Effects of Variation of Component Content on the Colored Flame of Firework Star Compositions

Kazuomi Itoh,[a] Hideo Watanabe,[b] Dayu Ding[a]* and Tadao Yoshida[a]

[a] Ashikaga Institute of Technology, 268-1 Omae-cho, Ashikaga-shi, Tochigi 326-8558, Japan

Email: *dding@ashitech.ac.jp

[b] Pyrotechnica Co. Ltd. 4179 Shimoakima, Annaka-shi, Gunma 379-0104, Japan

Abstract: *The spectra of the colored flames of firework compositions were measured with a spectrometer and processed into chromaticity coordinates. The change in color purity as a function of composition is shown using chromaticity diagrams. Firework star compositions of red, yellow, green and blue were tested. The components of the compositions were altered to investigate the influence of color agents, chlorine donors and high energy agents on the colored flames.*

Keywords: *firework composition, combustion, colored flame, chromaticity diagram*

Introduction

The light and color of fireworks are major effects in firework displays. These come mainly from the combustion of firework star compositions. Many colored flames of firework star compositions are formed by color generating chemical species which are produced by the combustion of firework stars.

To give insight into the relative importance and roles of some of the components, the effects of variation of single component content such as color agent, chlorine donor or high energy agent used in reference firework compositions on the colored flame of firework compositions were investigated in this study. Compositions used in the experiment are those of red, yellow, green and blue stars.

Experimental

Materials

Reference compositions were selected from a book[1] and are listed in Table 1. Hereafter, reference compositions in Table 1 are abbreviated as RC.

Magnalium (MgAl) is an alloy of magnesium (Mg) and aluminium (Al) and it is usually used as a high energy agent in firework compositions because of its high heat of combustion.

The experiments were carried out on the

Table 1 *Reference compositions (wt%).*

Component	Red	Yellow	Green	Blue	Role
Potassium perchlorate ($KClO_4$)	54	50	20	63	Oxidant
Strontium carbonate ($SrCO_3$)	12				Color agent
Sodium oxalate ($Na_2C_2O_4$)		15			Color agent
Barium nitrate ($Ba(NO_3)_2$)			37		Color agent
Cupric oxide (CuO)				10	Color agent
Magnalium (MgAl)	15	15	16	16	Fuel
Phenolic resin	8	7.5	6	12	Fuel
Chlorinated gum	6	7.5	16	10	Chlorine donor
Rice granules	5	5	5	5	Binder

Article Details ***Article No: - 0076***

Manuscript Received:-02/03/09 ***Final Revisions:-27/05/09***

Publication Date:-27/05/09 ***Archive Reference:-902***

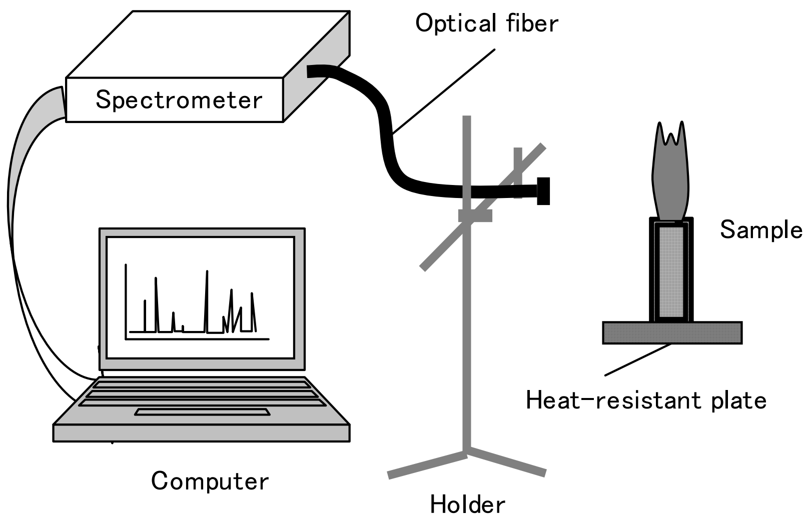

Figure 1 *Schematic diagram of the experimental setup.*

compositions by changing the content of specific components based on reference compositions and the ratios of other components were kept constant.

For all experiments, chemicals were used as supplied from Sunaga Fireworks Co. Ltd. The samples of compositions were prepared by mixing the chemicals as dry powders. About 1.4 g of the mixture was poured into a paper tube of 8.0 mm inner diameter, 0.2 mm thick and 30 mm long.

Methods

A schematic diagram of the experimental setup used in this work is shown in Figure 1. A PMA-11C7473-36 spectrometer from Hamamatsu Photonics Co. Ltd was used for measuring the spectrum of the firework flame. When a sample at the top was ignited which was placed verticallyon a heat-resistant plate, 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 experiments were conducted in a dark room and the chamber in which samples were burned was painted flat black to avoid reflections. Three samples for each formula were prepared and tested under the same conditions.

Results and discussion

Experimental data reduction

From the spectra measured, we can understand the properties and features of colored firework flames in which there are various desired or undesired emitters, and there is further discussion later. On the other hand, color sensations are not uniquely related to one wavelength of light, but related to the combinations of many wavelengths of light entering one's eyes. Firework flame is one kind of colored light source and light of various wavelengths is emitted. In order to quantify colored firework flames, the CIE1931 color system developed in 1931 by the International Commission on Illumination was used in the research. Using this color system, the color of a firework flame can be quantitatively evaluated with color coordinates x and y in a two-dimensional diagram called a chromaticity diagram, see Figure 2. Monochromatic light colors lie on the outer periphery of the tongue-shaped region called the monochromatic light line and for which the corresponding wavelengths are listed. The white light point ICI illuminant "C" lies at the center of the diagram.

In this study, all of the firework flame spectra were taken and saved to the computer. With the measured spectra and color-matching functions in the XYZ chromatic system, we calculated the color coordinates x and y. For an instance, the color coordinates x and y of a firework flame are calculated, then a color point A for the data is

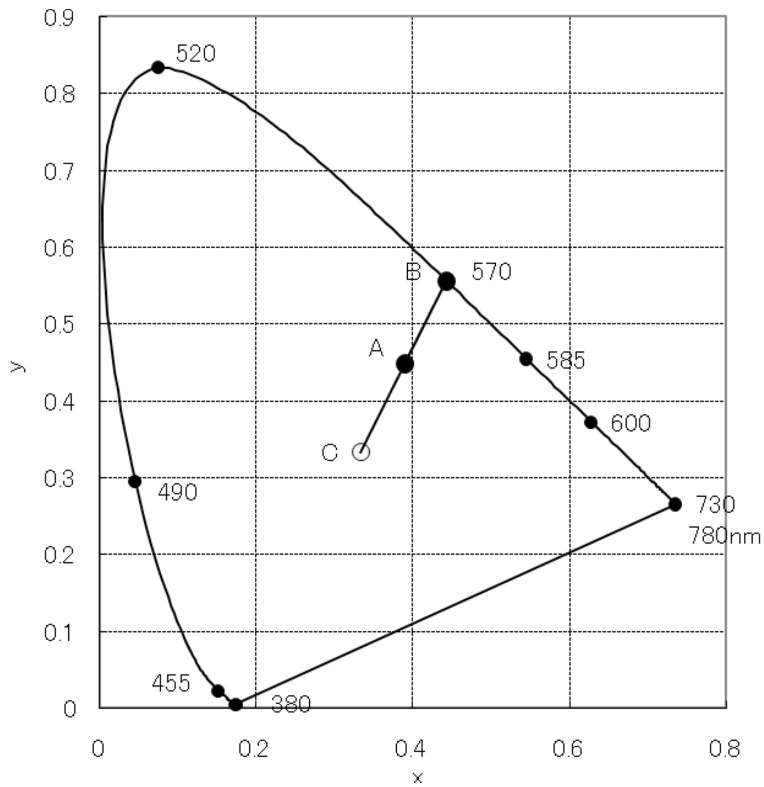

Figure 2 *Chromaticity diagram.*

plotted in the chromaticity diagram. 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 the excitation purity or purity, with white light point C having 0% purity and monochromatic light point B having 100% purity.

