

An Experimental Comparison of Selected Blue Flame Pyrotechnics

Dominykas Juknelevicius,^[a] Arno Hahma,^[a, b] Rutger Webb,^[c] Thomas M. Klapötke,^{*,[d]} and Arunas Ramanavicius^[a]

In memory to Dr. Bernard E. Douda

Abstract: In this research, 10 different pyrotechnic blue flame compositions were designed and compared. Chromaticity and luminosity parameters of the flame were measured using Ocean Optics JAZ-ULM VIS-Spectrometer equip-

ped with a cosine corrector. Color saturation, luminous intensity, specific luminous intensity, oxygen balance, burn rate, actual and theoretical maximum density, color coordinates (X, Y) are presented and discussed.

Keywords: Blue flare pyrotechnic · Copper chloride · Fireworks · Pyrotechnics · Illuminating flame

1 Introduction

A blue pyrotechnic flame color with high saturation or color purity (p_e), is one of the biggest challenges in pyrotechnics. While several suitable pyrotechnic compositions can be formulated with a reasonable effort for red, green, and yellow at high color purity and high luminous intensity (I_v), there are much fewer examples for blue illuminants available.

An excellent historic perspective on colored flame development is given in the thesis by *Sturman* [1]. He discusses the evolution of colored flames throughout the years, even from the period before the introduction of potassium chlorate into pyrotechnic compositions.

One of the first spectroscopic investigations that reported an analysis of blue flames was carried out by *Barrow & Caldin* [2]. They identified the emitting species as CuCl. Interestingly, mercury(I) chloride was used in these compositions as chlorine source.

Blue flames have been studied by several researchers and academics over the past decades. *Douda* has contributed significantly to the understanding of colored flames [3].

A systematic study of compositions, which are generating blue flames, was performed by *Shimizu* [4]. He utilized a self-made spectrograph containing a sample holder, a 0.04 mm slit, water prisms, lenses, and a photographic plate.

The proliferation of relatively low-cost spectrometers has been helpful for studying pyrotechnic flames. Pyrotechnic compositions are assessed in a “static” way, whereby the sample is burned, and the smoke is removed well enough to ensure a free line of sight to the sample. In 2003, *Brian Ingram* investigated the spectra of red, green, and blue pyrotechnic flames [5]. *Meyerriecks* and *Kosanke* studied the principal emitters in colored flames [6]. They

utilized solutions of various chemicals in combination with a nebulizer and an oxygen/propane/acetylene flame.

Several papers have been published about the desired emitter in pyrotechnic flames comprising a copper and a chlorine source [7]. *Dolata* speculated about the formation of a trimer of CuCl [8]. This was quickly followed by *Sturman*, who provided disproof of this hypothesis [9].

While static measurements are a sound and reproducible method for characterizing compositions, such measurements are not representative of the true environment in most applications. In actual use, pyrotechnic compositions

[a] D. Juknelevicius, A. Hahma, A. Ramanavicius
Department of physical chemistry Faculty of Chemistry
Vilnius University
Naugarduko st. 24, 03225, Vilnius, Lithuania
*e-mail: dominykas24@gmail.com

[b] A. Hahma
Diehl defence GmbH
Fischbachstraße 16, D-90552 Röthenbach an der Pegnitz, Germany
*e-mail: arno.hahma@diehl-defence.com

[c] R. Webb
NanoTechnas, Faculty of Chemistry
Vilnius University
*e-mail: rutgerwebb@gmail.com

[d] T. M. Klapötke
Department of Chemistry, Ludwig-Maximilian University of Munich
Butenandtstr. 5–13 (D), 81377 Munich, Germany
Fax: +49 (0)89-2180 77492
*e-mail: tmk@cup.uni-muenchen.de

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have to burn at various airspeeds. Consequently, mixing of ambient air will alter the flame stoichiometry and temperature. Furthermore, pyrotechnic stars may extinguish in flight [10, 11].

Few publications are available about "Round Robin trials" of spectral color measurements. Douda has reviewed 81 mm mortar flares as test objects [12].

