Special Materials in Pyrotechnics Part 2.[55] — Application of Cæsium and Rubidium Compounds in Pyrotechnics

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ABSTRACT

The application and thermochemical behavior of pyrotechnics based on rubidium and cæsium compounds are reviewed.

Keywords: alkali metal, cæsium, pyrotechnics, rubidium

Introduction

The application of the salts of sodium and potassium in pyrotechnics has a long tradition, but there is little information available on the application of the salts of the heavier alkali metals: rubidium (Rb) and cæsium (Cs). Although they are not used in civilian fireworks, compounds of these two elements do find application in technical and military pyrotechnics.

Application in Fireworks

a) Flame Color

The testing of both cæsium and rubidium salts for firework applications stems from the fact that alkali metals in general yield intense visible emission due to radiative transitions of the s^1-electrons. In addition, the names "cæsium" (derived from Latin "cæsius" ≡ sky blue) and "rubidium"(derived from Latin "rubidus" ≡ dark red) may imply that these elements impart sky blue and dark red color to flames. Unfortunately these incorrect suppositions have found their way into such fundamental pyrotechnic literature such as Douda's "Theory of Colored Flame Production"[1] and Ellern's *Military and Civilian Pyrotechnics.*[2] Actually the names originated with Kirchhoff and Bunsen, who discovered both elements in the spa of Bad Dürkheim, Germany, and they based the names on the sky-blue spectral lines of cæsium [455.5 and 459.3 nm] and the dark red spectral lines of rubidium [780.0 and 794.8 nm], respectively.[3a] Nevertheless, from the literature it is known that both elements when applied to the laboratory burner flame yield colors similar as potassium.[4] This is because the prominent color lines from which rubidium and cæsium were given their names are not the only features in the visible spectra of flames containing these elements. As well as its two deep red lines from the

$$5p^2P_{1/2, 3/2} \rightarrow 5s^2S_{1/2}$$
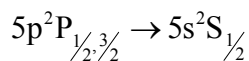
transition, the spectrum of rubidium has two blue-violet lines [421.6 and 420.2 nm] that come from the

$$6p^2P_{1/2, 3/2} \rightarrow 5s^2S_{1/2}$$
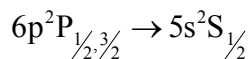
transition, which is analogous to the

$$7p^2P_{1/2, 3/2} \rightarrow 6s^2S_{1/2}$$
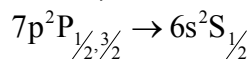
transition that produces the two sky blue lines in the spectrum of cæsium. The spectra of both elements also have lines in the red, orange, yellow and green regions that arise from electronic transitions between the excited states. In addition, the spectra also display continuous emissions, which have been attributed to several different processes described below:

The ease of ionization of both Rb and Cs gives rise to M^+ and e^- species yielding continuum radiation upon recombination (eq 1)

$$M^+ + e^- \rightarrow M + h \cdot \nu \qquad (1)$$

where M is Rb or Cs, h is Planck's constant [6.626×10^{-34} J·s^{-1}], and ν is the frequency [s^{-1}].

Furthermore, it is assumed that thermal line broadening of the minor series lines[5a] provides a quasi continuous spectrum, and finally the known reaction

$$M + OH \rightarrow M OH + h \cdot \nu \qquad (2)$$
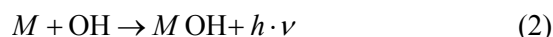
Table 1. Thermochemical Properties of Alkali Metal Sulfides and Sulfates.