The spectrometer used in our experiments can

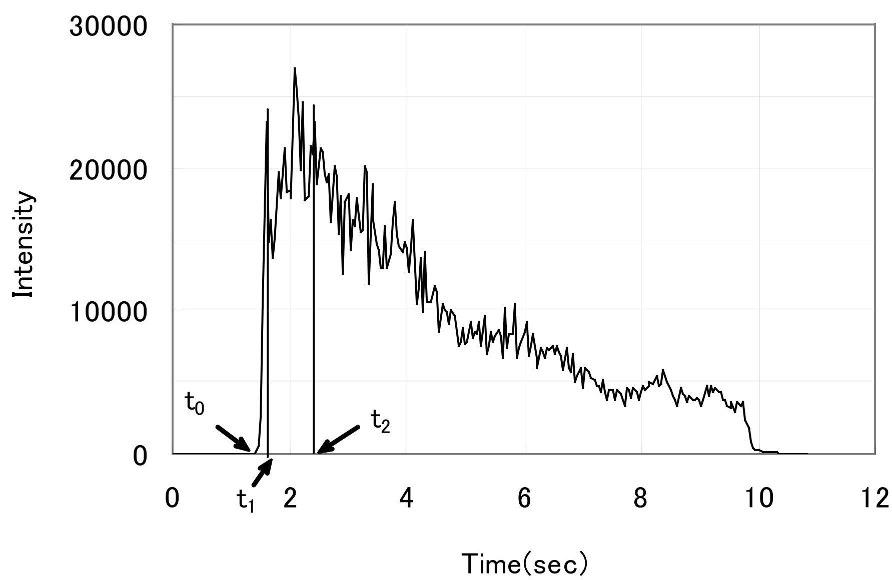

Figure 3 *Change of the spectrum with time.*

measure the change in the spectrum with time with a repeated measurement function. An example of spectral change with time (light emission at a particular wavelength) is shown in Figure 3. After ignition at time t_0, the sample began to burn and radiate light, and the flame reached approximate stability at time t_1. But after t_1, the intensity profile changed with time because of flickering of the flame as the air surrounding the flame was heated and movement of the air resulted. To eliminate the effects of flame flickering and to correctly evaluate the colored firework flame, the average intensity between t_1 and t_2 for each wavelength was used to calculate the CIE coordinates. The time between t_1 and t_2 was set to about one second for data reduction of all wavelength intensities of firework flames.

Red composition flame spectra

The spectrum of the red composition flame in Figure 4 shows several peaks of light intensity in the wavelength range 600–700 nm. The red color is responsible for characteristics of these peaks such as their position, width, and intensity. If the peaks are located at longer wavelengths, or the peaks are higher-intensity or sharper, a deeper red colored flame will be formed. The peak at 606 nm is due to strontium monohydroxide (SrOH) emissions and the peaks at 635, 660, and 673 nm are due to strontium monochloride (SrCl) emissions. SrCl is a desired emitter for forming a deeper red flame because the peak intensity of SrCl is higher than that of SrOH.

There was a ubiquitous sodium atomic emission at 589 nm, which contributed an undesirable yellow or orange-yellow light. Sodium or sodium compounds were not used in the red compositions, but they existed in the chemicals as impurities.

The very high peak at 767 nm was produced by potassium, which was also an undesired emitter, but there was little effect on the red color sensation because the peak was near the infrared range.

(1) Effects of $SrCO_3$

Experiments were carried out to vary the color agent $SrCO_3$ based on the red reference composition (see Table1). The $SrCO_3$ content was changed in 5% increments and the formulas are shown in Table 2. The chromaticity results of the compositions are shown in Figure 5.

The chromaticity coordinates of the formula move towards the red region with increasing $SrCO_3$ content. A reason for this is likely that the concentration of SrCl in the flame increased with $SrCO_3$ content. However, when the $SrCO_3$ content is about 17%, on adding more $SrCO_3$ the color movement towards the red region becomes

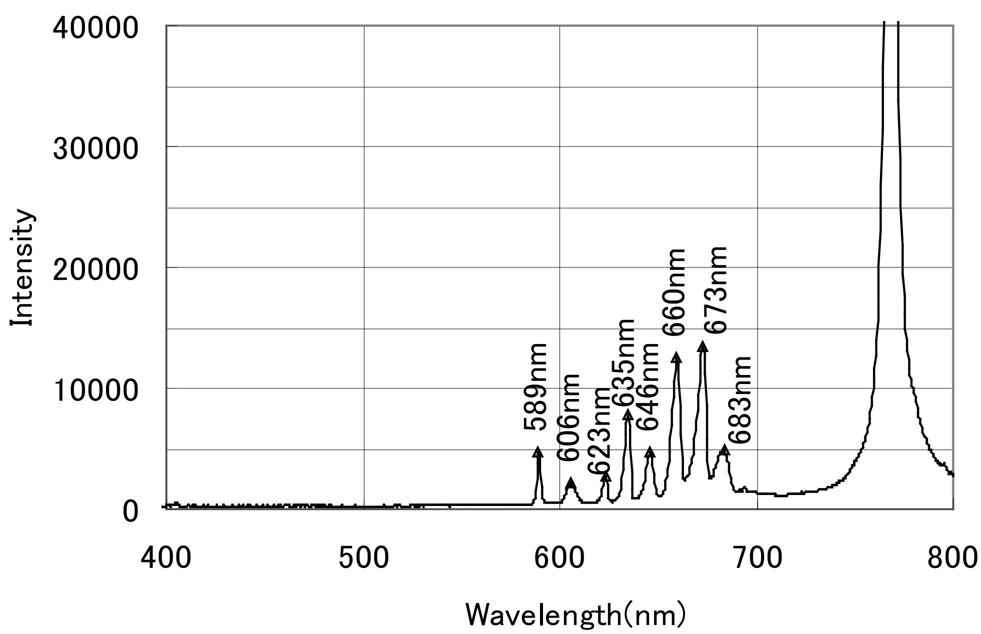

Figure 4 *Spectrum of red flame.*

Table 2 *Variation of color agent based on red formula (wt%).*

Component	Formula				
	R-1	R-2	R-3 (RC)	R-4	R-5
$KClO_4$	60.1	57.1	54	50.9	47.9
$SrCO_3$	2.0	7.0	12	17.0	22.0
MgAl	16.7	15.9	15	14.1	13.3
Phenolic resin	8.9	8.5	8	7.5	7.1
Chlorinated gum	6.7	6.3	6	5.7	5.3
Rice granules	5.6	5.3	5	4.7	4.4

very slight. Adding $SrCO_3$ to the red reference composition can improve the red colored flame, but once a certain amount of the color agent is attained, adding more does not improve the red flame.

(2) Effects of chlorinated gum

The percentage of chlorinated gum in the red reference composition was varied, and the formulas are listed in Table 3. The results of those experiments are shown in Figure 6. There is a tendency for the chromaticity coordinates

