Spectroscopic Measurement of Burning Stars

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Abstract: *The spectroscopic measurement of burning stars has been carried out in order to examine the spectra of the stars, the peak intensity profiles of the spectra, the burning time and behavior, and the effect of filters on the attenuation of peak intensity and the excitation purity.*

Keywords: *firework stars, spectroscopic measurement, burning time, emission spectra, three dimensional expression, peak intensity profile, excitation purity, filter*

Introduction

Light emission and the beautiful colors of burning stars are important effects in fireworks. Shimizu[1] and Douda[2] were pioneers in modern research into the colored flames of firework compositions. Subsequently the spectra of colored flames were studied in detail and assigned to the respective emitters by Meyerriecks and Kosanke[3] and others. Kosanke and Kosanke have published a comprehensive review on the chemistry of colored flames,[4] and Ingram has carried out color purity measurements on traditional pyrotechnic star formulas.[8]

The burning time and linear burning rate are also important characteristics of stars. The shape of a fire flower of stars in the sky depends on the burning time of the stars. A spherical shape is produced by stars with short burning times and a crown or willow shape with long burning times. The linear burning rate is also important for analyzing the exterior ballistics of burning stars.

Preliminary work on the burning time and linear burning rate was done by Ooki et al.[5] and Higaki et al.[6] using a high-speed video camera and a pressure vessel. In the present work, spectroscopic measurement is carried out to study the spectra and burning characteristics of spherical stars.

Experimental

Materials

The firework spherical stars used in this work were supplied by Sunaga Fireworks Co. Ltd. All stars are coated with prime for promoting ignition of the star composition.

Apparatus

The spectrometer PMA-11C5966-31 is a product of Hamamatu Photonics Co. Ltd. The spectrometer is composed of an optical fiber for light intake, photodetector, spectroscope, basic software and data analyzer. The analyzer automatically calculates and records the spectrum, the respective peak wavelength and intensity, the excitation purity, and so on.

The spectrometer is equipped with following functions: exposure time from 20 ms to 32767 ms, averaging repetition from 1 to 32767 times, exposure repetition from 1 to 32767 times, and sensitivity low and high. The dark electric current can be corrected for removing background noise.

The analyzer can print out the emission spectrum at a specified time, the peak intensity profile at a specified wavelength and the three dimensional picture of the spectrum with time.

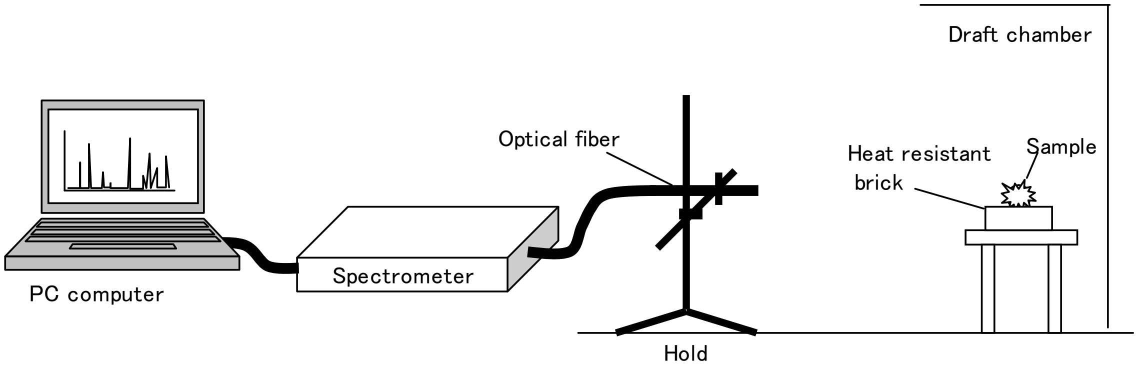


Figure 1. *Setup of measurement system.*

The two filters used are products of NELLES GRIOT: 03FNQ099 ($D = 0.5$) and 057 ($D = 1.0$) with attenuation ratios of 0.344 and 0.112, respectively.[7]

Procedure

The setup of the spectroscopic measuring system is shown in Figure 1. A star is placed on a heat resistant brick in a draft chamber and ignited by a torch burner. The tip of the optical fiber of the spectrometer is placed at 2.0 m or 4.0 m from the star. The power sources of the spectrometer and the PC are switched on successively. The measurement conditions such as instrument sensitivity, exposure time, averaging repetition numbers and exposure repetition are set and the dark electric current is measured. The spectrometer measurement is started with the ignition of the star.

Results and Discussion

Summary of experimental results

The experimental results are listed in Table 1 and Table 2.

Examples of three dimensional pictures and peak intensity profiles of emission spectra

Examples of the three dimensional pictures of the emission spectra of stars for a no. 5 shell are shown in Figure 2. We can easily determine the outline of the spectrum and the progress of events from the pictures. In the cases of the stars tested, the peak of incandescent emission was large compared to the other peaks which were due to specific color emissions. Each peak in the color spectrum was broad compared to that observed in the flame from liquid color.[7]

The highest peaks of the color spectra were assigned to SrCl (667 nm) for red, Na (587 nm) for yellow, BaCl (520 nm) for green and CuCl (440 nm) for blue.[3] The spectra of the other colors were mixtures of the above-mentioned spectra. The silver color was composed of larger K and incandescent, and smaller Na emissions.

