

# Spectroscopic Measurement of Light and Flame of LEDs and Liquid Colors

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**Abstract:** *Spectra and color values of the light from LEDs and liquid colors were measured using the PMA-11C7473-36 spectrometer as a preliminary study of the color of firework flames. The light from LEDs was stable and reproducibly measured. The color values of the light from LEDs did not vary with change in the exposure time of the spectrometer and the distance between the light and the incident point. The color values of the flames of liquid colors were less stable than those from LEDs owing to the flickering of the flame, but nearly constant with the change of exposure time and distance. The peak heights of the flame spectra of the liquid colors were proportional to the exposure time, but when the highest peak was saturated the proportionality changed. The red and yellow spectra of the liquid colors consisted of the single peaks from Li and Na atoms, respectively, with high excitation purity. The green and blue spectra consisted mainly of the molecular spectra of  $BO_2$  and  $CuCl$ , respectively, with moderate excitation purity. The concentrations of the principal color emitters of the flames of alcohol colors were calculated using a computer program for chemical thermodynamics.*

**Keywords:** *flame spectra, liquid colors, LED, spectroscopic measurement, thermodynamic modeling*

## Introduction

The objective of this work is to establish the measuring conditions for spectroscopy of the flames of liquid colors with the PMA-11C7473-36 spectrometer as a preliminary study of the spectroscopic measurement of colored firework flames.

It has been known for a long time that flammable liquids containing certain color imparting materials give colored flames on burning in air. Weingart<sup>1</sup> reported that alcohol containing some compounds gives green, red, yellow or blue colored flames on burning in air. Shimizu<sup>2</sup> preliminarily examined the flame color of copper using a gas burner. Jennings-White<sup>3</sup> described how lithium compounds show a beautiful scarlet color in gas or alcohol flames but not in a pyrotechnic flame.

Jennings-White and Wilson<sup>4</sup> carried out a colored flame ball display using liquid color and a concussion apparatus as follows: certain color imparting materials were dissolved in about 500 ml of methanol, and the formulation was poured directly over a 5 g charge of commercially available theatrical concussion powder which was

waterproofed and set in a concussion mortar. The charge was fired and the colored flame column emitted rose to a height of about 20 feet by 8 feet in width.

Meyerriecks and Kosanke<sup>5</sup> introduced color imparting materials dissolved or suspended in water or other liquids into a propane gas burner, showed the flame spectra of the colored species formed and gave the calculated results on a chromaticity diagram. Yamamoto, Wada, Matsunaga et al.<sup>6</sup> obtained the reference spectrum of SrOH from the combustion flame spectrum of methanol containing  $Sr(NO_3)_2$ .

The Saint Cross Co. Ltd. in Korea patented<sup>7</sup> and sells the colored flame torch with a trade name of Magic Corona which is used in this work.

The torch using liquid color burns for a longer time than ordinary fireworks and is a convenient tool for testing a spectroscopic instrument for fireworks. LEDs (Light Emitting Diodes) emit a stable light for a long time. We examined the performance of a spectroscopic instrument using liquid colors and LEDs. The excitation purity of color is regarded as an important color value in

fireworks.<sup>8</sup> We therefore paid particular attention to the excitation purity of the liquid color flame.

## Experimental

### Materials

Red, green and blue LEDs of 6 mm in diameter were produced by Toshiba, Stanley Electric and Opto Supply Companies, Ltd., respectively. The oil colors are the products of the Saint Cross Company Ltd.<sup>7</sup> The methanol and ethanol colors were prepared by the authors and compositions are listed in Table 1.

### Apparatus

A Photonic Multichannel Analyzer PMA-11 C7473-36 (Hamamatsu Photonics Co. Ltd.) was used. The spectrometer is composed of an optical fiber for light intake, photo detector, spectroscopy, basic software and data analyzer. The analyzer automatically calculates and records the spectrum and the excitation purity of the incident color.

**Table 1.** Compositions of alcohol colors.

No.	Alcohol	Ingredient
1	Methanol 100 ml	LiCl 0.10 g
2	Methanol 100 ml	NaNO <sub>3</sub> 0.10 g
3	Methanol 100 ml	H <sub>3</sub> BO <sub>3</sub> 4.0 g
4	Methanol 100 ml	CuCl <sub>2</sub> 1.0 g, CHCl <sub>2</sub>
5	Ethanol 100 ml	LiCl 0.10 g
6	Ethanol 100 ml	NaNO <sub>3</sub> 0.10 g
7	Ethanol 100 ml	H <sub>3</sub> BO <sub>3</sub> 4.0 g
8	Ethanol 100 ml	CuCl <sub>2</sub> 1.0 g, CHCl <sub>3</sub> 10 ml

The three filters used are products of NELLES GRIOT: 03FNQ099 ( $D = 0.5$ ), 057 ( $D = 1.0$ ) and 065 ( $D = 2.0$ ).