Recent efforts have been made to identify alternatives to well-known copper-chlorine based systems. Some of us have published work on copper(I) bromide and compared it to copper(I) chloride [13]. The work includes the 1931 CIE coordinates for the isolated spectra of CuCl and CuBr. In the same year, Koch compared all four copper(I)halides [14]. He provided values of the 1931 CIE coordinates, as well as the dominant wavelength and color purity. He has concluded that copper(I) bromide provided good efficiency, even outperforming the classical copper(I)chloride. The copper(I) fluoride and the copper(I) iodide based system were found to be inferior to the bromide and chloride. The formulations tested by Koch were optimized for the formation of K_2SO_4 , to enable spectral measurements minimizing the interference of potassium.

Recently, the flame color of pyrotechnics containing metallic indium has been investigated. These results do not indicate that indium is, even from a purely technical point of view, a viable alternative emitter [15].

The goal of the present study was to compare the p_c and dominant wavelength of the best-known blue flame (star) compositions. An overview of pyrotechnic blue illuminants helps to select the best compounds for achieving the highest color saturation in a practical application.

2 Experimental Section

The following chemicals were used: Ammonium perchlorate, potassium perchlorate (d50 10 μ m), potassium chlorate (20 μ m) were all reagent grade, 5-AT from Sigma 02312TE, Hexamine B. Kraft 16932.5600, Stearic acid Merck 673, Paraffin wax ($C_{31}H_{64}$) Te-ce-wax H994 powder, Dextrin Roth 6777.1, Lactose monohydrate Roth 8921.1, Redgum ($C_6H_6O_{2.6}$) Ilotulitus Oy, Hyrylä, Finland, MgAl MX 077 Eckart Werke in Fürth, Sulfur JT Baker 0335 USP, PVDC Solvin 910 Solvay, Belgium, ground to 20 μ m, CP ($C_{10}H_{15}Cl_7$) Leuna-tenside GmbH CP135, Chlorinated rubber ($C_{10}H_{11}Cl_7$) S10 Covestro 00549421, HCB old sample, PVC Solvin 374MB, Cu powder electrolytic Ecka 71, Eckart Werke, basic copper carbonate ($Cu_2(CO_3)(OH)_2$ malachite) Sigma 20.789-6, Copper benzoate was synthesized from potassium benzoate and a soluble copper salt, Paris green ($Cu_4As_6C_4H_6O_8$ was synthesized from arsenic trioxide and copper acetate, CuOCl (synthesized), CuO Omikron GmbH 10-0334.

The compositions were prepared by mixing the dry ingredients and passing through a 40-mesh sieve. The homogeneous powder mixture was moistened with a solvent to activate the particular binder. The compositions #1, #6 were moistened with dichloromethane to dissolve the CP. Com-

position #2 was moistened with n-Hexane to dissolve the paraffin and all the others, except composition #3, were moistened with water to dissolve dextrin. Composition #3 was used without any binder.

The compositions were pressed to nominally 10 g pellets having a nominal diameter of 16,80 mm at 115 MPa pressure. Five pellets were pressed for each composition and measured with a digital caliper at ± 0.01 mm precision. The dimensions were used for calculating the densities and percentage of the TMD as well as the burn rates of each pellet.

The spectra were recorded with Ocean Optics JAZ-ULM VIS-Spectrometer equipped with a cosinus corrector. The spectrometer was run in its high-speed absolute calibration mode and placed 0.5 meters apart from the pellet. The cosinus corrector has an angle view of ± 60 degrees and could record the entire flame despite the short distance needed because of the low light output of blue illuminants. The resulting spectra were recorded already calibrated. The calibration was verified against a NIST traceable calibration lamp. The verification confirmed the factory calibration is correct and precise. Hence, no correction of the raw data was necessary.

The combustion times were recorded using a Casio Exilim EX-FH20 camera at 210 Hz frame rate and VGA-resolution. This camera has a considerably higher time resolution and precision than the spectrometer, which often had to be run at 500 ms integration. In addition, the video recordings remain as a reference for each pellet. The video recordings were automatically edited to include one second before and after the combustion. The combustion times were defined as the beginning and the end of the sum curve exceeding a threshold level set at 10% of the maximum intensity of the pellet.