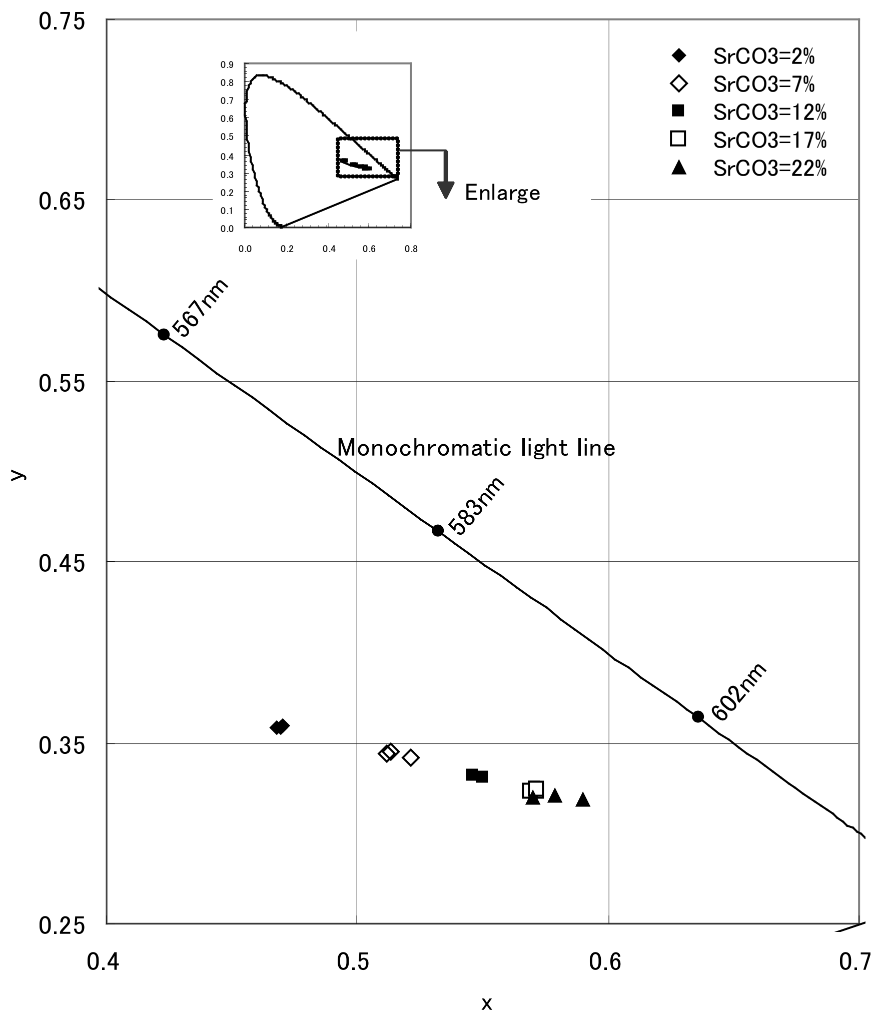

Figure 5 *Chromaticity of variation of color agent based on red formula.*

Table 3 *Variation of chlorinated gum based on red formula (wt%).*

Component	Formula				
	R-6	R-7	R-3 (RC)	R-8	R-9
$KClO_4$	56.3	55.1	54	52.9	51.7
$SrCO_3$	12.5	12.3	12	11.7	11.5
MgAl	15.6	15.3	15	14.7	14.4
Phenolic resin	8.3	8.2	8	7.8	7.7
Chlorinated gum	2.0	4.0	6	8.0	10.0
Rice granules	5.2	5.1	5	4.9	4.8

to move towards the red region with increasing chlorinated gum content. The predominant peaks in the spectrum are the emissions from SrCl and a chlorinated gum added to the composition will provide Cl and so the amount of SrCl will increase.

(3) Effects of MgAl

To assess the effect of MgAl, experiments were conducted to vary the amount of MgAl based on the red reference formula. The percentage of MgAl was changed in 5% increments and the formulas are listed in Table 4. The chromatic performance

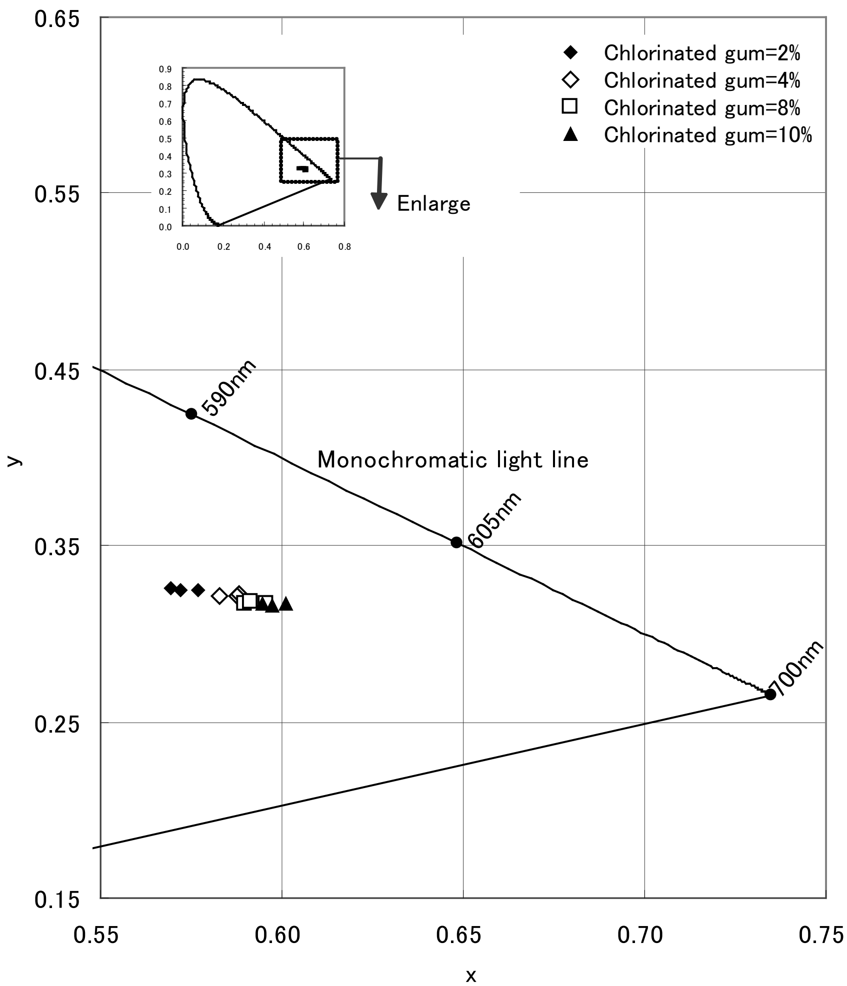

Figure 6 *Chromaticity of variation of chlorinated gum based on red formula.*

Table 4 *Variation of MgAl based on red formula (wt%).*

Component	Formula				
	R-10	R-11	R-3 (RC)	R-12	R-13
$KClO_4$	60.4	57.2	54	50.8	47.6
$SrCO_3$	13.4	12.7	12	11.3	10.6
MgAl	5.0	10.0	15	20.0	25.0
Phenolic resin	8.9	8.5	8	7.5	7.1
Chlorinated gum	6.7	6.4	6	5.6	5.3
Rice granules	5.6	5.3	5	4.7	4.4

data of the compositions are shown in Figure 7.

MgAl is used in most modern firework stars as a bright agent. When the amount of MgAl increased from 5% to 10%, the chromatic performance improved a little. A likely reason for this is that as more MgAl is added, the heat generated by the composition increases, heating the flame towards the optimum temperature for emission from SrCl excitation. However, once the percentage of MgAl exceeds 10%, the chromatic performance will

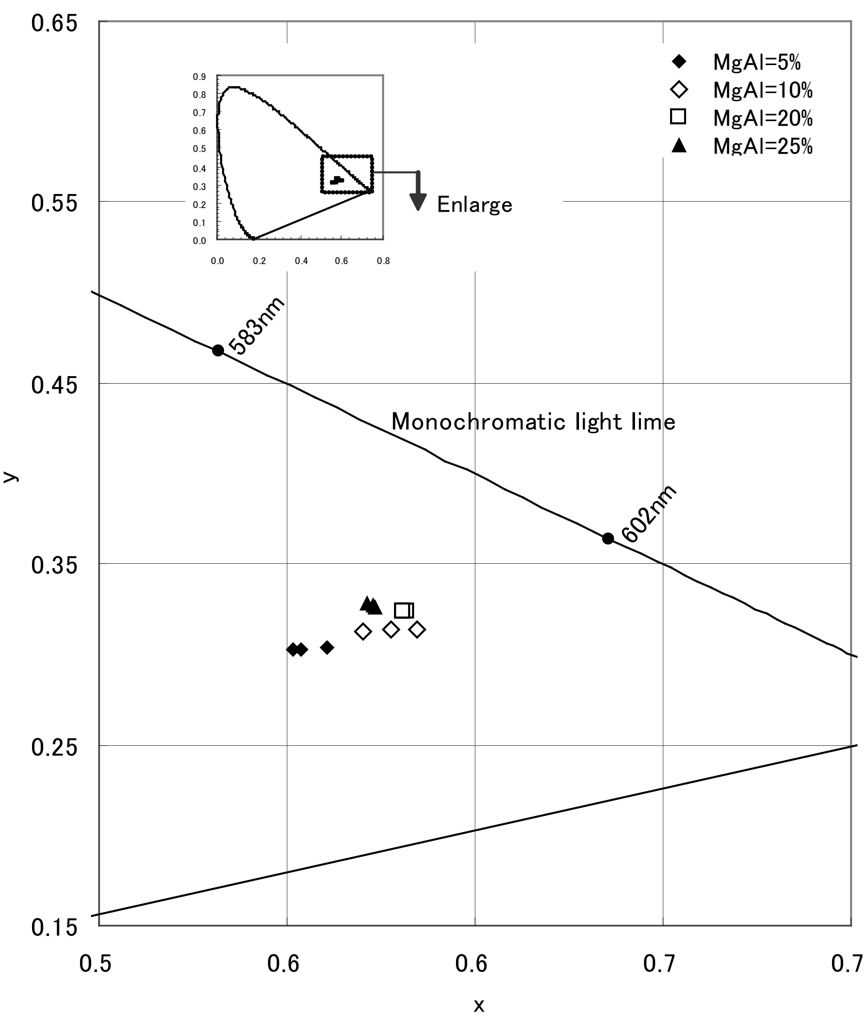

Figure 7 *Chromaticity of variation of MgAl based on red formula.*

decrease.