Examples of peak intensity profiles of the emission spectra are shown in Figure 3. The wavelength of the specific color peak was chosen, but for some stars the K peak was used because the intensity of the specific color peak was too small compared to the K peak and inaccurate. The intensity increases sharply at first, reaches a maximum and then decreases slowly. The sharp initial increase may correspond to the spread of the fire over the surface of the star and the slow decrease to the decrease in the diameter of the spherical star. The profiles are not smooth but irregular, probably because of fluctuating burning on the star surface.

Effect of prime on the intensity profile

Ordinary stars are composed of color composition and prime which covers the color composition in order to promote the ignition of the composition. The burning time of a star is the sum of those of the prime and the composition.

The effect of the prime appears in the pressure profile in the burning of a star in a pressure vessel[6] and the emission spectrum of a burning star as shown in the present work. In the pressure profile of a burning star in a closed vessel, a sharp pressure rise owing to the combustion of the prime appears in the initial stage of the burning, then the pressure drops a little followed by a moderate pressure peak owing to the combustion of the main color composition.

Table 1. *Experimental conditions and burning time of stars.*

Sample star[a]	Star size/ mm	Experimental conditions[b]	Measurement distance/mm	Filter[c]	Burning time (s)
No. 2 Silver willow	9.454	20 ms*5Av*60	2	None	2.10
No. 2 Green peony	9.710	20 ms*5Av*60	2	None	2.00
No. 2 Yellow spangles	10.250	20 ms*200	2	None	1.44
No. 2 Yellow peony	10.127	20 ms*200	2	None	1.62
No. 2 Silver peony	10.746	20 ms*200	2	None	0.76
No. 2 Silver crown	10.099	20 ms*200	2	None	2.04
No. 2.5 Silver willow	11.392	20 ms*200	2	None	2.66
No. 2.5 Green peony	10.558	20 ms*200	2	None	2.00
No. 2.5 Yellow spangles	10.490	20 ms*200	2	None	1.30
No. 2.5 Red peony	10.815	20 ms*200	2	None	2.08
No. 2.5 Green peony	10.694	20 ms*200	2	None	2.48
No. 3 Green peony	11.352	20 ms*200	4	None	2.28
	11.548	20 ms*300	2	1+0.5	2.38
No. 3 Yellow spangles	11.457	20 ms*200	2	None	1.38
	11.517	20 ms*300	4	1+0.5	1.48
No. 3 Silver peony	12.302	20 ms*200	2	None	0.94
	11.533	20 ms*300	4	1+0.5	0.82
No. 3 Red peony	12.362	20 ms*200	2	None	2.38
	11.362	20 ms*300	4	1+0.5	2.38
No. 3 Pink peony	12.287	20 ms*200	2	None	1.88
	11.735	20 ms*300	4	1+0.5	1.78
No. 3 Blue peony	11.954	20 ms*200	2	None	2.26
	11.822	20 ms*300	4	1+0.5	2.24
No. 3 Light blue peony	11.538	20 ms*200	2	None	1.40
	12.489	20 ms*300	4	1+0.5	1.98
No. 3 Purple peony	11.619	20 ms*200	2	None	1.82
	12.045	20 ms*300	4	1+0.5	1.98
No. 3 Silver crown	11.865	20 ms*200	2	None	2.74
	12.273	20 ms*300	4	1+0.5	3.00
No. 4 Green peony	13.259	20 ms*200	4	1	1.98
No. 4 Yellow spangles	13.563	20 ms*200	4	1	1.18
No. 4 Silver peony	13.383	20 ms*200	4	1	0.98
No. 4 Red peony	13.916	20 ms*200	4	1	2.56
No. 4 Purple peony	13.059	20 ms*200	4	1	2.06
No. 4 Silver crown	13.316	20 ms*200	4	1	2.78
No. 5 Silver willow	14.486	20 ms*300	4	1+0.5	4.24
No. 5 Green peony	14.530	20 ms*300	4	1+0.5	3.18
No. 5 Yellow spangles	14.553	20 ms*300	4	1+0.5	1.86
No. 5 Red peony	14.493	20 ms*300	4	1+0.5	3.04
No. 5 Blue peony	13.461	20 ms*300	4	1+0.5	2.70
No. 5 Light blue peony	14.676	20 ms*300	4	1+0.5	1.94
No. 5 Purple peony	14.553	20 ms*300	4	1+0.5	2.36
No. 5 Silver crown	14.784	20 ms*300	4	1+0.5	3.18

[a] No. 2, No. 2.5, No. 3, No. 4 and No. 5 are the stars used for no. 2 shells, no. 2.5, no. 3, no. 4 and no. 5 shells, respectively. [b] Experimental condition: exposure time*(averaging repetition)*exposure repetition. [c] None is no filter, 1 is the filter with $D = 1.0$, and 0.5 is the filter with $D = 0.5$.