### Procedure

An LED was put on a base plate and placed in front of the tip of the optical fiber of the spectrometer. A liquid color was poured into the container of a commercial alcohol lamp and burnt using a wick. The distance between the center of the emitter and the tip of the optical fiber was fixed or varied according to the object of the measurement.

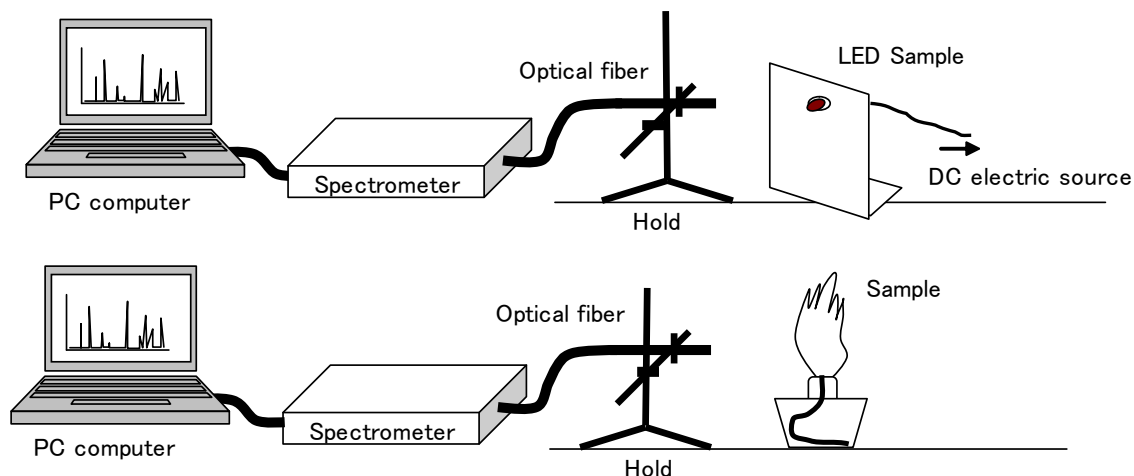
At first, the measuring conditions such as the sensitivity, the exposure time, and the averaging repetition of the instrument were set, the dark electric current was corrected in the dark room, and then the LED was switched on or the liquid lamp ignited. The setup of the spectroscopic measurement system is shown in Figure 1.