All pellets were measured in a free state without wind. The pellets were lacquered with 30% solution of Synthesia E37 nitrocellulose in ethanol: diethyl ether 1:2 to make them burn only at the end face (cigarette burning). This way, the burn time reflects the true burn rate, when divided by the pellet length. We did, however, encounter some problems with the lacquer film peeling off due to poor adhesion. This may have caused some loss of the composition, however, the losses were less than 0.2 g for each pellet and were ignored.

3 Results and Discussion

Pyrotechnic blue illuminant formulations were gathered from different sources. Ten of them having the highest color saturation based on the information in the literature were selected for this experiment. All the selected blue flame compositions contain four main components: an oxidizer, a fuel, a copper source, and a chlorine source. The variety of chemical components was another criterion for the compositions being as different one from another as possi-

ble. This can provide more information about the best compositions and the best chemical components for generating blue flames with high color saturation. The selected compositions are presented in Table 1 and their combustion characteristics are given in Table 2.

50 g of each composition (except 25 g of No. 5) were prepared. Five 10 g pellets (16.80 mm diameter) were pressed out of each composition. The values presented in Table 2 are an average over 5 parallel measurements. It must be noted that even though pellets were ignited from the top, not all of them burned evenly (cigarette burning). For compositions 5–10, that were based on potassium chlorate and perchlorate, the surface flame propagation was more pronounced than that to the depth of the pellet. For that reason, the recorded burn rate data presented in Table 2 is not as precise as it was expected.

The first composition #1 burned with a uniform tall flame, especially during the first seconds. It was one of the very few compositions passing the 50% p_e threshold and had dominant wavelength (DW) of $\lambda = 445$ nm, which is the lowest of all 10 compositions. This composition also possesses the highest I_v and L_{sp} values among all ammonium perchlorate (AP) based compositions tested in this study.

Composition #2 was different from #1 due to wax and stearic acid as fuels. Occasionally, large yellow spots appeared in the blue flame envelope due to soot formation. This can be addressed to the largest oxygen deficit resulting in a reduced p_e . The burn rate was also the lowest among the ten compositions studied.

Composition #3 was unique because of its high nitrogen content, which was achieved by using 5-aminotetrazole (5-AT) as the main fuel. The poor fuel properties of this compound resulted in a composition, which could not sustain combustion on its own. The heat feedback from the flame wasn't sufficient enough to sustain combustion. However, the composition could be burned by holding a glowing sparkler wire on the burning surface. It should be noted that this composition is a derivative from the original presented by Naud [17].

Composition #4 has the fewest number of components with AP as an oxidizer and chlorine source, copper(II) benzoate serves as a fuel and a copper source. This nearly oxygen-balanced composition ($\Omega = -5.4$) passed the 50% p_e threshold while its I_v and L_{sp} values remained on the average level.

Composition #5 was unique due to the use of copper acetoarsenite. An interesting note is stated by Shimizu

Table 1. Experimental compositions: chemicals, ratios, sources.

No.	Source	Composition & ratio	Ratio	Comments
1	Hahma	AP/Cu/CR/Hexamine/CP	62/14/4/10/10	Optimized for maximum $([HCl + Cu]/[CuO])$ formation
2	McGriffen ¹⁶	AP/Cu/Stearic acid/Paraffin	74/11/11/4	Ashless blue flare
3	Naud ¹⁷	AP/5-AT/BCC	47.5/47.5/5	N-rich blue
4	Dumont ^{18,19*}	AP/Copper benzoate/Dex	79/17.5/3.5	Classic AP/Cu benzoate blue
5	Hardt ²⁰	KC/Paris green/Stearic acid/HCB/Dex	62/21/8/4/5	Copper acetoarsenite containing
6	Ofca ²¹	KC/CuOCl/Lactose/CP/Dex	65/13/13/5/4	Chlorate-lactose blue
7	Veline ²²	KP/CuO/Red Gum/CR/MgAl/Dex	53/14/9/14/6/4	Firework star with MgAl
8	Stanbridge ²³	KP/CuO/HCB/S/Dex	39/37/6.5/15/2.5	Chinese blue for small pellets
9	Naud ²⁴	KP/CuO/PVC/Hex/Red Gum/Dex	61/17/10/6/3/3	Naud Ref. blue
10	Pihko**	KP/CuO/Hexamine/CR	62/13/10/15	Perchlorate-Hexamine blue