Table 2. *Experimental results of emission spectra of burning stars.*

Sample star	Peak (1)		Peak (2)		Peak (3)		Excitation purity (%)
	λ/nm	Intensity (counts)	λ/nm	Intensity (counts)	λ/nm	Intensity (counts)	
No. 2 Green peony	378	6165	520	62577			
			586	19191	(766)	PS[a]	54
No. 2 Silver willow	588	34182	693	50944	(766)	PS[a]	
No. 2 Yellow spangles	588	58686			(766)	PS[a]	82
No. 2 Yellow peony	588	41654			(766)	PS[a]	84
No. 2 Silver peony					768	94838	42
No. 2 Silver crown	586				(766)	PS[a]	17
No. 2.5 Silver willow	586	66850			(766)	PS[a]	26
No. 2.5 Silver peony	520	123846	586	43730	(766)	PS[a]	42
No. 2.5 Yellow spangles	588	46304			(766)	PS[a]	81
No. 2.5 Red peony			639	142275	(766)	PS[a]	80
No. 2.5 Silver crown	588	50000			(766)	PS[a]	29
No. 3 Green peony	518	32386	586	16919	(766)	PS[a]	53
	517	1363	586	849	766	23173	45
No. 3 Yellow spangles	588	60350			(766)	PS[a]	81
	588	1996			765	10496	78
No. 3 Silver peony	586	81376			(766)	PS[a]	19
	587	4437			766	96104	34
No. 3 Red peony	586	9242	603	14308			
	638	53107	664	118810	(766)	PS[a]	84
			667	6656	766	15264	81
No. 3 Pink peony	586	3381	603	4581	630	11425	
	638	11827	667	28136	(766)	PS[a]	62
	441	378	587	784	602	1193	
	631	2838	639	3049	657	5611	
			667	7108	766	7108	56
No. 3 Blue peony	448	4147	586	4348	766	149964	4
	441	285	543	282	589	260	
					766	7832	1
No. 3 Light blue peony	380	7102	446	27811	518	60379	
			586	39367	(766)	PS[a]	16
	447	1418	519	3334	586	2020	
					766	37058	19
No. 3 Purple peony	438	2042	587	3873	603	4040	
	631	10249	637	10033	656	20906	
			668	26608	766	129456	44
	438	386	586	351	603	373	
	630	1363	639	1399	656	2599	
			666	3332	766	10800	43
No. 3 Silver crown	586	20025			(766)	PS[a]	40
	585	1391	692	2081	766	21604	21

[a] PS: Peak saturated.

Table 2 continued. *Experimental results of emission spectra of burning stars.*

Sample star	Peak (1)		Peak (2)		Peak (3)		Excitation purity (%)
	λ/nm	Intensity (counts)	λ/nm	Intensity (counts)	λ/nm	Intensity (counts)	
No. 4 Green peony	519	5263	586	2899	766	74658	48
No. 4 Yellow spangles	587	9350			767	45888	78
No. 4 Silver peony	586	20660			(766)	PS[a]	36
No. 4 Red peony	586	2334	603	3729	630	12341	
	638	12708	659	23712	667	30139	
					766	75570	83
No. 4 Purple peony	441	742	585	871	605	999	
	631	3569	837	3583	656	6850	
			667	8609	765	26423	44
No. 4 Silver crown	586	8692			768	111806	26
No. 5 Silver willow	586	3527			769	40493	30
No. 5 Green peony	520	1211	586	827	766	26615	46
No. 5 Yellow spangles	588	3087			767	16936	76
No. 5 Red peony	588	712	603	1021	631	3266	
	638	3266	657	6550	667	8279	
					766	24162	81
No. 5 Blue peony	444	255	542	273	586	263	
					767	7918	5
No. 5 Light blue peony	441	1327	523	2511	586	1886	
					767	43721	16
No. 5 Purple peony	437	367	587	383	667	3422	
					767	12145	42
No. 5 Silver crown	586	2348			767	31605	31

[a] PS: Peak saturated.

The spectrum of the color composition and the prime of a star are different and therefore the combustion of the composition and the prime can be differentiated. The main peak of both composition and prime is the incandescent emission peak. The color composition has a color spectrum, but the prime does not.

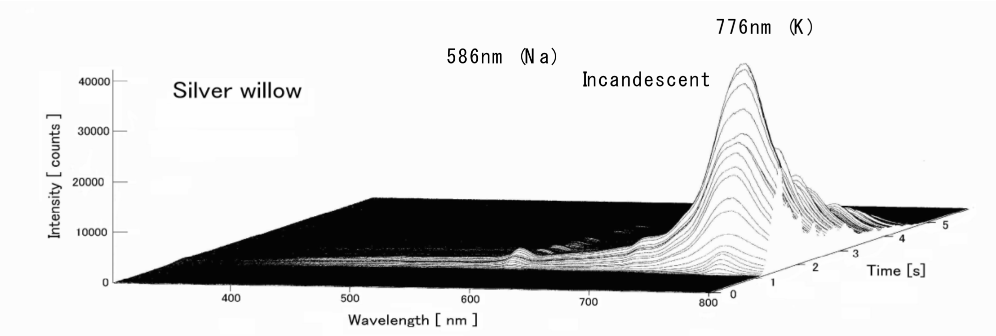
In the first stage of a star burning, the incandescent peak appears and the color peak or peaks do not. After few moments, a color peak begins to appear. In the prime, a small amount of sodium is a contaminant. But the amount of contaminating sodium is much less than that of the yellow color composition, so there is no problem in differentiating the spectra of the yellow composition and the prime.