## Results and Discussion

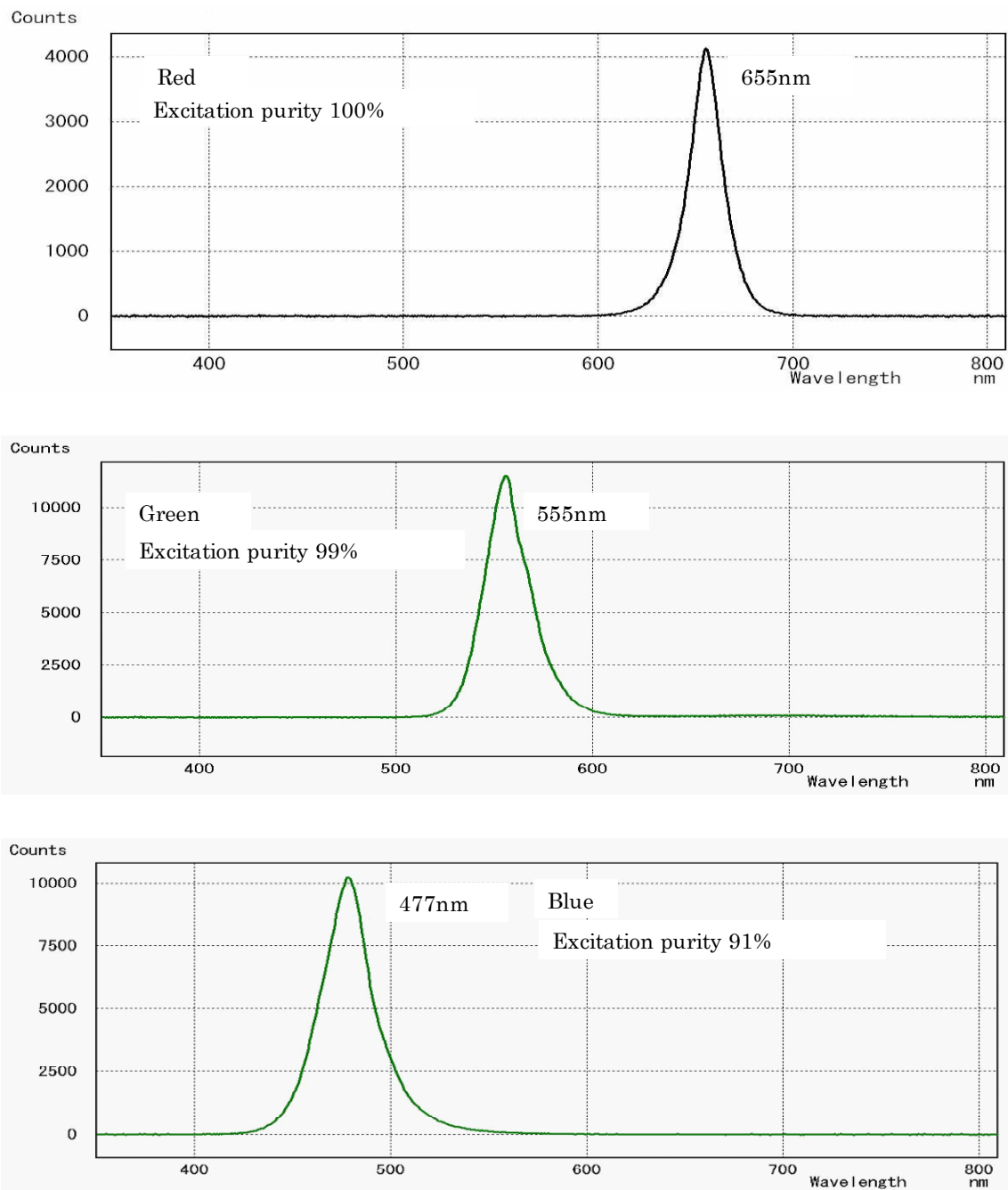
### Spectra of LED and liquid colors

Emission spectra and LED chromaticity are shown in Figure 2. The excitation purities of spectra of the red and green LEDs were nearly 100%. That of the blue LED was about 90%. The spectra of the red, green and blue LEDs tested have a single peak each as shown in Figure 2.

Figure 3 shows the emission spectra of the red, yellow, green and blue flames of the methanol colors. The spectra of the ethanol and oil colors were similar to those of the methanol colors except for excitation purity and base line.