Yellow composition flame spectra

The spectrum of a flame of yellow composition is shown in Figure 8. In forming a yellow flame, the atomic emitter sodium (Na) is responsible for the deep yellow flame, with emission at 589 nm. There are only two intensity peaks in the wavelength range 380–780 nm. One (desired) peak is at 589 nm due to sodium (Na) emission, and the other (undesired) peak is at 767 nm due to potassium (K) emission.

(1) Effects of $Na_2C_2O_4$

Experiments were carried out to vary the color agent $Na_2C_2O_4$ based on the yellow reference composition (see Table 1). The percentage of $Na_2C_2O_4$ was changed in 5% increments and the formulas are shown in Table 5. The chromaticity results of the compositions are shown in Figure 9.

The results show that the yellow flame attained an optimum chromatic performance when the percentage of color agent $Na_2C_2O_4$ was about 15% in the yellow formula, and the chromatic performance would decrease if the amount of $Na_2C_2O_4$ was below or above this level. When only a little color agent was added, the atomic emitter sodium (Na) of the yellow color in the flame was not enough, and as more color agent was added, the heat of combustion was lost in heating the excess color agent, cooling the flame temperature for the emitting sodium (Na) excitation.

(2) Effects of MgAl

The percentage of MgAl was changed in 5% increments based on the yellow reference composition and the formulas are listed in Table 6. The experiment results are shown in Figure 10.

The chromatic coordinates shifted to a monochromatic light line at wavelength 589 nm when the percentage of MgAl increased. The chromatic performance of the yellow flame can be improved by adding MgAl. But once the amount of MgAl was at or over 15%, the effect of MgAl on the performance was very slight.

Green composition flame spectra

A typical spectrum of green composition flame is shown in Figure 11. The molecular emitter barium monochloride (BaCl) is responsible for emissions at 514 and 525 nm, and the emitter barium monohydroxide (BaOH) is responsible for emissions at 487, 515, and 527 nm.[2] According to Kosanke and Kosanke,[3] barium monohydroxide is

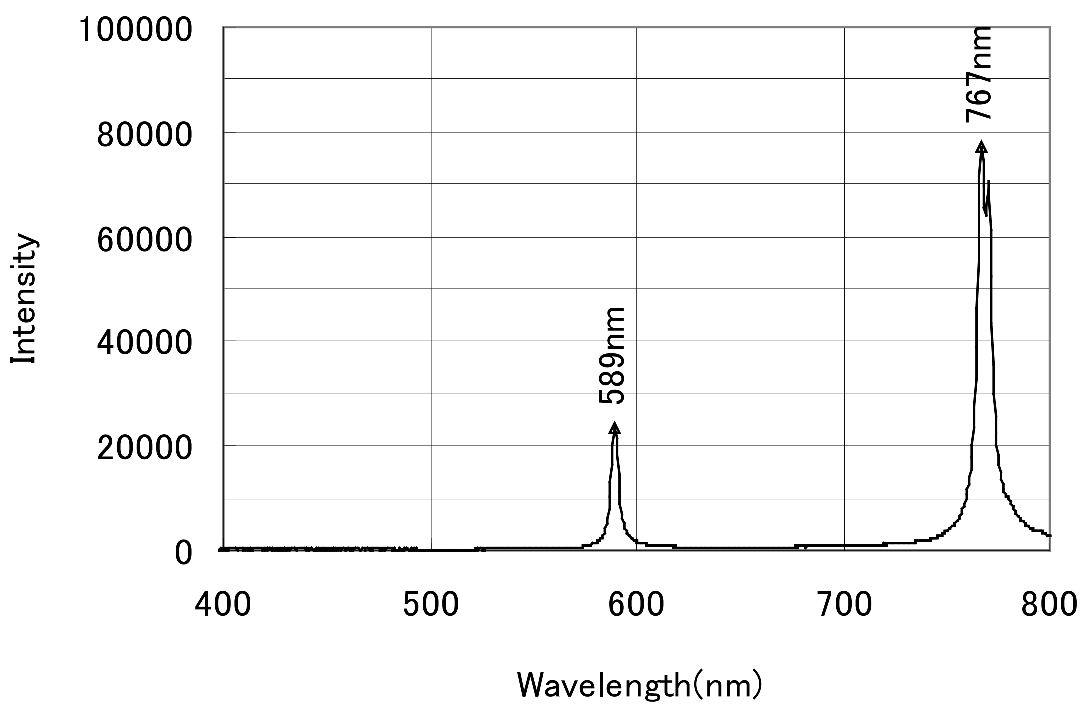

Figure 8 *Spectrum of yellow flame.*

Table 5 *Variation of $Na_2C_2O_4$ based on yellow formula (wt%).*

Component	Formula				
	Y-1	Y-2	Y-3 (RC)	Y-4	Y-5
$KClO_4$	55.9	52.9	50	47.1	44.1
$Na_2C_2O_4$	5.0	10.0	15	20.0	25.0
MgAl	16.8	15.9	15	14.1	13.2
Phenolic resin	8.4	7.9	7.5	7.1	6.6
Chlorinated gum	8.4	7.9	7.5	7.1	6.6
Rice granules	5.6	5.3	5	4.7	4.4

quite a weak emitter by comparison with barium monochloride, so the desired emitter in a green firework flame is barium monochloride. There is a relatively strong interfering emission at 589 nm, originating from atomic sodium (Na). There are also interfering emissions from the glowing matter in the flame. When the temperature of the matter is high enough, it can emit light across the entire visible wavelength 380–780 nm, but the intensity of light becomes high with increasing wavelength. If the interfering or undesired emissions between 550 and 780 nm are decreased or eliminated, the

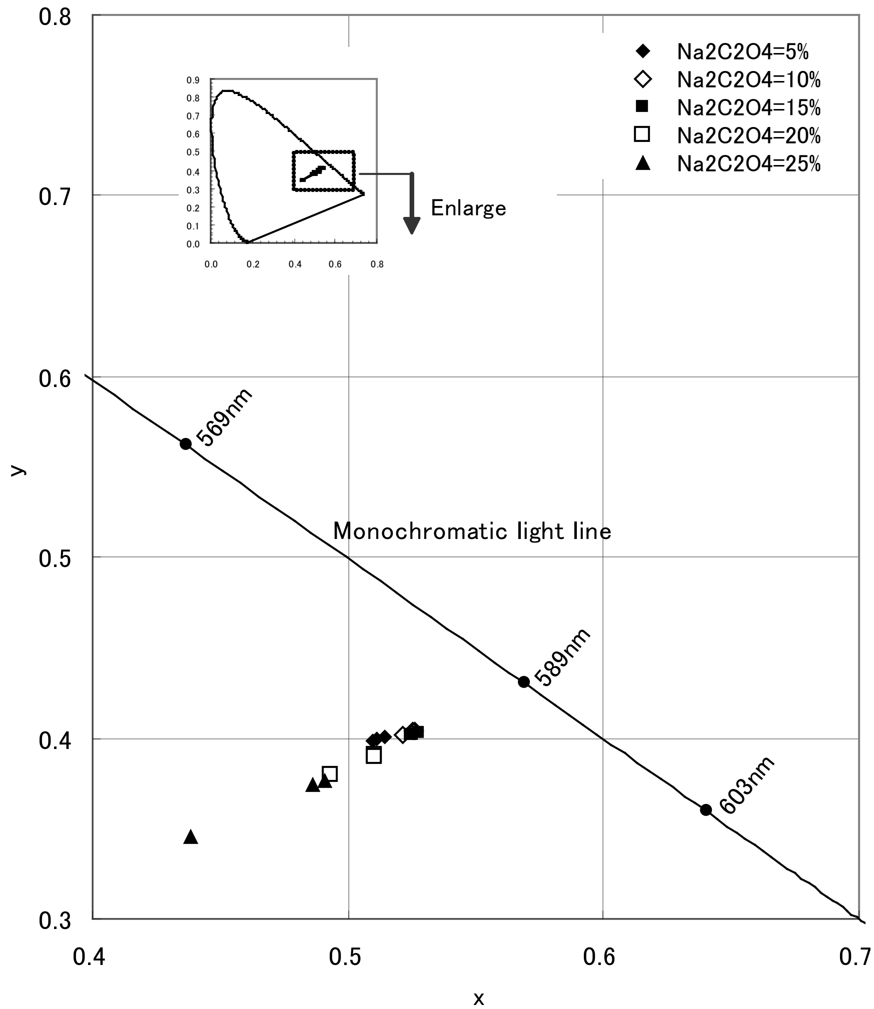

Figure 9 *Chromaticity of variation of $Na_2C_2O_4$ based on yellow formula.*

Table 6 *Variation of MgAl based on yellow formula (wt%).*

Component	Formula				
	Y-10	Y-11	Y-3 (RC)	Y-12	Y-13
$KClO_4$	55.9	52.9	50	47.1	44.1
$Na_2C_2O_4$	16.8	15.9	15	14.1	13.2
MgAl	5.0	10.0	15	20.0	25.0
Phenolic resin	8.4	7.9	7.5	7.1	6.6
Chlorinated gum	8.4	7.9	7.5	7.1	6.6
Rice granules	5.6	5.3	5	4.7	4.4

color will be favorably moved toward the center of the green area of the chromaticity diagram, and the performance of the green flame will be significantly improved.

