrO and SrOH in the flame.

The charcoal used in the compositions of group 1 contains mainly carbon and a small amount of hydrogen. Rice granules, which mainly contain carbohydrate, are used in the compositions in group 2 as the fuel. Therefore, when the compositions of group 1 and group 2 are burning, the strontium-containing emission species in the flame are mostly strontium oxide (SrO) and strontium monohydroxide (SrOH).

Either SrO or SrOH emits light near 606 nm. The band emission at 606 nm in Figure 3 or Figure 4 is strong.

The complex band emissions in the range 630–700 nm are almost continuous, which is mostly due to SrOH.

For a chlorine donor such as chlorinated gum or potassium perchlorate added to the composition of group 3 and group 4, the emitter SrCl is present in the flame besides the emitters SrO and SrOH.

Any of the emission species SrO, SrOH and SrCl can form a red flame, but the red color purities due to these species are different. SrO or SrOH is responsible for an orange-red light, but SrCl is responsible for a deepest red color.

The experimental results in Figure 5 or 6 show that the emission at 606 nm, which contributes an orange-red light, becomes weak when a chlorine donor is used in the compositions. This suggests that if a source of chlorine atoms is available in the flame, the emissions due to SrO and SrOH can be diminished by the emitter SrCl. The reason is probably due to strontium monochloride (SrCl) which may form from the chemical reaction as follows:[4]

$$SrO + HCl \rightarrow SrCl + OH$$

Further, by comparison of Figure 5 and Figure 6, it can be seen that to diminish the light due to the emission at 606 nm, a chlorine donor serving as the fuel such as chlorinated gum is more effective than potassium perchlorate, which serves as an oxidant.

For the compositions of group 3, chlorinated gum (= chlorine donor) serving as fuel is rich with a negative oxygen balance, so that the deeper red colored flame is formed. In contrast, for the compositions in group 4, potassium perchlorate (= chlorine donor) serving as oxidant decreases to the negative oxygen balance, but the red colored flame is deeper than that with a positive oxygen balance. This probably can be explained by the following chemical reaction.[4]

$$SrCl + O \rightarrow SrO + Cl$$

In this equation, the loss of strontium monochloride (SrCl) due to the formation of SrO can be diminished by decreasing the amount of oxygen in the flame with a fuel-rich composition, i.e., with a negative oxygen balance composition. Therefore, it can be concluded that it is advantageous to form SrCl in the flame when the oxygen balance of the composition is negative, and a deeper red colored flame can be formed.

Conclusions

The effects of varying the oxygen balance of compositions and chlorine on the colored flame of fireworks compositions have been investigated in this study. Some conclusions are obtained as follows.

(1) The red color saturation can be improved with a negative oxygen balance, i.e., a fuel-rich composition.

(2) Strontium concerning species SrO, SrOH and SrCl can form a red flame, but SrO and SrOH are responsible for an orange-red light, whereas SrCl is responsible for a deepest red color.

(3) Emissions due to SrO and SrOH can be diminished by the emissions due to SrCl.

(4) To form a red flame, a suitable chlorine donor is not an oxidant like potassium perchlorate but a fuel like chlorinated gum.

References

1 T. Shimizu, “Studies on Colour Flame Composition of Fireworks 4. On Flame Spectra of Red, Yellow and Green Colour Compositions”, *Selected Pyrotechnic Publications of Dr. Takeo Shimizu, Part 3. Studies on Fireworks Colored Flame Compositions* (translated from Japanese), Journal of Pyrotechnics, Inc., 1999.

2 W. Meyerriecks and K. L. Kosanke, “Color Values and Spectra of the Principal Emitters in Colored Flames”, *Journal of Pyrotechnics*, Issue 18, Winter 2003, pp. 1–22.

3 B. V. Ingram, “Color Purity Measurement of Traditional Pyrotechnic Star Formulas”, *Journal of Pyrotechnics*, Issue 17, Summer 2003, pp. 1–18.

4 K. L. Kosanke and B. J. Kosanke, “The Chemistry of Colored Flames”, *Pyrotechnic Chemistry*, Journal of Pyrotechnics Inc., 2004, Chapter 9.

5 B. T. Sturman, “Notes on chlorinated rubber and some other chlorine donors”, *Journal of Pyrotechnics*, Issue 22, Winter 2005, pp. 63–66.

6 R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, Chapman and Hall Ltd., 4th edn, 1976, pp. 334–340.