**Figure 1.** Setup of spectroscopic measurement system.

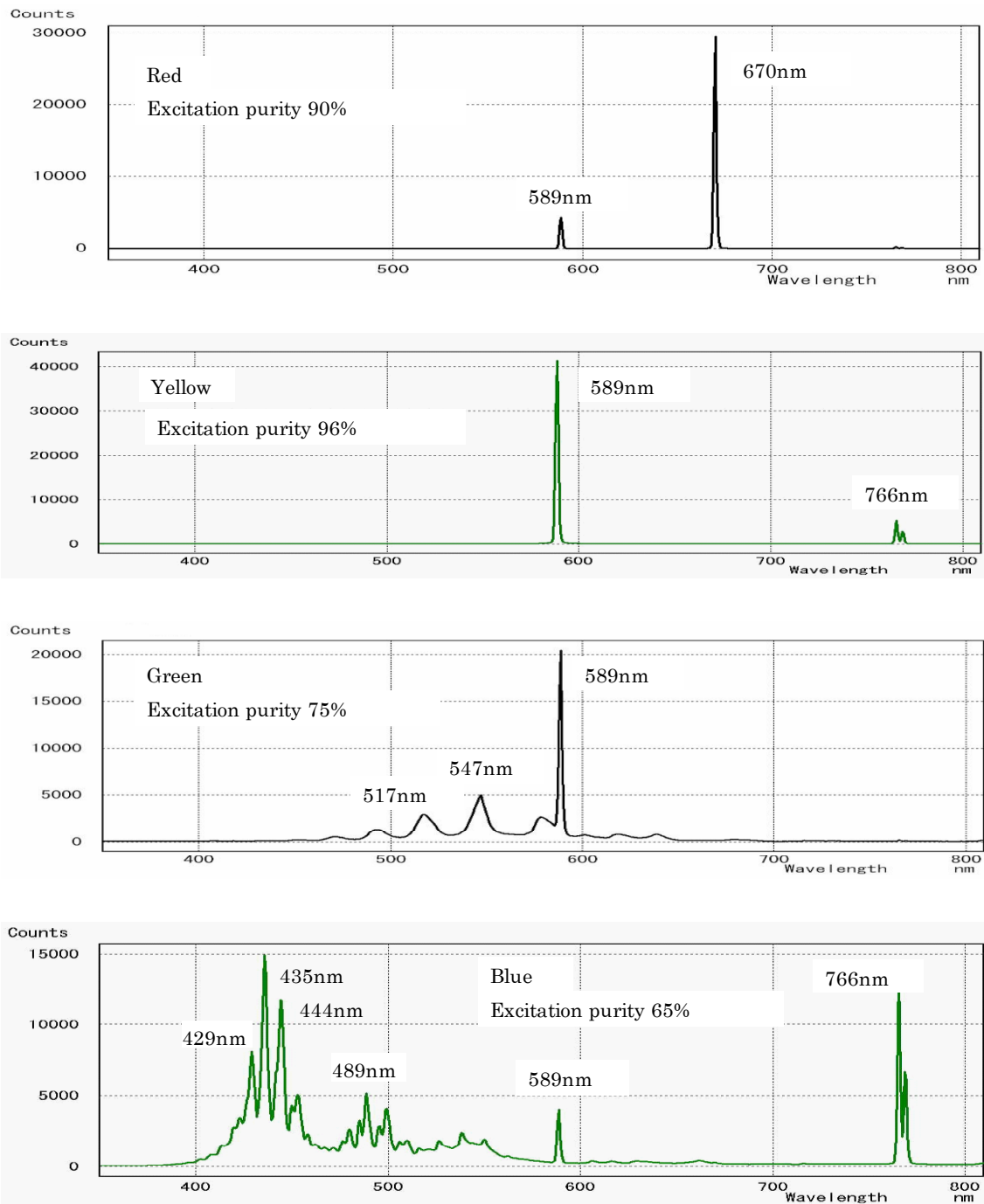


**Figure 2.** Spectra and excitation purity of LEDs.

The main peak of the spectrum of the red methanol color is the lithium atom line spectrum. The second peak is the contaminated sodium atom line spectrum. In the ethanol color flame base line drift is observed in the higher wavelength region which may come from the incandescent emission of the solid combustion products of ethanol. As the result the excitation purity of the flame of an ethanol

color is lower than that of the corresponding methanol color.

The main peak of the yellow methanol color is the sodium atom line spectrum and the second peak is that of the contaminated potassium atom line spectrum. The baseline drift is common to the ethanol color. The highest sharp peak of the green spectrum of the methanol color flame using



**Figure 3.** Spectra and excitation purity of the methanol color flames.

boric acid is the contaminated sodium atom line spectrum. The broad band spectrum with 517, 547 and 578 nm and other peaks is the molecular spectrum of  $\text{BO}_2$ .<sup>9</sup>

The highest sharp peak of the spectrum of the blue methanol color flame using  $\text{CuCl}_2$  and  $\text{CHCl}_3$  is also the line spectrum of the sodium atom, the

second that of the potassium atom. The band spectrum from 412 nm to 552 nm was assigned to  $\text{CuCl}$ .<sup>5</sup>

The spectra of the flames of the red and yellow oil colors are very similar to those of the red and yellow methanol colors suggesting that the emitters of the oil and methanol colors are same.

The excitation purities of both colors are similar and higher than the corresponding ethanol color. In the oil color spectra, no drift was observed in the baseline as shown in the spectra of the flame of the ethanol colors.

Figure 4 shows the chromaticity diagrams of the flames of ethanol and oil colors. The excitation purity of an oil color was higher than that of corresponding ethanol color.

### Reproducibility of excitation purity

In order to examine the reproducibility of the observed excitation purity data, the experiments were repeated five times under the same conditions. The results are shown in Figure 5. The circles are averaged values and the ends of the lines are the extreme values. The scatter of the observed values does not necessarily decrease as the times of averaging repetition increase. The averaging repetition here is the repetition times of exposure in the spectrometer for averaging. This result may be attributable to the flickering of the flame. On the other hand, the average experimental values of excitation purity approach a constant value with increase of averaging repetition.

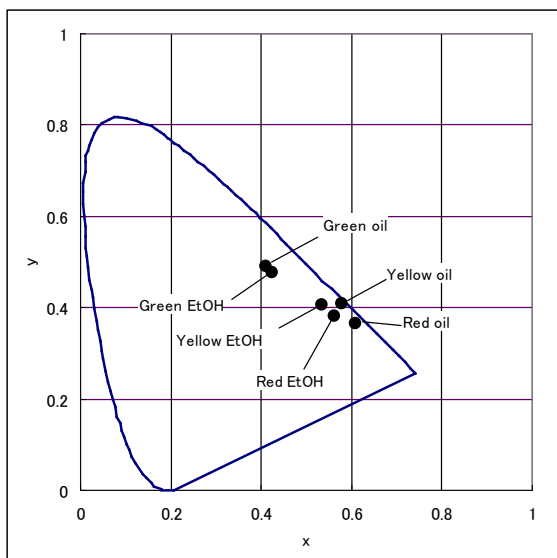


Figure 4. Chromaticity diagrams of ethanol and oil colors.

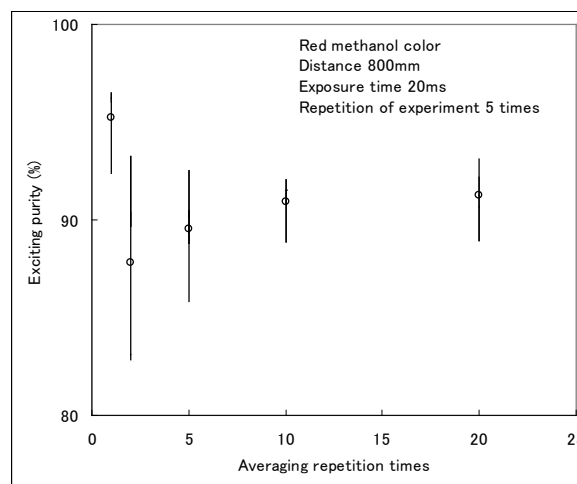


Figure 5. Plot of excitation purity vs. averaging repetition.