(1) Effects of Ba $(NO_3)_2$

The experiments were conducted by changing the percentage of $Ba(NO_3)_2$ in 5% increments and the formulas are listed in Table 7. The chromaticity results of the compositions are shown in Figure 12.

As can be seen, the chromatic data shifted slightly toward the green area with increasing $Ba(NO_3)_2$

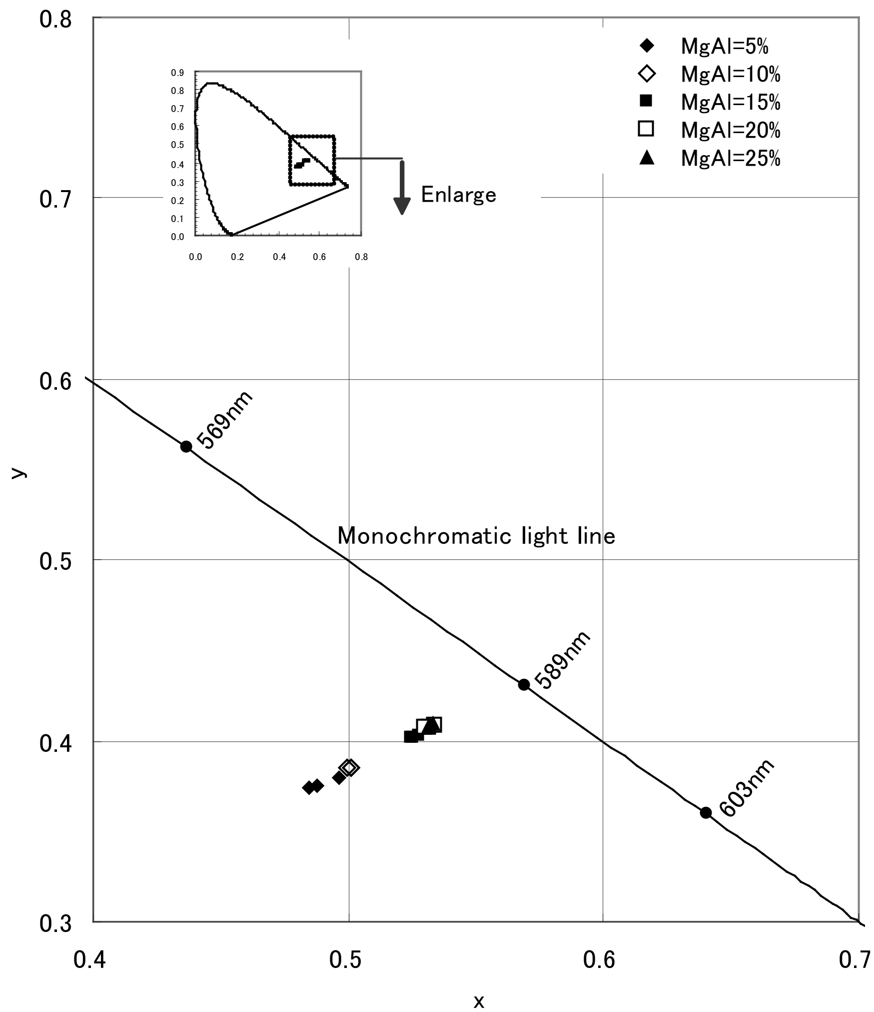

Figure 10 *Chromaticity of variation of MgAl based on yellow formula.*

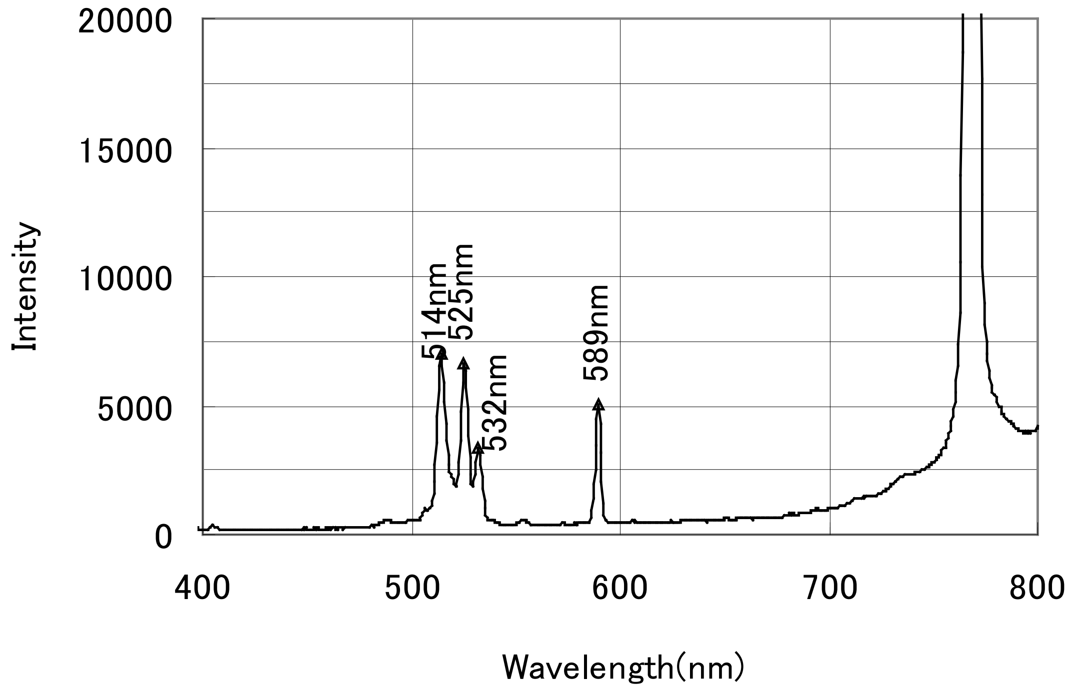

Figure 11 *Spectrum of green flame.*

content. The results possibly indicate that the color agent does not have a great effect on the chromatic performance.

(2) Effects of chlorinated gum

Experiments were done according to the formulas listed in Table 8. The percentage of chlorinated gum in the green formula was varied in 5% increments. The results of these experiments are shown in Figure 13.

When the amount of chlorinated gum was varied from 6% to 16%, the chromatic data showed a very slight change. But once the chlorinated gum content was above 16%, the performance decreased obviously. This may indicate that the flame temperature decreased with increasing chlorinated gum content because the combustion heat was lost in heating excess chlorinated gum.

(3) Effects of MgAl

The percentage of MgAl was changed in 5% increments based on the green reference composition and the formulas are listed in Table 9. The flame spectra were collected and analyzed. Those results are shown in Figure 14.

When the amount of MgAl increased from 6% to 21%, the chromatic coordinates moved towards the green region. However, when the MgAl content was above 21%, the chromatic coordinate changes were very slight.

Note that when the MgAl amount was below 16%, the chromatic coordinates quickly moved towards the orange-yellow region. A reason for this may be that as the MgAl amount decreased, the heat generated by MgAl burning decreased and there was not enough heat for the desired emitter excitation. The results suggest that a high energy agent such as MgAl is necessary for forming a deep green firework flame.

Blue composition flame spectra

A blue composition flame spectrum is shown in Figure 15. There were several peaks from approximately 400 to 560 nm which were from emissions of copper monochloride (CuCl) and copper hydroxide (CuOH). According to other researchers,[2] the molecular emitter copper monochloride (CuCl) is responsible for the emissions at 430, 436, 484, 489, and 527 nm. The emission at 465 nm is also from the emitter CuCl. Either emitter CuCl or emitter CuOH emits light over a wider wavelength range. The collection of emissions from 400 to 480 nm is recognized

Table 7 *Variation of $Ba(NO_3)_2$ based on green formula (wt%).*

Component	Formula				
	G-1	G-2	G-3 (RC)	G-4	G-5
$KClO_4$	23.2	21.6	20	18.4	16.8
$Ba(NO_3)_2$	27	32	37	42	47
MgAl	18.5	17.3	16	14.7	13.5
Phenolic resin	7	6.4	6	5.6	5
Chlorinated gum	18.5	17.3	16	14.7	13.5
Rice granules	5.8	5.4	5	4.6	4.2

as violet-blue, and that from 480 to 560 nm is recognized as greenish-yellow. The dominant wavelength is possibly in the blue region, but it is difficult to improve the purity of the blue flame. Therefore, as long as compounds of copper are used as color agents in firework compositions, it is very difficult to produce a deepest blue flame. In addition, the presence of the strong sodium peak at 589 nm and a continuum extending throughout longer wavelength region deteriorate the purity of the blue flame.