Private communication: *Modification by Hahma (2012), ** Petri Pihko (1988)

Table 2. Experimental results: Oxygen balance (Ω), Burn time, average pellet length, burn rate, TMD - theoretical maximum density TMD % (indicates the fraction of measured density divided by TMD), I_v , L_{sp} , and color coordinates are presented. The mass of all pellets was in the range 9.5–11.7 g, except composition #5, which was limited to 4.8–5 g for each pellet. The white point was set at $x = 1/3$, $y = 1/3$.

No.	Ω [%]	T [s]	L [mm]	BR [mm·s ⁻¹]	TMD [g·cm ⁻³]	TMD [%]	I_v [cd]	\pm	L_{sp} [cd·s·g ⁻¹]	\pm	p_e [%]	DW [nm]	CIE x	CIE y	
1	-20.2	17.5	23.2	1.3	1.98	96%	91	6.6	162	12.1	51.6	± 1.2	453.7	0.240	0.173
2	-26.3	42.5	26.0	0.6	2.01	85%	22	2.5	94	4.1	30.4	± 4.1	556.2	0.328	0.251
3	-15.1	27.5	32.7	1.2	1.75	83%	10	2.3	26	3.2	38.1	± 1	432.8	0.269	0.210
4	-5.4	12.5	26.0	2.1	1.75	95%	79	18.3	98	2.5	52.0	± 1.6	463.2	0.233	0.179
5	-12.7	9.0	11.3	1.3	2.17	90%	58	0.8	107	4.3	45.3	± 1.9	469.6	0.240	0.208
6	3.7	8.0	23.5	3.0	2.18	86%	46	3.2	37	1.8	28.6	± 3.4	462.8	0.278	0.250
7	-12.8	11.6	24.7	2.1	2.16	83%	388	27.6	454	22.9	29.8	± 2	464.1	0.276	0.246
8	-3.2	6.9	19.8	2.9	3.02	73%	108	21.7	75	8.0	55.7	± 2.6	467.9	0.221	0.175
9	-5.5	8.0	22.9	2.9	2.31	82%	267	19.7	218	15.9	40.8	± 1.6	477.3	0.242	0.240
10	-5.8	11.1	23.1	2.1	2.30	82%	365	48.4	414	35.8	38.6	± 0.2	481.1	0.242	0.261

[10,25]: “copper acetoarsenite was used in Japan in almost all blue compositions in 1980’s as it produces a very pretty blue”. Nowadays, such compositions are nearly obsolete due to toxicity and environmental concerns. This composition produces more smoke compared to AP compositions (1–4) due to the presence of potassium, which creates solid particles.

Composition #6 had the highest oxygen balance of $\Omega = +3.7$. Chlorinated paraffin (CP) was difficult to mix evenly with other components the composition, which in addition to the positive Ω may have contributed to the lower performance of the composition. Also, a decrease in color saturation was observed during the combustion of each pellet.

Composition #7 is a popular one in fireworks. The metallic fuel MgAl increases the flame temperature and light output accordingly but results to reduced color saturation. With p_e of 30%, composition #7 had the highest I_v and L_{sp} of the tested compositions.

Composition #8 had the highest p_e of 55.7 wt.-%. This composition is unique for its high copper oxide content (37%), low potassium perchlorate content of 39 wt.-%, and the absence of an energetic fuel such as wax, hexamine, etc. Sulfur is used as the main fuel instead. Sulfur helps to scavenge potassium in the flame resulting in an increased chlorine concentration promoting CuCl emitter formation [10, 14]. HCB acts as a chlorine donor.