### Effect of exposure time on excitation purity

The PMA-11C7473-36 is a highly sensitive spectrometer and the peaks of the recorded spectrum saturate easily in the experiments. The distance between the emitter and point of incidence is limited when saturation is avoided. In order to know the effect of the saturation, the effect of the exposure time on the excitation purity and the peak height was examined.

Figure 6 shows the plot of excitation purity against exposure time for the LED and liquid colors. The excitation purities of LED and liquid colors were nearly constant in the range of the scatter with the increase of exposure time even when the highest peak saturated.

### Effect of exposure time on peak height

The peak heights of the emission spectra of LEDs and the liquid color flames were measured with different exposure times. Plots of peak heights of the LED spectra are shown in Figure 7. The peak heights were linearly proportional to the exposure time without scatter. The 547 nm peak height of the  $\text{BO}_2$  band spectrum was nearly proportional to the exposure time as shown in Figure 8. In this case no saturation of the Na peak was observed, but some scatter was observed compared with the LED case. The situation was similar in the ethanol

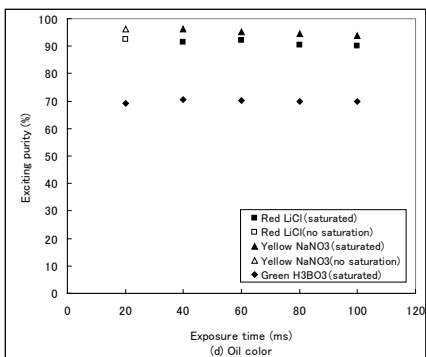
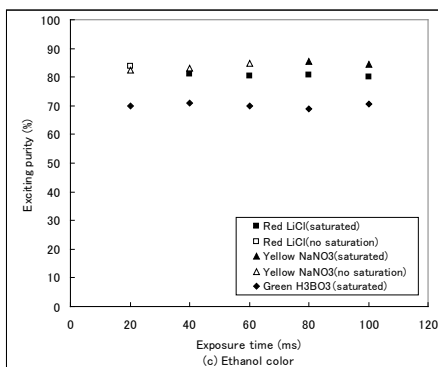
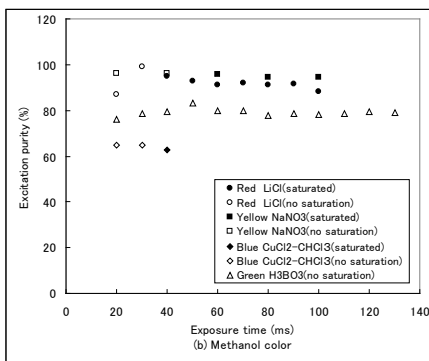
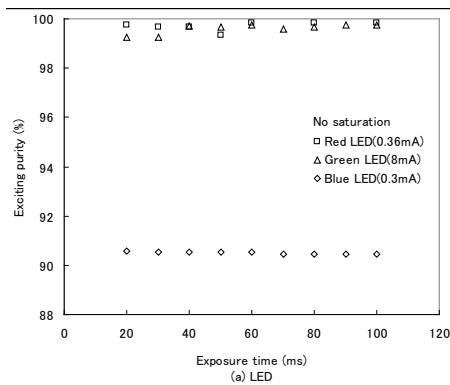


Figure 6. Plot of excitation purity vs. exposure time.

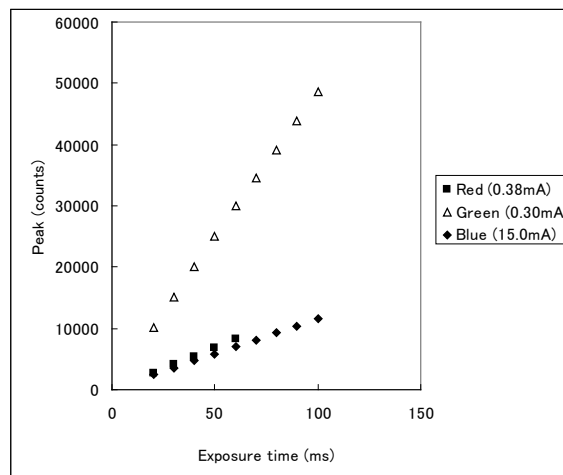


Figure 7. Plot of peak height vs. exposure time for LEDs.

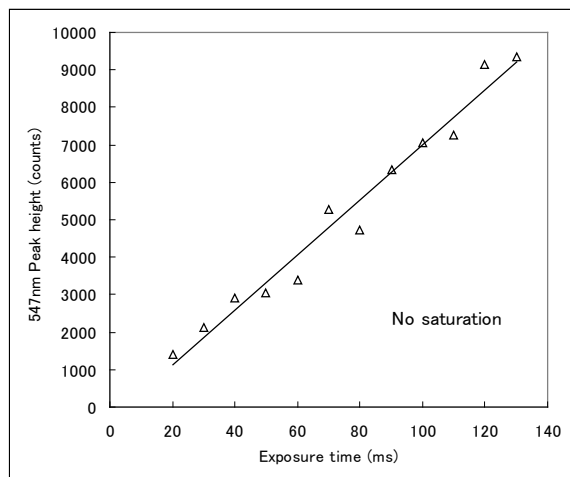


Figure 8. Plot of 547 nm  $BO_2$  height vs. exposure time for green methanol color.