	K_2S	K_2SO_4	Rb_2S	Rb_2SO_4	Cs_2S	Cs_2SO_4
CAS-Nr.	1312-73-8	7778-80-5	31083-74-6	7488-54-2	12214-16-3	10294-54-9
m_r[g·mol^{-1}]	110.263	174.261	203.002	267.00	297,877	361.875
mp [°C]	948	1069	425	1050	515	1005

where M is Rb or Cs and is also assumed to contribute to the continuous radiation.[6] Thus atomic emission of cæsium or rubidium with traditionally composed pyrotechnics cannot yield distinct colors other than whitish pink to violet. In terms of suppressing the minor line radiative transitions it is known that a cooler flame or generally speaking an excitation at lower temperature may help to suppress radiative transitions between higher quantum levels.[7] This is in accord with Boltzmann's equation (eq 3), which calls for a higher number of atoms in the excited state with rising temperature. That is,

$$\frac{N_e}{N_g} = \frac{P_e}{P_g} \cdot e^{\left(-\frac{E_e}{kT}\right)} \tag{3}$$

where N_e and N_g designate numbers of atoms in either excited or ground state, P_e and P_g designate statistical factors that are derived from the number of states energetically equivalent at a given quantum level, E_g designates the energy difference between the ground and excited state in Joules, k is Boltzmann's constant [$1.38 \cdot 10^{-23}$ J·K^{-1}], and T designates the absolute temperature in Kelvin. Indeed, references 5 and 8 both state that with rising flame temperature the metal spectra become more brilliant and display more lines than at lower temperatures.

Weingart[9] confirms that lowering the flame temperature may be a feasible approach to reduce unwanted radiative transitions. He proposes that simple blue colors can be made by dissolving cæsium carbonate in ethanol and then burning it with a cotton wick. Although this experiment yields a gray-blue colour at the side of the flame, the top of the flame, which is known to be the hottest part of the flame, still yields a whitish pink flame.[4]

Jennings-White[10] applied both nitrates and perchlorates of rubidium and cæsium in pyro-technic formulations. In these experiments the flame color was always white or whitish pink-violet. Especially in the case of formulations containing halogens, this is not surprising since rubidium chloride (RbCl) as well as cæsium chloride (CsCl) are known to produce emissions exclusively in the UV.[11a,b]

Hiskey,[12] in his reply to a comment by Webb, states that he tried CsCl as a replacement for copper(I) chloride (CuCl) in high nitrogen containing pyrotechnics, but had no luck in obtaining a blue color.

b) Glitter Formulations

Verifying different theoretical approaches for glitter stars, Jennings-White[13] tested both cæsium nitrate (CsNO$_3$) and rubidium nitrate (RbNO$_3$) as substitutes for potassium nitrate (KNO$_3$) in glitter formulations. Oglesby's theory,[14] whereby the glitter effect is based on the intermediate formation of potassium sulfide (K_2S) that would be subsequently oxidized in air to potassium sulfate (K_2SO_4), was confirmed. Table 1 gives the melting points of the sulfides and sulfates of potassium, cæsium and rubidium. In addition, cæsium sulfide is known to oxidize easily in air when ignited with a propane flame.[5b] Jennings-White describes glitters with either RbNO$_3$ or CsNO$_3$ as showing bright silver and impressive terminal delayed flash. As expected, these formulations did not impart any color to the flame.

Table 2 lists formulations with both nitrates and perchlorates of Rb and Cs tested by the author[4] and Jennings-White.[10,13] None of these formulations provided a distinct color.

No successful experiments have been reported in the literature to produce colored flames with either rubidium or cæsium salts.

Table 2. Formulations with Nitrates and Perchlorates of Rb and Cs.

	1	2	3	4	5	6	7	8	9	10	11
$RbNO_3$								~80		55	
$RbClO_4$									~80		
$CsNO_3$	90.93	81.1			70		~80				55
$CsClO_4$				83		80					
Cs_2SO_4			17								
$KClO_4$			8								
Guanidine nitrate			42								
Nitrocellulose	1.17		4								
Tetrachloro-phthalic acid anhydride $(C_6Cl_4)C_2O_3$			12								
Mg	7.90		17								
Mg / Al 50:50										10	10
Sb_2S_3										10	10
Si					20						
$CaSi_2$		18.9									
S_8										10	10
Charcoal										10	10
Dextrin										5	5
Shellac							~20	~20	~20		
Gum acca-roides											
Methaldehyde					10						
Hexamine				17							
$Zr(C_5H_7O_2)_4$ Zirconium(IV)-pentandionate						20					
Flame color	white	whitish blue	white	whitish pink	bluish cone	whitish pink	white	pale pink	?	bright silver	bright white
Effects		sparks	strobes	strobes	violet aureole					glitter	large glitter
Reference	4	4	4	4	4	4	10	10	10	13	13