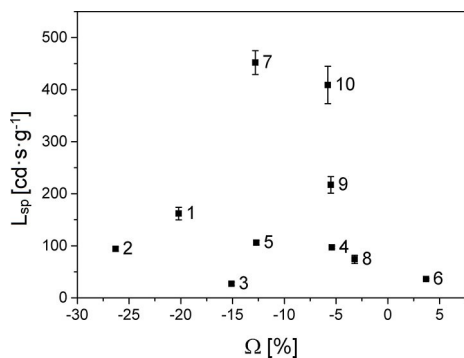


Figure 1. L_{sp} dependence on the oxygen balance.

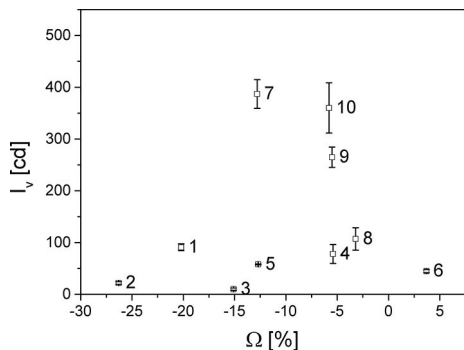


Figure 2. I_v dependence on the oxygen balance.

Composition #9 was chosen as a reference from Naud [24]. It was similar to composition #10 with a similar p_e of 41% It had only a slightly lower L_{sp} and I_v values.

Composition #10 was an efficient blue flame composition yielding p_e of 39% with L_{sp} of $414 \text{ cd s}^{-1} \text{ g}^{-1}$. It also produced the largest amounts of glowing slag on the test plate, where pellet was fixed.

The Ω of all compositions lies in the range of -26 to $+4\%$. The compositions at the extreme ends (#6 and #2) had low L_{sp} and I_v values, which may be related to the unbalanced system. Too low Ω results in soot formation, while too high Ω may cause the emitter species to be oxidized. The L_{sp} and I dependence on Ω are depicted in Figures 1 and 2.

The measured p_e lies in the range of 28–56% (Figure 3). The lowest p_e of $\sim 30\%$ was measured for compositions #2,6,7 and the highest exceeding 50% for compositions #1,4,8. Deep blue flame compositions with high p_e are usually observed to burn with a relatively dim flame compared to the bright ones having a low p_e . In this work, composition #8 flame was indeed the least luminous of the $KClO_4$ compositions (107 cd , $74 \text{ cd s}^{-1} \text{ g}^{-1}$). However, p_e reached 56% on average from 5 pellets, with one pellet reaching 57.7%. By observing the p_e vs time graphs some pellets of composition #8 peaked at 65% p_e during the first seconds of combustion before the p_e dropped to 50–57%. Possibly the reduction of the color purity is associated with slag formation on the burning surface. Composition #8 is designed to be used as small stars in fireworks. Therefore, it possibly did not deliver the best performance when burned as a 16 mm diameter, 10 g pellet.

The emission spectra were recorded for each of 10 compositions. The main focus of interest was to observe how the CuCl emissions compare to the CuOH, CuO, Na, and black body emissions. In figure 4 $KClO_3$ compositions 5,6 are compared. Composition #5 has a less pronounced grey body radiation and strong CuCl emissions at 400–470 nm, hence it possesses a higher color purity than composition #6. In Figure 5, the spectra of compositions #8 and #10 are compared. The CuOH emission from composition #10 appears much more pronounced compared to composition #8. This emission decreases the color purity of composition

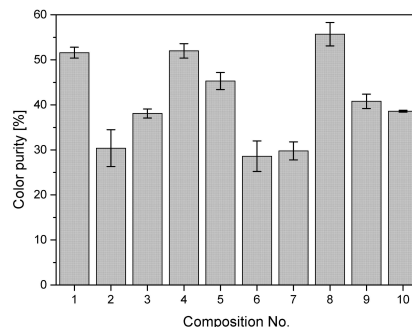


Figure 3. The distribution of p_e .