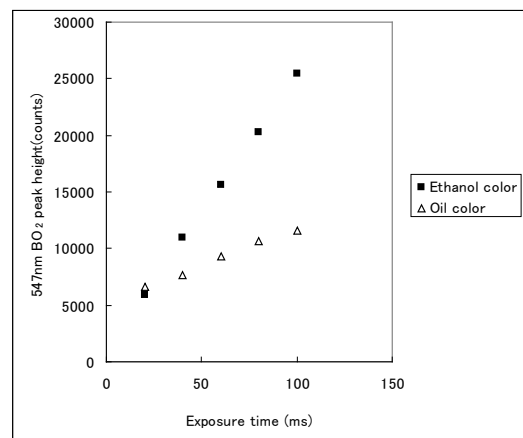


Figure 9. Plot of 547 nm  $BO_2$  peak vs. exposure time for green alcohol color.

and oil colors except that the oil color line deviated from zero as shown in Figure 9.

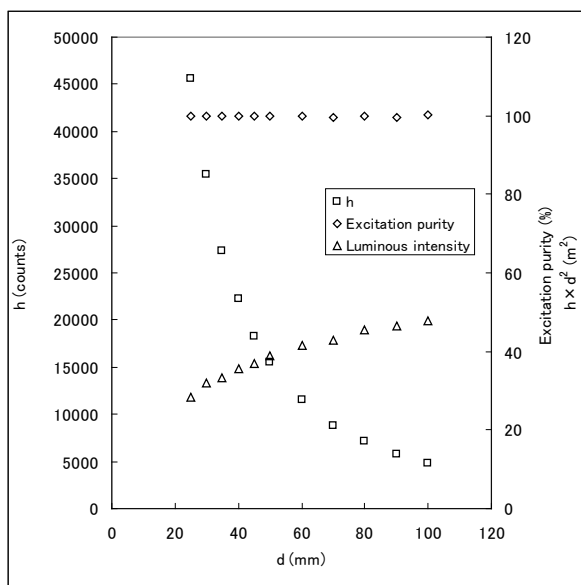
### Effect of the distance between the emitter and the sensor on the excitation purity and the peak height

The plot of excitation purity against the distance between the emitter and the sensor is shown in Figure 10 for a red LED. The excitation purity did not change with distance. The scatter of the purity was small because of the stable light emission of the LED. The plot of counts of the peak height for the red LED against the distance is also shown in Figure 10 indicating that the counts decrease with the distance. The peak height ( $h$ ) is proportional to the illuminance at the sensor and the illuminance is related to the luminous intensity of the emitter provided the emitter is a point:<sup>11</sup>

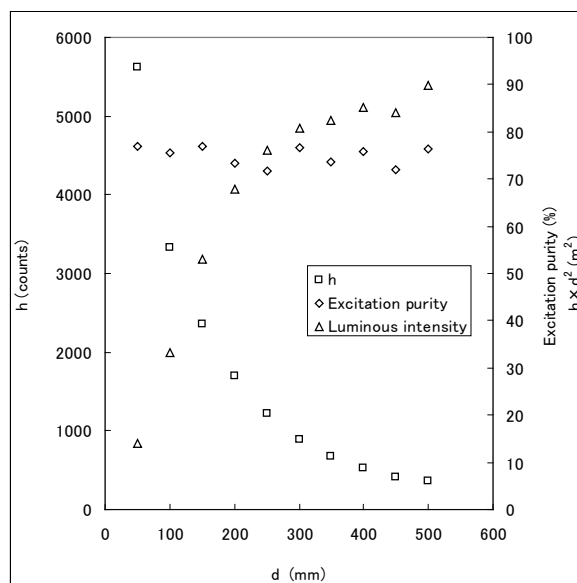
$$\begin{aligned} \text{Luminous intensity} &= \text{illuminance} \times \text{distance} (d)^2 \\ &= h \times d^2 \end{aligned}$$

$h \times d^2$  is also plotted against  $d$  in Figure 10.  $h \times d^2$  increased with  $d$  probably because the LED is not a point in the range of the measurement.  $h \times d^2$  looks like approaching a constant value when  $d$  increases further.