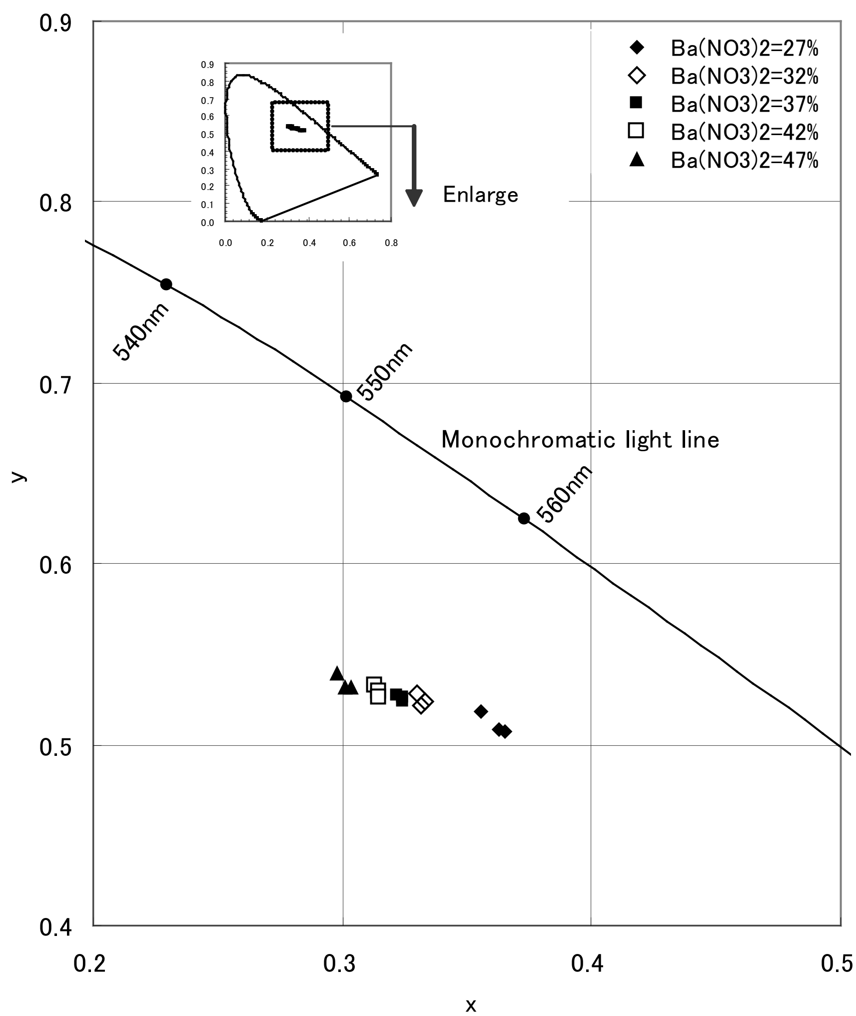

Figure 12 *Chromaticity of variation of $Ba(NO_3)_2$ based on green formula.*

Table 8 *Variation of chlorinated gum based on green formula (wt%).*

Component	Formula				
	G-6	G-7	G-3 (RC)	G-8	G-9
$KClO_4$	22.4	21.2	20	18.8	17.6
$Ba(NO_3)_2$	41.4	39.2	37	34.8	32.6
MgAl	17.9	17	16	15.1	14.1
Phenolic resin	6.7	6.3	6	5.6	5.3
Chlorinated gum	6	11	16	21	26
Rice granules	5.6	5.3	5	4.7	4.4

Effects of CuO

The formulas with varying contents of the color agent CuO are listed in Table 10. The experimental results for these formulas are shown in Figure 16.

The results show that the chromatic coordinates moved towards the blue region when the CuO content was increased, but once the amount of CuO was above 6%, the color performance hardly changed. It indicates that there is not a great dependence of the color performance on the amount of CuO.

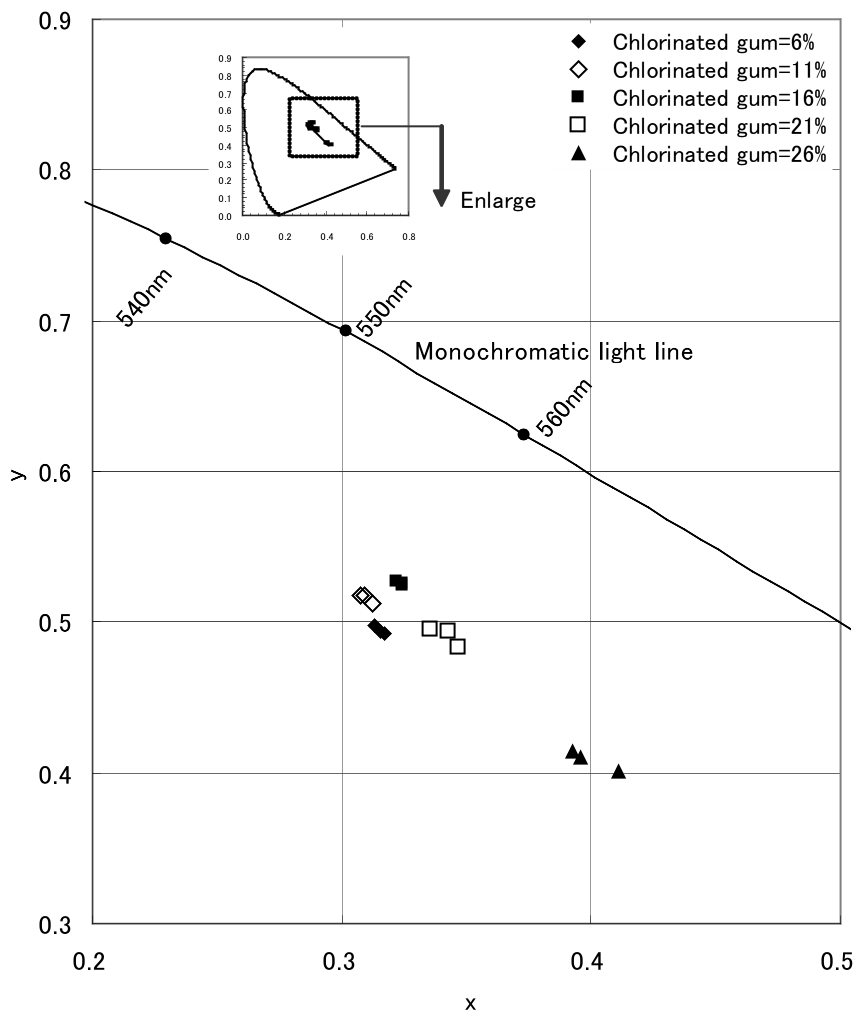

Figure 13 *Chromaticity of variation of chlorinated gum based on green formula.*

Table 9 *Variation of MgAl based on green formula (wt%).*

Component	Formula				
	G-10	G-11	G-3 (RC)	G-12	G-13
$KClO_4$	22.4	21.2	20	18.8	17.6
$Ba(NO_3)_2$	41.4	39.2	37	34.8	32.6
MgAl	6	11	16	21	26
Phenolic resin	6.7	6.4	6	5.7	5.3
Chlorinated gum	17.9	16.9	16	15	14.1
Rice granules	5.6	5.3	5	4.7	4.4

Effects of chlorinated gum

The percentage of chlorinated gum in the blue reference composition was varied, and the formulas are shown in Table 11. The experimental results are shown in Figure 17. The results show that the chromaticity coordinates shift towards the blue region with increasing chlorinated gum content. The predominant peaks in the spectrum are the emissions from CuCl. Therefore, adding a chlorinated gum to the composition will provide more Cl and will result in an increase in the amount of CuCl. But once the amount of chlorinated gum