An example of plot of the intensity of incandescent (766 nm) and color (520 nm) peaks against time is shown in Figure 4. It can be seen that the start times of both peaks are different. The incandescent peak appears first. The intensity of the 766 nm peak increases at first showing that the fire spreads over the surface of the prime, then the 520 nm peak intensity starts to increase showing that the color composition ignites from the prime combustion. Then both peaks reach maxima and decrease with time showing that the burning surface of the color composition decreases in the course of combustion with time.

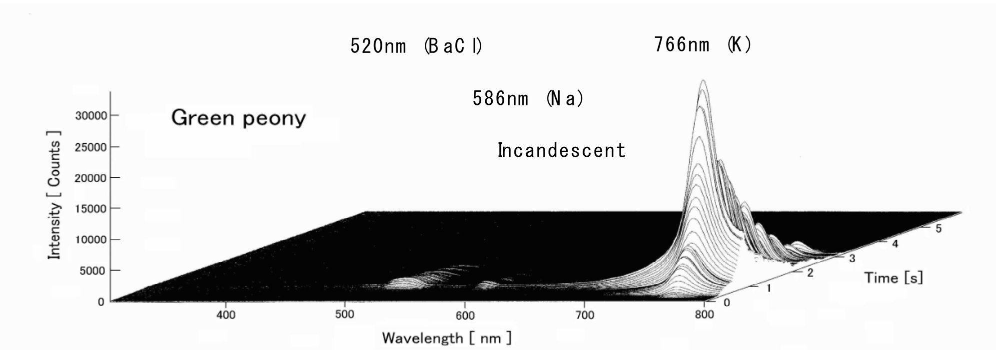
Excitation purity: reproducibility and dependency on combustion time

The excitation purity of the flame color of a star is important for evaluating the star. The available statistical values of the excitation purities are listed in Table 3 for some stars.

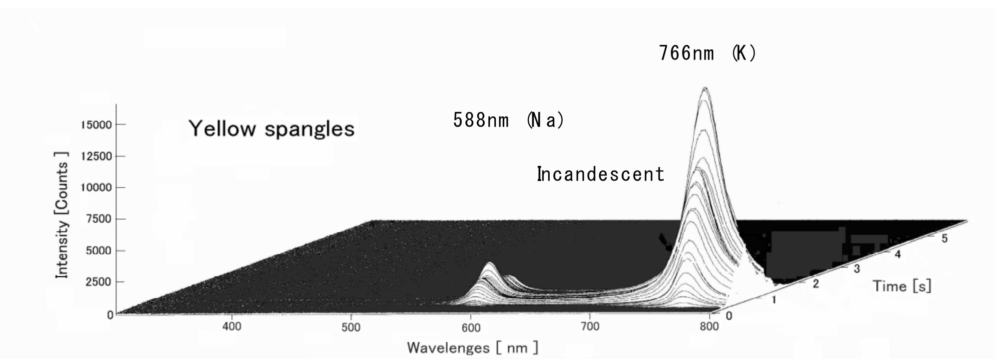
The time dependence of the excitation purity is shown in Figure 5. The initial increase of the



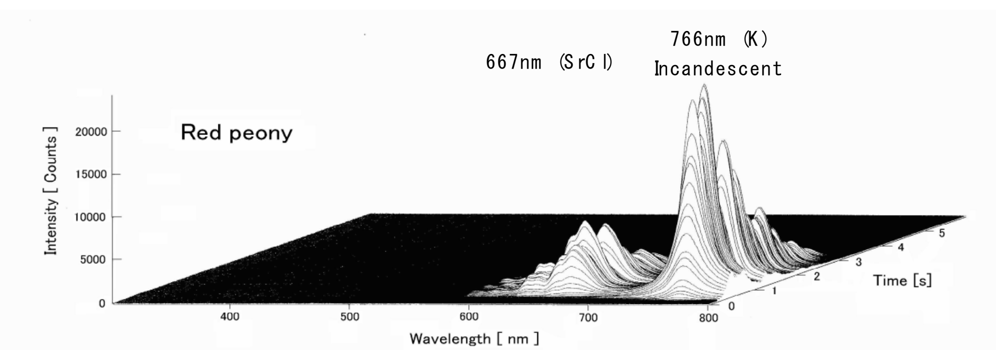
(a) Na (yellow), incandescent and K (infrared) emmisions