Figure 11 shows the plot of the excitation purity, peak height ( $h$ ) and  $h \times d^2$  for the green methanol color. The plot of excitation purity against distance has a larger scatter for the flame of the



**Figure 10.** Plot of excitation purity, peak height ( $h$ ) and  $h \times d^2$  vs. distance ( $d$ ) for the red LED.

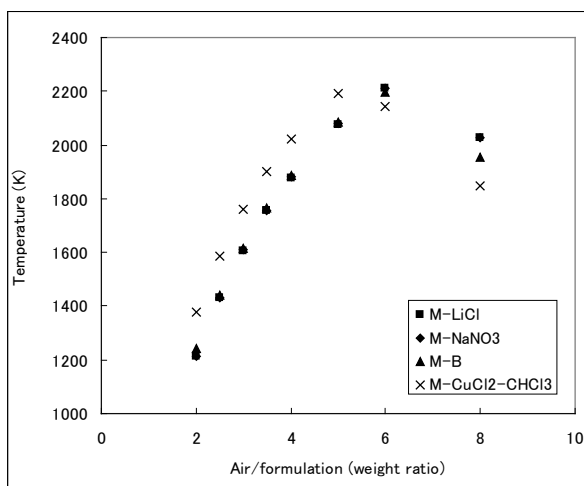


**Figure 11.** Plot of excitation purity, peak height ( $h$ ) and  $h \times d^2$  vs. distance ( $d$ ) for the green methanol color.

green methanol color than that for the red LED, because the LED emits stable light, but the flame is flickering and inhomogeneous. The height of the 547 nm  $\text{BO}_2$  peak of the green flame decreased with the distance.  $h \times d^2$  increased and approached a constant value with increasing distance at a much greater distance than for LED, because the volume of the torch flame is much larger than the LED emitter.

### Thermodynamic analysis

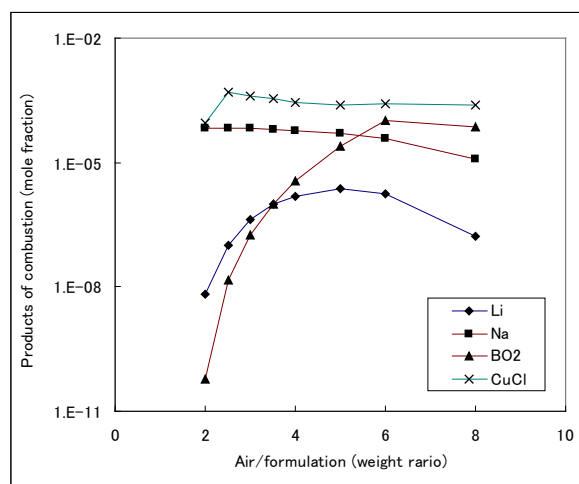
The thermodynamic calculations were performed by several authors<sup>6,12-14</sup> for investigating the emitter concentrations in the flame of firework compositions. A thermodynamic calculation was performed using a NASA program<sup>10</sup> for calculating the emitter concentrations in the methanol colors and the adiabatic combustion temperatures of the solutions. Figure 12 shows the adiabatic temperature of the flames of the methanol colors against the air/methanol solution ratio. The temperature profiles of the red, yellow and green colors were very similar because the solutes in the methanol were in small proportions and the effect of the solutes on the heat of combustion of the solutions was low. The temperature of the blue color was different from those of the other colors. This may be attributable to the relatively high concentration of chloroform in the solution.



**Figure 12.** Plot of adiabatic temperature air/methanol solution (wt/wt).

The mol fractions of principal emitters of flames of methanol colors are listed in Table 2 and shown in Figure 13 against the air/methanol solution ratio. The concentrations of Li and  $\text{BO}_2$  which are the principal emitters<sup>11,9</sup> of red and green colored flames were small when the air/methanol solution ratio was small, and increased with the increase of the ratio and reached maxima. This means that the red and green colors are more intense at higher temperatures in the flame.

On the other hand, the concentrations of Na and CuCl which are the principal emitters<sup>5</sup> of yellow and blue flames did not change greatly with the change in air/methanol solution ratio. This means that the intensities of these colors do not change



**Figure 13.** Plot of mole fractions of principal emitters vs. air/methanol solution (wt/wt).

greatly with the change of temperature of the flame.

The spectrum of the red methanol color consists of a Li atom line peak along with a small contamination from a Na atom line peak and the excitation purity of the color was over 90% as shown in Figure 3. The other emitters were not found in the observed spectrum. In the calculated equilibrium products, several lithium containing compounds such as LiCl and LiOH appeared in larger concentrations than Li. LiCl and LiOH may be weaker emitters than Li.

The spectrum of the yellow methanol color consists of a Na atom line peak along with the contaminating K peaks. No other peak was observed in the spectrum. NaOH appeared in the calculated products in comparable concentration with Na. NaOH may be also a weaker emitter than Na.

$\text{HBO}_2$  and  $\text{B}_2\text{O}_3$  were formed according to the calculation in the green colored flame of B containing methanol in larger and comparable concentrations, respectively. No peak other than  $\text{BO}_2$  was found in the spectrum of the flame of green methanol color.

### Preliminary test of filters

The spectrometer PMA-11C7473-36 was a suitable instrument for measuring the spectra of the light and flame of LED and liquid colors. However it was expected that the spectrometer would be too sensitive to measure the spectra of firework flames and their compositions in the laboratory. As a measure to overcome this the use of attenuation filters was considered. Three pieces of attenuation filters were tested using red and blue LEDs as light emitters. Results are listed in Table 3. At the moment, the B, C and combined B and C filters may be useful for measuring the spectra of fireworks in the laboratory and the A filter not.