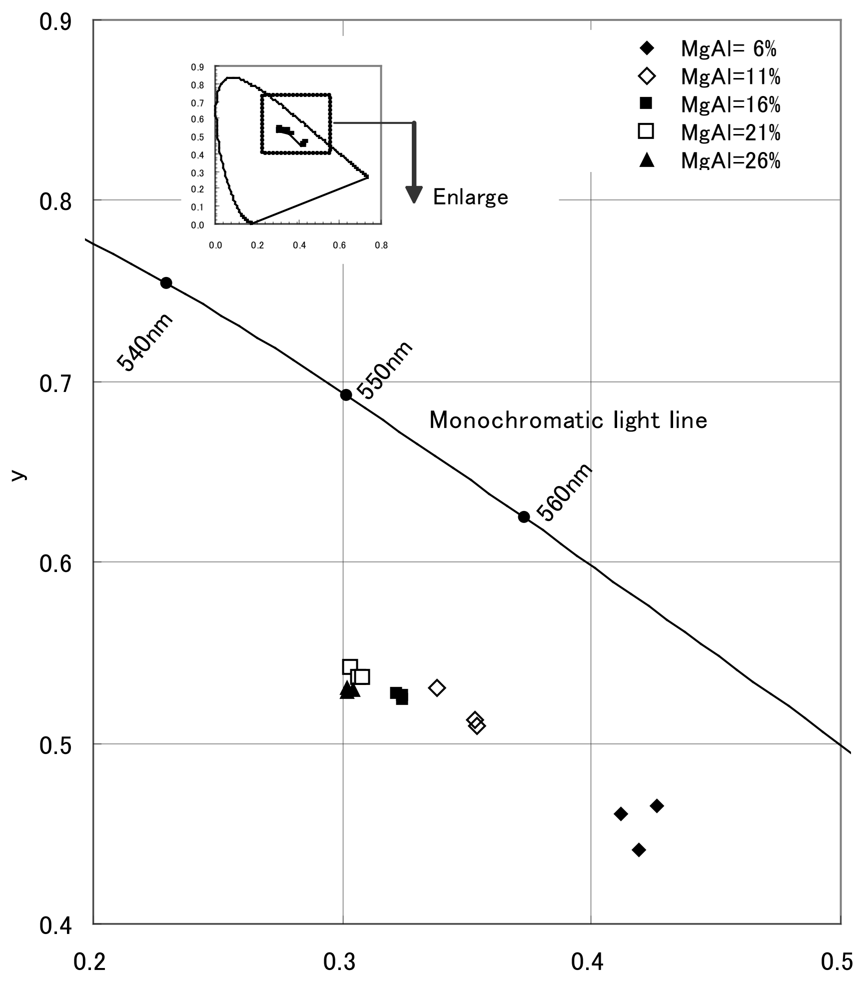

Figure 14 *Chromaticity of variation of MgAl based on green formula.*

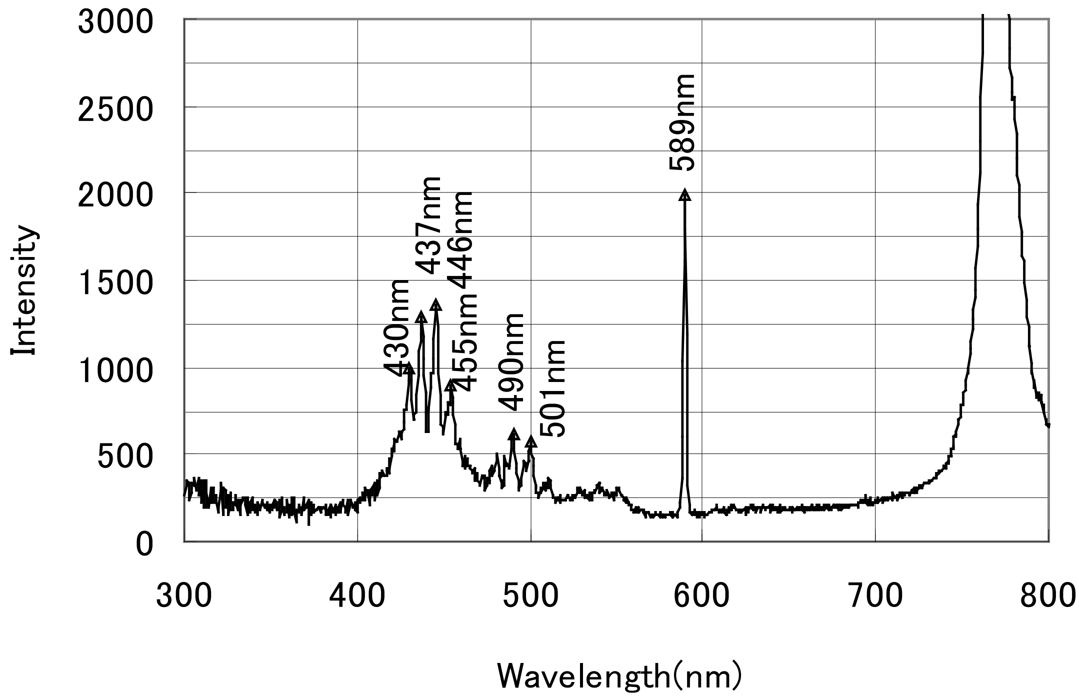

Figure 15 *Spectrum of blue flame.*

is at or above 14%, the chromaticity coordinates shift back to the white light region.

Effects of MgAl

MgAl powder was added to the blue reference composition with 5% increments from 5% to 25%, respectively, and the experiments were conducted. Those experimental results are plotted in Figure 18. For the comparison, the results for the blue reference composition are also plotted in the same figure. The point C indicates the ICI white light chromatic coordinate.

The results show that as MgAl metal powder above 5% was added to the blue reference composition, the chromatic coordinates would move towards the white light region and the purity of the blue flame would deteriorate. In fact, the flame could not be perceived as blue if above 5% metal powder MgAl was added to the blue reference composition. The reason is that the intensity of the sodium peak at 589 nm and continuous emission of light extending throughout the longer wavelength region will increase due to the high combustion heat of MgAl.

Conclusions

The effects of variation of content of color agent, chlorine donor or high energy agent on the colored flame of firework compositions have been investigated in this study. The quality of a colored flame mainly depends on the competition between desired emitters and undesired emitters. From the spectra measured, the emitting light peak and wavelength information due to the emitters is obtained. The atomic sodium peak at 589 nm is an undesired emission when forming a deep red, green or blue flame, but not for a yellow flame. Continuous radiation extending throughout the longer wavelength region is also undesirable for all colored flames. It is easier to form a deep red or yellow flame with the proper formula, but it is difficult to form a deep blue flame. In particular, a firework formula to which a metal powder such as MgAl is added cannot form a deep blue flame.

Table 10 *Variation of CuO based on blue formula (wt%).*

Component	Formula				
	B-1	B-2	B-3 (RC)	B-4	B-5
$KClO_4$	68.6	65.8	63	60.2	57.4
CuO	2.0	6.0	10	14.0	18.0
Phenolic resin	13.1	12.5	12	11.5	10.9
Chlorinated gum	10.9	10.4	10	9.6	9.1
Rice granules	5.4	5.2	5	4.8	4.6