(b) BaCl (green), Na (yellow), incandescent and K (infrared) emmisions

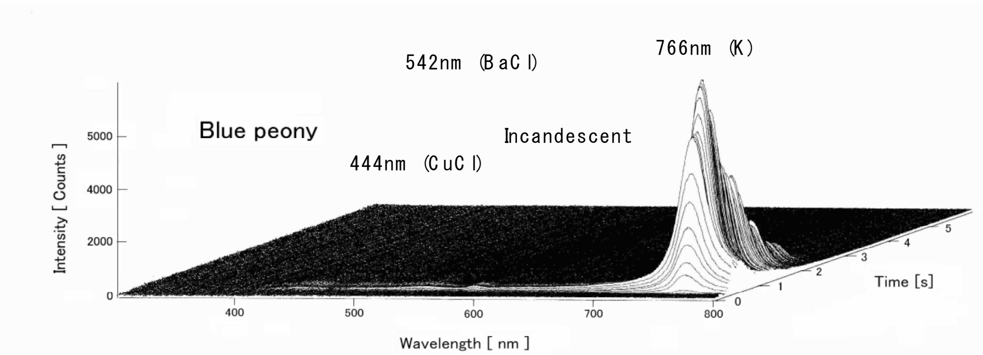


(c) Na (yellow), incandescent and K (infrared) emmisions

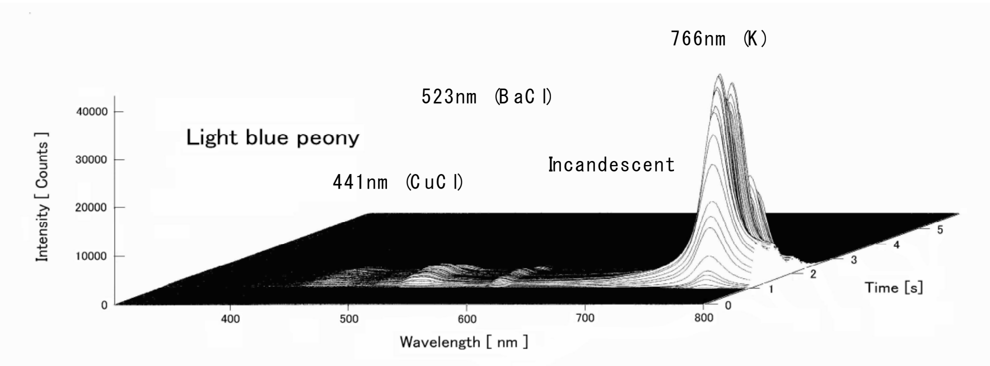


(d) SrCl (red), incandescent and K (infrared) emmisions

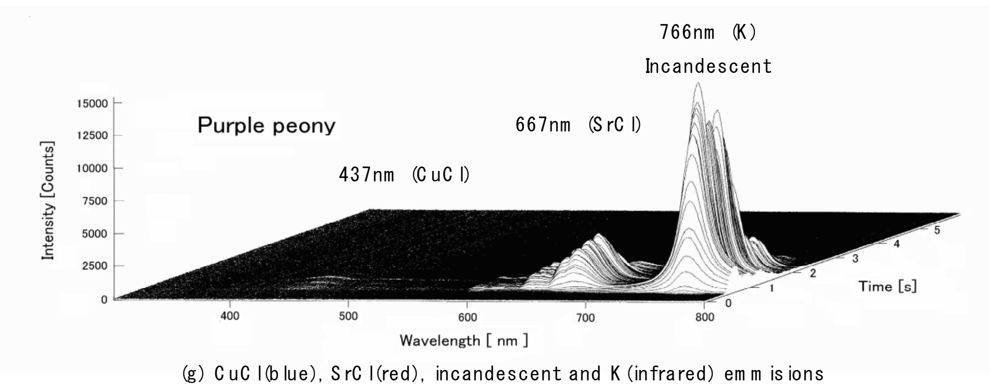
Figure 2. *Three dimensional pictures of emission spectra of burning stars.*



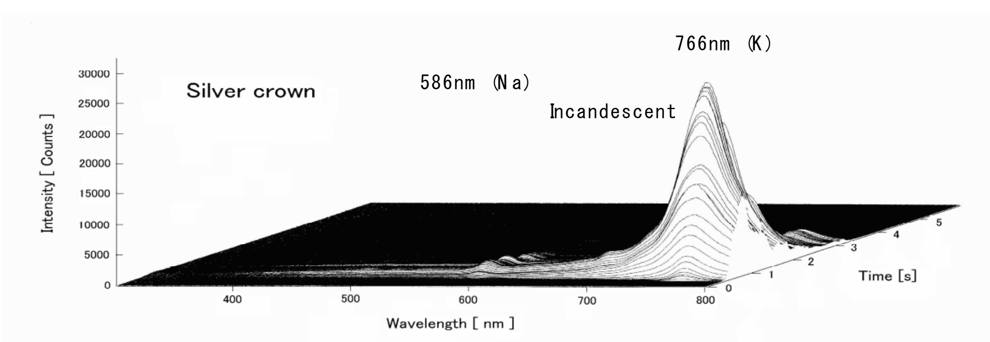
(e) CuCl(blue), BaCl(green), incandescent and K (infrared) emmisions



(f) CuCl(blue), BaCl(green), incandescent and K (infrared) emmisions



(g) CuCl(blue), SrCl(red), incandescent and K (infrared) emmisions



(h) Na (yellow), incandescent and K (infrared) emmisions

Figure 2 continued. *Three dimensional pictures of emission spectra of burning stars.*