Technical and Military Applications

Although of no practical use for fireworks, both rubidium and cæsium have been thoroughly investigated by technical researchers and have subsequently found application in military and technical pyrotechnics. Admittedly, rubidium compounds have found only very minor application, because there are no rubidium minerals and because rubidium compounds are available only as by-products of the extraction of lithium and cæsium.[3b] The interest in rubidium and cæsium is mainly due to their emissions in the far red (Rb) and the near infrared (Cs), and to the low ionization energy of both metals and the consequent ease of thermal electron emission, which gives rise to a number of interesting applications.

a) Devices Using Ionization of Cæsium and Rubidium

Ionization of chemical species in flames has long been known. As early as World War II German researchers, developing the A4 liquid propellant powered ballistic missile, found that the highly ionized plume (estimated ~10⁶ ions

1. Undistorted ray
2. Diffraction at underdense plasma
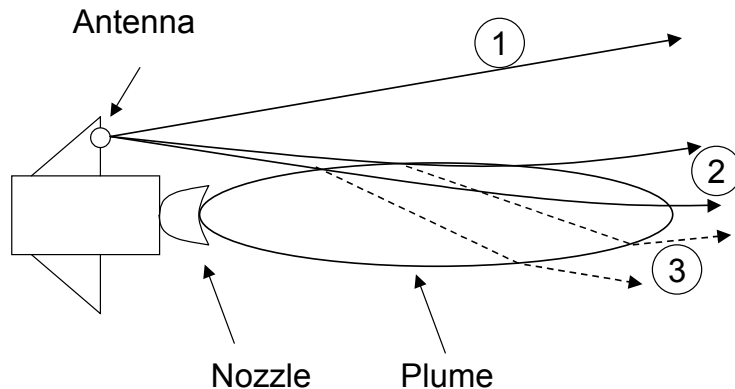3. Diffraction at overdense plasma

Figure 1. Antenna pattern in the wake of a missile with either an underdense or overdense plume.

per cubic centimeter) interfered severely with then applied 50 MHz radio guidance system.[15] In the 1950s to 1960s as missile development grew in the U.S. this problem was addressed by Balwanz.[16] He investigated the distortion of the antenna pattern of guided rockets from the effects of the plume (Figure 1).

This interaction between rocket plume and radio signals is due to thermal ionization of the main flame gas constituents and, in the case of composite propellants, due to thermoionic emission from either aluminum oxide and/or ionization of alkali metal impurities (Na, K, Cs) in the composite propellant. Flames possessing high electron densities may be considered as low temperature plasmas. The electrical properties of plasma may be described by the so-called plasma frequency ω_p.

$$\omega_p = \sqrt{\left(\frac{4\pi e^2 n_e}{m_e}\right)} \qquad (4)$$

where e denotes the charge of the electron, n_e denotes the electron density and m_e denotes the mass of the electron.

In the interaction of an electromagnetic wave and plasma, if the plasma frequency ω_p is much larger than the angular frequency ν of the incident wave, the plasma may be considered a good reflector to the wave and is thus designated as "overdense" (Figure 1). As soon as this effect was recognized, it was studied primarily with the aim of finding ways of reducing it as has been done, for example, by Sukhia[17] who investigated the antenna pattern distortion of towed aerial targets by the burning of IR tracking flares.