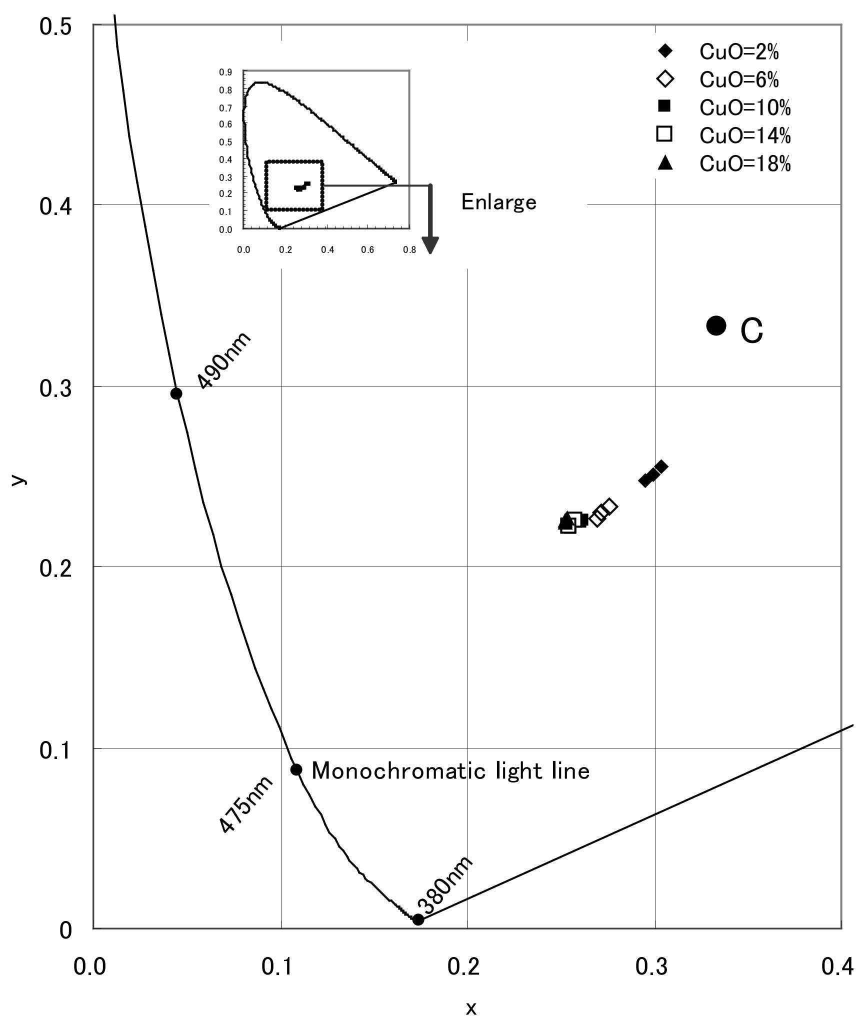

Figure 16 *Chromaticity of variation of CuO based on blue formula (● sign indicates white light point ICI illuminant "C").*

Table 11 *Variation of chlorinated gum based on blue formula (wt%).*

Component	Formula				
	B-6	B-7	B-3 (RC)	B-8	B-9
$KClO_4$	68.6	65.8	63	60.2	57.4
CuO	10.9	10.4	10	9.6	9.1
Phenolic resin	13.1	12.5	12	11.5	10.9
Chlorinated gum	2.0	6.0	10	14.0	18.0
Rice granules	5.4	5.2	5	4.8	4.6

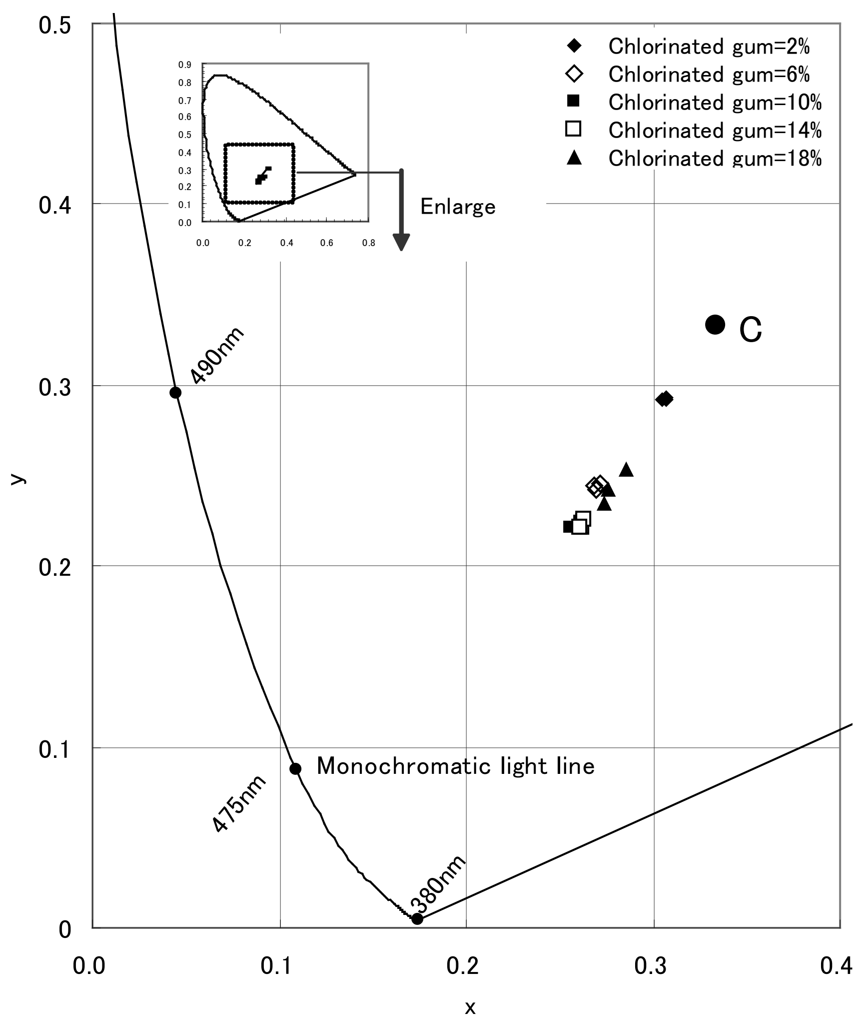

Figure 17 *Chromaticity of variation of chlorinated gum based on blue formula (● sign indicates white light point ICI illuminant "C").*

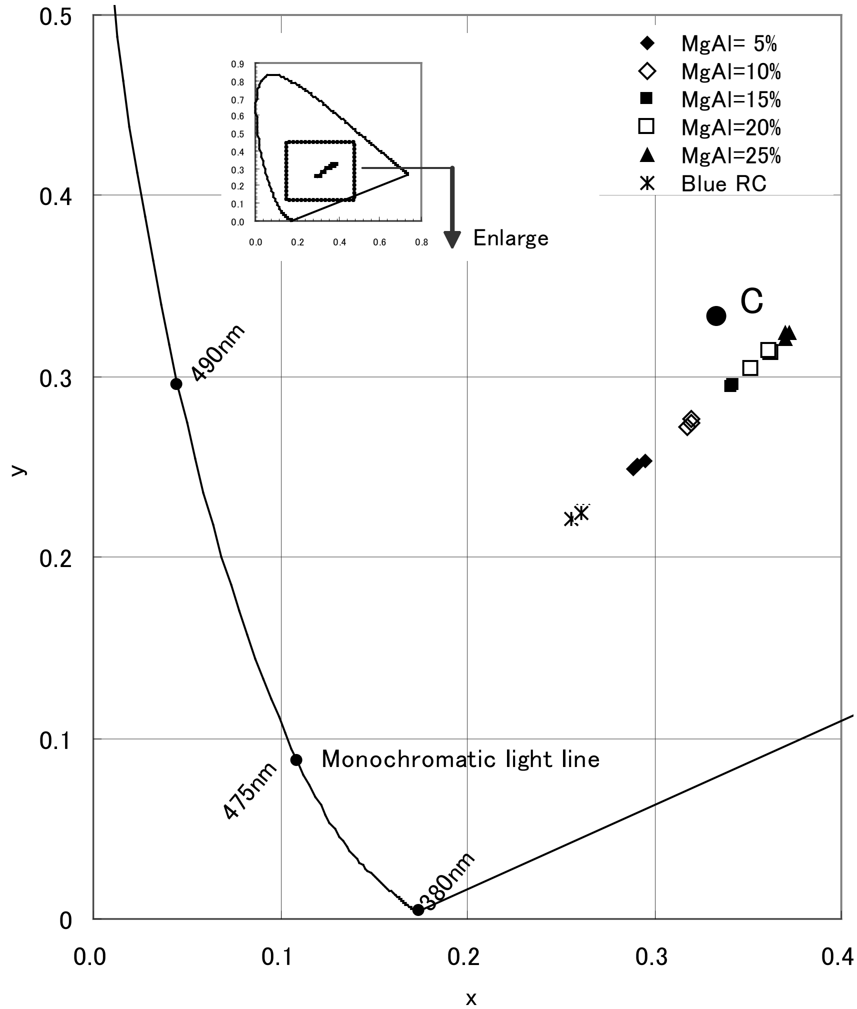

Figure 18 *Chromaticity of variation of MgAl added to blue reference formula (● sign indicates white light point ICI illuminant "C").*

References

1 Y. Sashimura, Fireworks, Personal publication, Printed by Nanfudo, Japan, Feb. 1, 2007, pp.166-173

2 Brian V. Ingram, "Color Purity Measurement of Traditional Pyrotechnic Star Formulas", *Journal of Pyrotechnics*, Issue 17, Summer 2003, pp. 1–18.

3 K. L. Kosanke and B. J. Kosanke, "The Chemistry of Colored Flames", *Pyrotechnic Chemistry*, Ch. 9, pp. 42–44, Journal of Pyrotechnics Inc., 2004.

4 K. Itoh, D. Ding, Y. Sashimura, H. Watanabe and T. Yoshida, "Effect of Composition on Color Values of Green Star Flame", 11th International Symposium on Fireworks, Puerto Vallarta, México, April 20-24, 2009, pp.115-126.