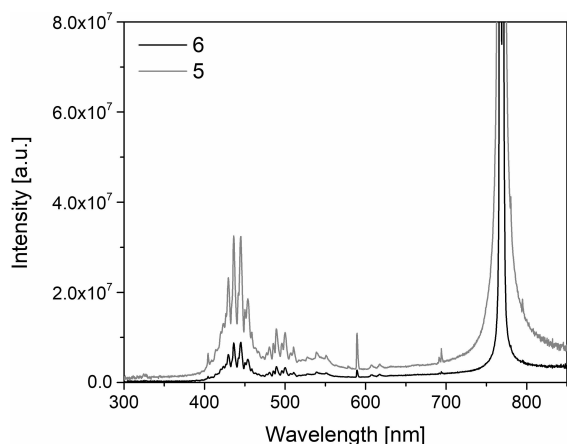


Figure 4. Emission spectra of compositions #5 and #6.

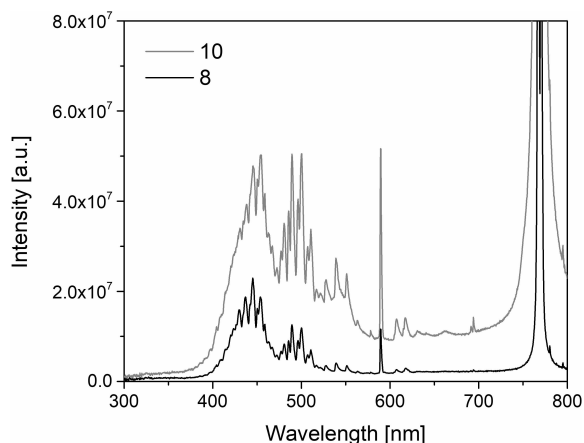


Figure 5. Emission spectra of the compositions #8 and #10.

#10, however the latter is much brighter burning. In Figure 6, the raw spectra of composition #6 are depicted at selected times. The intensity decreased as a function of time. This phenomenon was not observed with other compositions, at least not to such a strong extent. This effect may have resulted from both (i) the CP being unevenly distributed in the composition and (ii) also the slag formation.

Finally, the CIE x/y coordinates plotted in the CIE 1931 color diagram (Figure 7) are located in the blue and blueish-white region of the chromaticity diagram. Compositions #1,4,8 show a noticeable shift towards the blue region of the chromaticity diagram.

Video captures of the burning pellets are collected in Figure 8. From these photos, the flame size, shape, smoke, and slag formation can be estimated. The AP based compositions #1, 2, 3, 4, tend to burn with little smoke and no slag formation. The flame, especially in the beginning of the combustion, is tall and narrow. Later on, it evolves to a shape seen in Figure 8. The KClO_3 and KClO_4 compositions (#5 - #10) produce some slag and a significant amount of

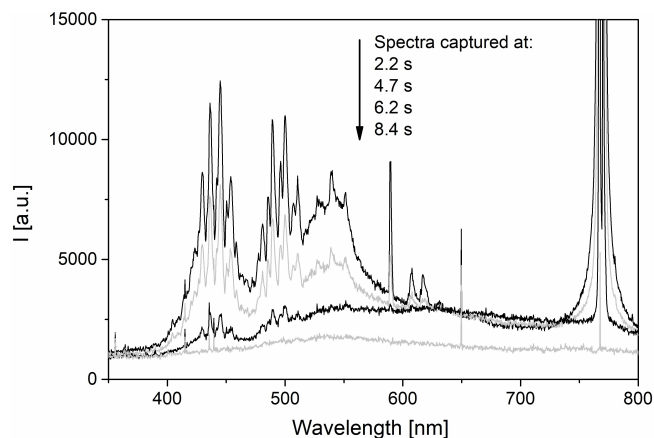


Figure 6. The composition #6 pellet flame's raw emission spectra recorded at 2.2, 4.7, 6.2, 8.4 s after ignition. A decrease in intensity is observed. The strongest emission in the blue region is observed after the ignition and the least intense emission is observed in the last seconds of combustion process.