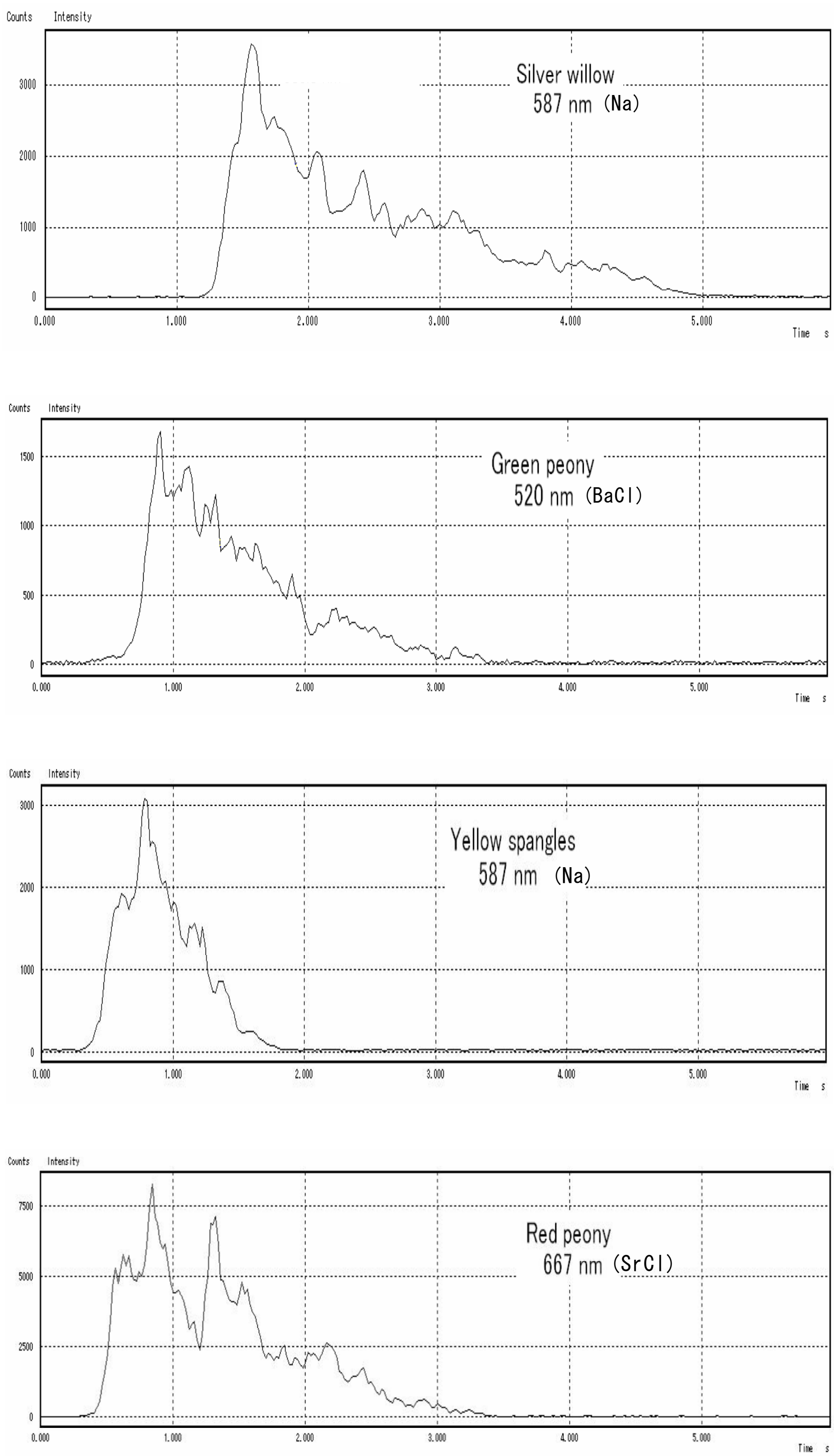


Figure 3. *Peak intensity profiles of emission spectra.*

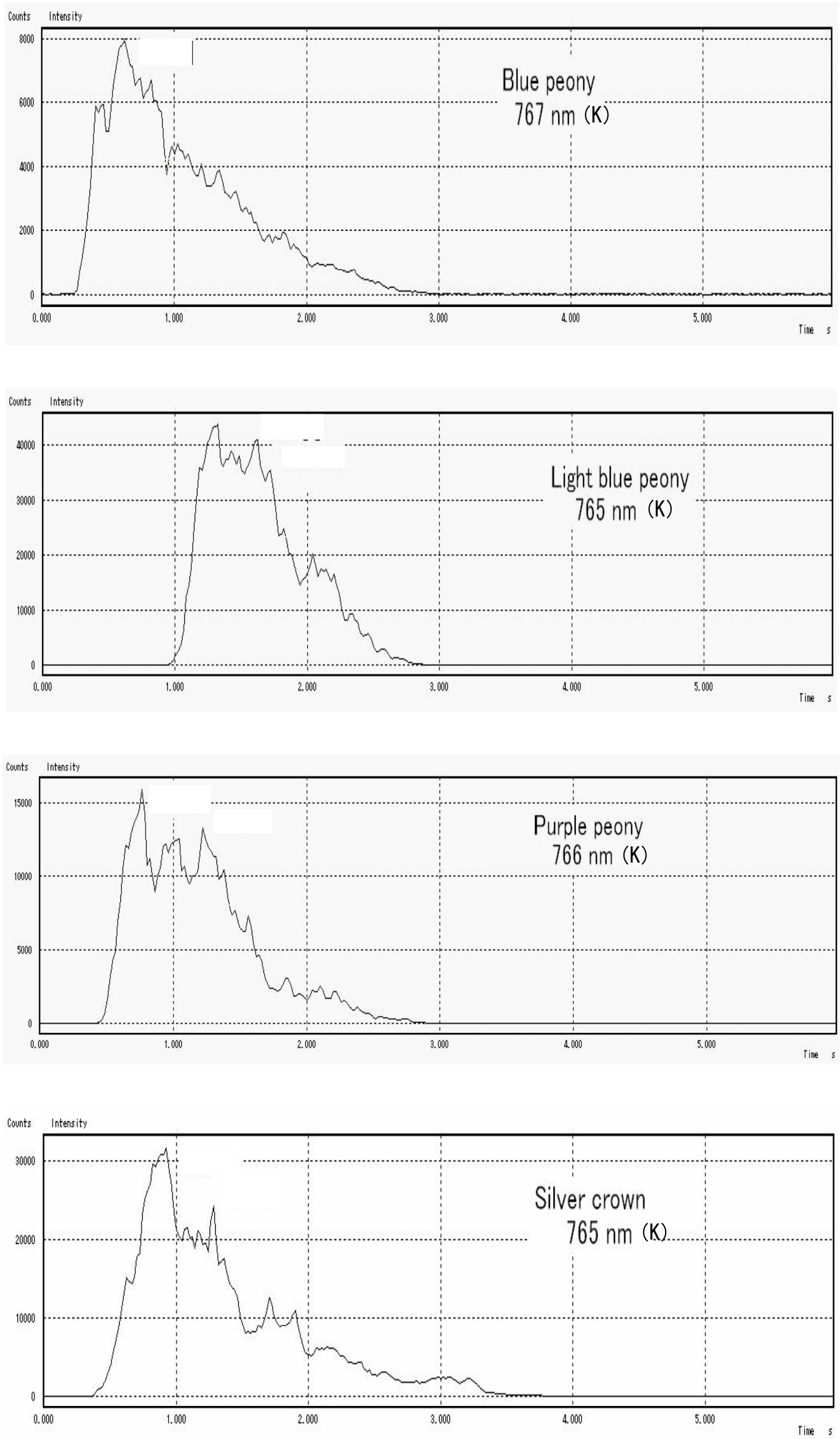


Figure 3 continued. *Peak intensity profiles of emission spectra.*

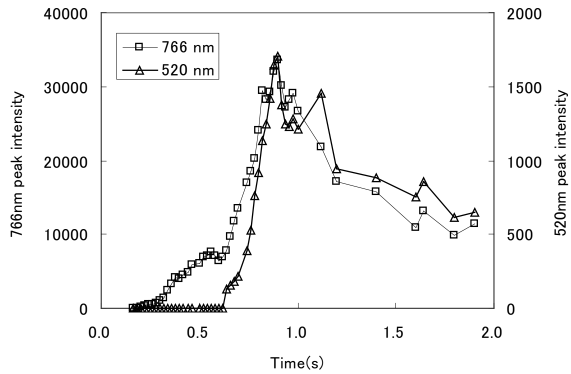
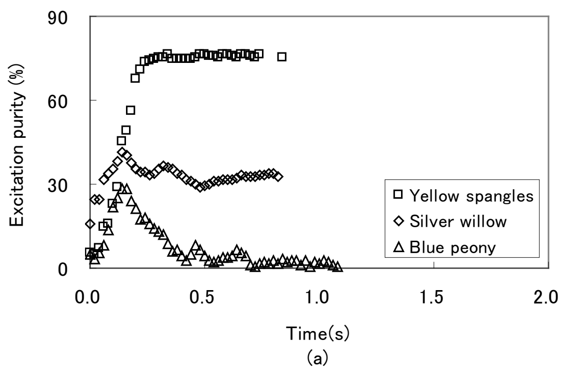


Figure 4. *Plot of 766 nm and 520 nm peak intensities vs. time for a green peony star.*



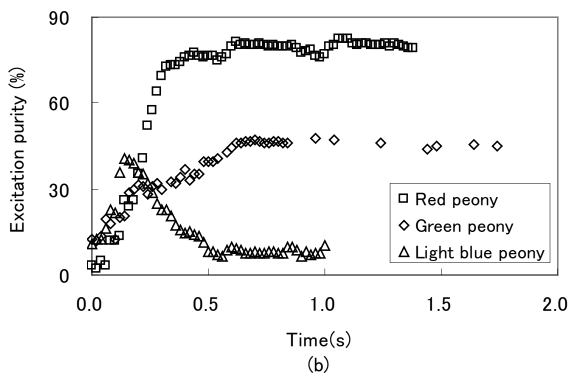


Figure 5. *Plot of excitation purity vs. time.*

purity corresponds to the flame spreading over the surface of the prime showing that the purity increases with the luminescence intensity of the incandescent emission.

Burning time against type and diameter of stars

The burning time is one of important properties of firework stars. The shape of a fire flower of burning stars depends on the speed of ejection from the shell and the burning time of the stars. The stationary and moving burning times of stars were measured previously using a high-speed video camera.[5,6]

In this work, the stationary burning time of stars was measured using a PMA-11C5966-31 spectrometer. The results are listed and shown in Table 1 and Figure 6, respectively.