**Table 2.** *Adiabatic temperature and concentration of species in the flame of methanol colors.*

Color	Air/solution (wt/wt)	Temperature/K	Species	Concentration (mole fraction)	
Red	2.0	1214	Li	$6.7 \times 10^{-9}$	
			LiCl	$1.7 \times 10^{-4}$	
			LiOH	$2.1 \times 10^{-5}$	
	4.0	1879	Li	$1.6 \times 10^{-6}$	
			LiCl	$3.6 \times 10^{-5}$	
			LiOH	$1.1 \times 10^{-4}$	
	6.0	2209	Li	$1.8 \times 10^{-6}$	
			LiCl	$9.2 \times 10^{-6}$	
			LiOH	$1.1 \times 10^{-4}$	
	8.0	2027	Li	$1.7 \times 10^{-7}$	
			LiCl	$1.2 \times 10^{-5}$	
			LiOH	$8.3 \times 10^{-5}$	
Yellow	2.0	1215	Na	$6.7 \times 10^{-5}$	
			NaOH	$3.1 \times 10^{-5}$	
	4.0	1880	Na	$5.8 \times 10^{-5}$	
			NaOH	$1.5 \times 10^{-5}$	
	6.0	2209	Na	$3.8 \times 10^{-5}$	
			NaOH	$1.9 \times 10^{-5}$	
	8.0	2027	Na	$1.2 \times 10^{-5}$	
			NaOH	$3.3 \times 10^{-5}$	
	Green	2.0	1242	BO <sub>2</sub>	$5.8 \times 10^{-11}$
				B <sub>2</sub> O <sub>3</sub>	$3.0 \times 10^{-8}$
				HBO <sub>2</sub>	$5.1 \times 10^{-4}$
		4.0	1888	BO <sub>2</sub>	$3.6 \times 10^{-6}$
B <sub>2</sub> O <sub>3</sub>				$3.2 \times 10^{-6}$	
HBO <sub>2</sub>				$3.9 \times 10^{-3}$	
6.0		2196	BO <sub>2</sub>	$1.0 \times 10^{-4}$	
			B <sub>2</sub> O <sub>3</sub>	$2.8 \times 10^{-6}$	
			HBO <sub>2</sub>	$2.9 \times 10^{-3}$	
8.0		1955	BO <sub>2</sub>	$7.4 \times 10^{-5}$	
			B <sub>2</sub> O <sub>3</sub>	$1.6 \times 10^{-6}$	
			HBO <sub>2</sub>	$2.3 \times 10^{-3}$	
Blue	2.0	1376	CuCl	$9.16 \times 10^{-5}$	
	4.0	2022	CuCl	$2.85 \times 10^{-4}$	
	6.0	2144	CuCl	$2.64 \times 10^{-4}$	
	8.0	1845	CuCl	$2.42 \times 10^{-4}$	

**Table 3.** Test results of three filters. Test conditions: sensitivity low, distance 100 mm, exposure time 20 ms and averaging 10 times.

LED	Electric current (mA)	Filter	Excitation purity (%)	Peak height (counts)	Attenuation
Red	3.00	No	100	45 151	
Red	3.00	A*	99	707	0.0157
Blue	1.20	No	94	40 614	
Blue	1.20	A*	93	342	0.00840
Blue	1.20	No	94	40 549	
Blue	1.20	B*	94	4558	0.112 <sup>a</sup>
Blue	1.20	C*	94	13 955	0.344 <sup>b</sup>
Blue	1.20	B + C*	94	1539	0.0380

$a \times b = 0.112 \times 0.344 = 0.0385$ . \* Filter A: 03FNQ065,  $D = 2.0$ . The excitation purity changed with the filter and the attenuations were different with different colors. Filter B: 03FNQ057,  $D = 1.0$ . The excitation purity did not change with the filter and the attenuations were same with different colors. Filter C: 03FNQ099,  $D = 0.5$ . The excitation purity did not change with the filter and the attenuations were same with different colors. Filter B + C: The excitation purity increased a little with the filters and attenuation was nearly the product of each attenuation of the B and C filters.

## Conclusions

The spectra of light of three LEDs each showed a single peak and gave from 91 to 100% excitation purities. The principal color emitters of liquid colors were Li for red, Na for yellow,  $\text{BO}_2$  for green and  $\text{CuCl}$  for blue, and the excitation purities of the colors were 90%, 96%, 75% and 65% in the methanol colors, respectively. The torch flame of liquid colors flickers and gives scatter in the observed data. The error in measurement was small when the averaging repetition time of the spectrometer was more than 10 for the red methanol color. The exposure time had little influence on the excitation purities for LED light and liquid colors. The adiabatic temperature and the concentration of the principal emitters in the flame of the methanol colors were calculated. It was shown that the concentrations of Li and  $\text{BO}_2$  were influenced by the air/solution ratio but those of Na and  $\text{CuCl}$  were not.

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