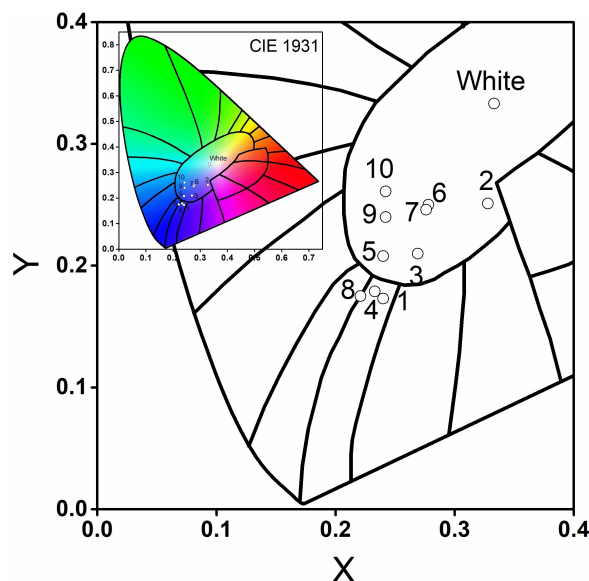


Figure 7. Zoomed in chromaticity diagram including the evaluated compositions with the full diagram in the upper left corner.

smoke. Some of them had higher I_v , L_{sp} , and p_e values than AP compositions, which are often considered superior blue flame compositions. The reason for the higher light output can be associated with smoke reflection during the measurements. If the smoke in the measurement chamber reflects some of the emitted light from the flame towards the spectrometer, the reflected light adds to the recorded data. This effect could not be completely avoided, because it is not possible to extract the smoke at the edge of the flame completely. On the other hand, the eye will also perceive this and the pyrotechnic composition will appear brighter

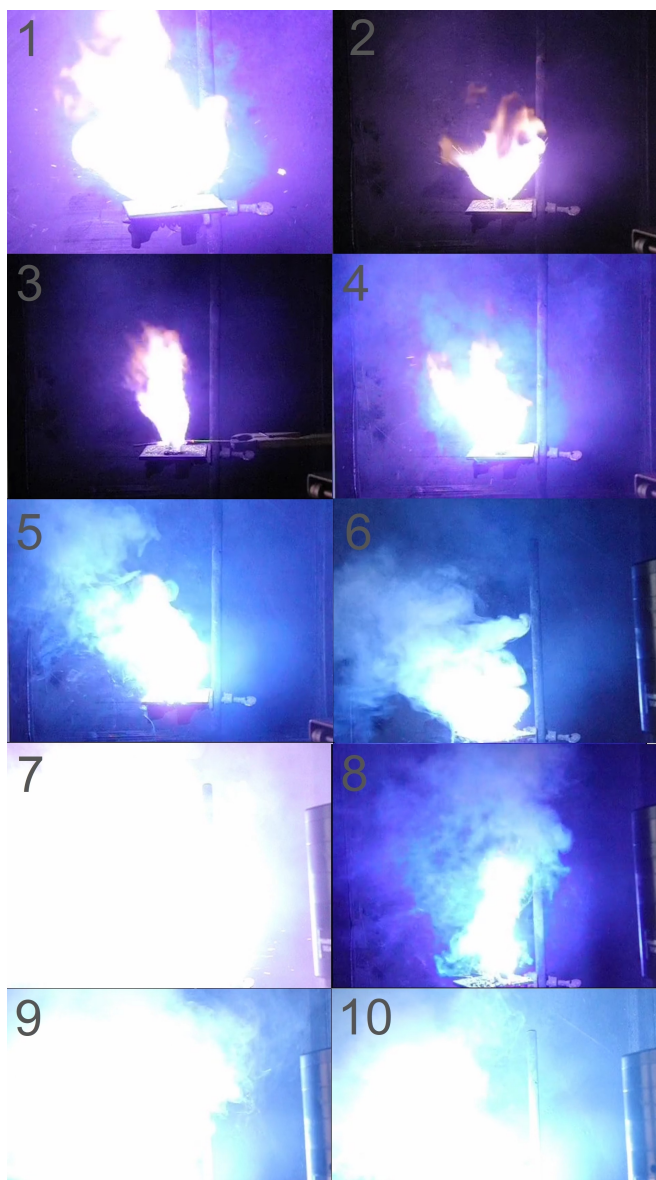


Figure 8. Video captures each burning composition.

than it is. In that sense, no error is produced, when the back reflection is ignored.