Though there is some scatter in the measured burning time, the burning time increases with increasing star diameter. If the linear burning rate of a star is assumed constant during the combustion, the burning time will be proportional to the diameter of the star. The average linear burning rate (r) can be estimated from the diameter (d) of a star and the burning time (t) using the following equation:

$$r = d/t$$

Average linear burning rates from this work are listed in Table 4.

Effect of filter

The intensities of emission of the stars used in this work were so strong that the most intense peaks of incandescence were often saturated. Two filters were used to avoid this difficulty. The performance of the filters was determined by comparing the peak intensities with and without filters. The

Table 3. *Statistical values of excitation purity for some stars.*

Star	Number of tests (n)	Mean (%)	Standard deviation (%)	Relative standard deviation
Green peony	6	48	4.9	0.10
Yellow spangles	6	79	2.5	0.03
Silver peony	4	33	9.5	0.29
Silver crown	6	27	8.0	0.29
Red peony	5	82	1.5	0.02

Table 4. *Average linear burning rate of stars.*

Star	Average burning rate/mm s^{-1}
Silver peony	14.3
Yellow spangles	7.7
Light blue peony	7.1
Pink peony	6.7
Purple peony	6.1
Red peony	5.3
Green peony	5.1
Silver crown	5
Silver willow	3.6

results are listed in Table 5. The attenuations achieved by combining two filters (($D = 1.0$) + ($D = 0.5$)) were 0.05 and higher. The attenuation of the green, yellow, silver, red, blue and light blue peonies was about 0.05. The other stars showed higher attenuation. At the moment, the reason for the difference is not clear and a subject for study in the future.

The change in the excitation purity by the filters is not so large for the green, yellow, red, pink, light blue and purple peonies, but large for the silver peony, blue peony and silver crown.

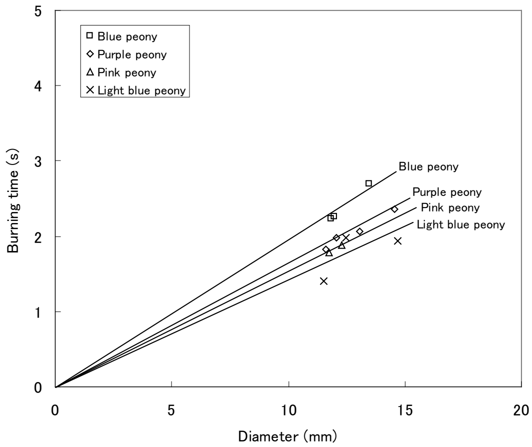
Conclusions

The burning time, peak spectral intensity and excitation purity of burning commercial firework stars were measured using a spectrometer. The burning time varied with the type and diameter of the stars. The intensity of the specific peaks of the emission spectrum changed with time, and showed fluctuation probably owing to the fluctuating burning at the star surface.

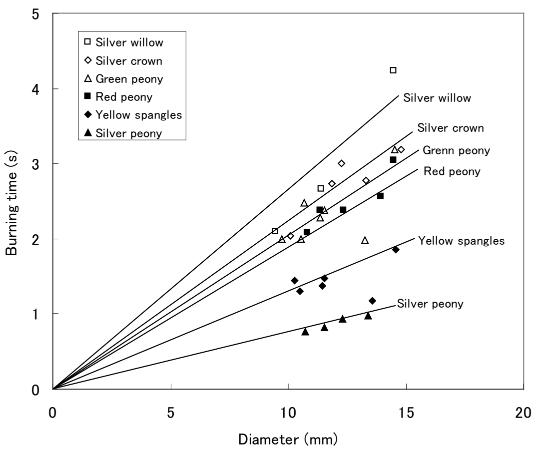
The effect of the prime coating the star surface was shown in the intensity profile of the K and visible color peaks. The 766 nm K peak appeared in the first stage of the star burning corresponding to the combustion of the prime and the visible colored flame peak appeared later. The excitation

Table 5. *Peak intensities and excitation purities with and without filters for no. 3 stars.*

Star	λ/nm	Filter		Attenuation	Purity no/(1.0+0.5)
		None	1.0+0.5		
Green peony	518	32386	1363	0.042	45/53
	586	16919	845	0.050	
Yellow spangles	588	60350	3087	0.051	78/81
Silver peony	586	81376	4437	0.055	34/19
Red peony	664	118810	6656	0.056	81/84
Pink peony	586	3381	784	0.232	56/62
	630	11425	2838	0.248	
	638	11827	3049	0.258	
	667	28136	7108	0.253	
Blue peony	448	4147	285	0.069	1.2/4.5
	586	4348	260	0.060	
	766	149964	7832	0.050	
Light blue peony	446	27811	1418	0.051	19/16
	518	60379	3334	0.055	
	586	39367	2020	0.051	
Purple peony	631	10249	1363	0.133	43/44
	637	10033	1399	0.139	
	656	20906	2599	0.124	
	668	26608	3331	0.125	
	766	129456	10800	0.083	
Silver crown	586	20025	1391	0.069	40/21



(a)



(b)

Figure 6. *Plot of burning time vs. diameter of stars.*

purity of the star flame was higher in the yellow and red stars and lower in the silver stars. The relative standard deviation of the excitation purity was smaller in the yellow and red stars and larger in the silver stars. The effect of the filter changed with the type of stars.

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