NASA CEA2 code was used to estimate the transient species present in the flames of tested compositions (supporting information). Only composition #5 was omitted, as there was no data on arsenic species. The adiabatic flame temperatures range from 1840 K for composition #8, to 2690 K for composition #10. Besides the high concentration of typical combustion products i.e. H_2O , CO_2 , CO , H_2 , N_2 substantial amount of HCl (0.15 mol-%) was produced for AP compositions #1–#4. Moreover, both KCl, HCl were present in KC and KP based compositions #6–#10. The target species for this experiment is CuCl. While most compositions had around 0.03–0.05 mole-% of CuCl produced, com-

position #8 had 0.07 mole-% of CuCl, which is in relation to the high performance of this composition described earlier. This can be associated with very high concentration (37 wt.-%) of CuO used in the compositions, that shifts the equilibrium towards CuCl formation.

4 Conclusions

Ten different blue pyrotechnic flame compositions were compared with the focus at the color saturation p_e . The measured values lie in the range of 28–58%. The highest average p_e of 55.7% (and up to 58% for a single pellet) was observed from composition #8 with 108 cd, 75 cd s g^{-1} . The peak $p_e = 65\%$ was registered during the first 1 to 3 seconds of combustion. The dominant wavelength of this composition was 468 nm.

KClO_4/S system used in composition #8 was found useful for producing a blue flame with high purity. It also proves that KOH continuum and $\text{K}_{(\text{g})}$ do not interfere significantly with desired CuCl emissions when sulfur is used as fuel.

Similar to composition #8, but brighter and more efficient was the AP based composition #1 with 91 cd and 162 cd s g^{-1} . The p_e was just slightly under 52% with a very low dominant wavelength of 453 nm.

Composition #7 lies at the other extreme with 388 cd, 454 cd s g^{-1} . This was the brightest composition but had a mere 29.8% saturation.

Composition #10 appeared to be well balanced, simple, and practical. Yielding a 365 cd bright flame and L_{sp} of 414 cd s g^{-1} it is almost as bright as composition #7. With a p_e of 38.6%, it has one of the best brightness to p_e ratios.

Hexamine was found to be a useful fuel in blue flame compositions. It has a high energy density of 30 MJ/kg being a good, energetic, non-metallic fuel burning with a non-sooty flame. Moreover, it is a synthetic compound that can be obtained in high purity.

5-AT containing composition #3 burned with significant difficulties. Most probably a fuel mixture of hexamine and 5-AT would have been more useful for this composition.

Even though highly regarded in older literature, Paris green composition did not surpass the other top compositions in color purity nor luminous intensity. Hence, Paris green and HCB (which can be easily replaced by a non-toxic chlorine source for composition #8) are discouraged from being used in practice.

This kind of experimental examination has not been done to date, wherein a rather diverse range of blue flame pyrotechnic compositions are examined quantitatively with a spectrometer. Very few researchers, in general, have reported CIE coordinates with p_e , I_v , L_{sp} values for blue flames. In addition, some old-fashioned ingredients were tested to demonstrate that arsenic-containing ingredients (Paris Green) offer no benefit in the color purity, and other, more novel, compositions show better performance.

Contributions

D.J.: Conceptualization, investigation, data analysis, writing – original draft. A.H.: Conceptualization, methodology, investigation, writing – review & editing, validation. R.W.: Writing - original draft (introduction part), writing – review & editing, validation. T.K.: Conceptualization, supervision, revision, funding acquisition. A.R.: Supervision, writing - review & editing, funding acquisition, submission.

Abbreviations

AP	ammonium perchlorate
5-AT	5-amino tetrazole
BCC	basic copper carbonate (malachite)
Dex	dextrin
HCB	hexachlorobenzene
CuOCl	copper oxychloride
CR	chlorinated rubber
CP	chlorinated paraffin
MgAl	powdered magnesium-aluminum 50/50 alloy
PVC	polyvinyl chloride
Ω	oxygen balance
I_v	light intensity (cd)
p_e	color saturation or purity
L_{sp}	specific luminous intensity (cd s / g)

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Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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