The ease of ionization of the heavy alkali metals such as rubidium and cæsium in flames was envisioned as being useful for certain technical and military applications.

Shidlovsky as early as 1964 refers to the work of Fagg and Friedman producing cæsium plasma by combustion of cæsium perchlorate ($CsClO_4$)/aluminum (Al) mixtures.[18] Fagg also investigated $CsNO_3$/Al pyrotechnic mixtures for producing cæsium plasma in upper atmosphere electron diffusion studies.[19] In this work the electron density of both stoichiometric $CsClO_4$ and $CsNO_3$/Al plasmas was measured by determination of the half-widths of the 546.7, 550.4, 563.8 and 566.4 nm Cs lines and was compared to thermochemical calculations.

Figures 2a and 2b give the molar fraction of electrons and temperature in flames produced by $CsClO_4$/Al and $CsNO_3$/Al mixtures, calculated for a pressure of 0.1 MPa. Figures 3a and 3b give the respective values for the rubidium systems.
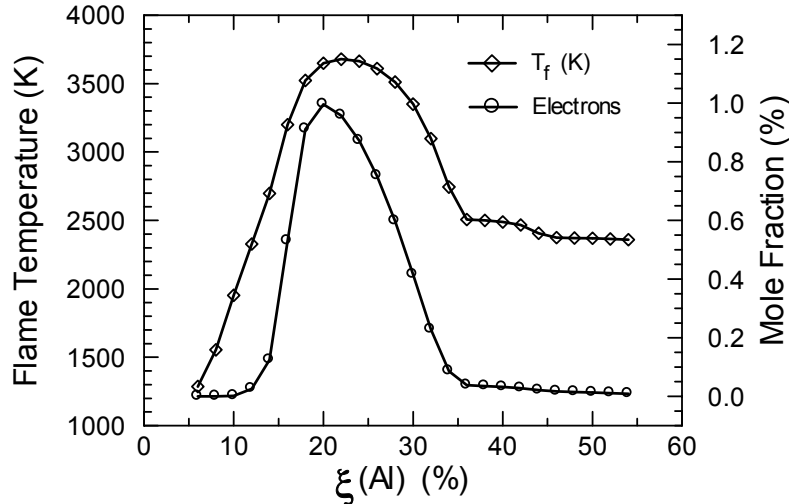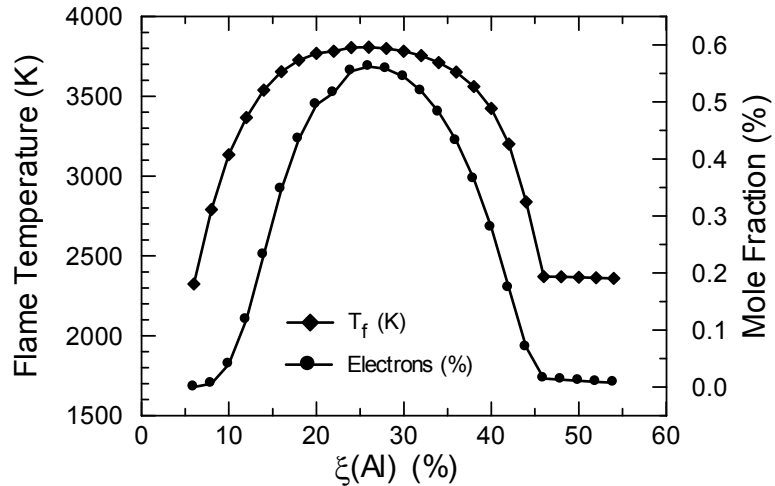
Figures 2a and 2b. The molar fraction of electrons as a function of ξ (Al) in $CsClO_4$/Al (upper) and $CsNO_3$/Al (lower) mixtures at 0.1 MPa pressure.[56]

It can be seen that within a given chemical system that the electron fraction is mainly a function of the temperature of the system. The Saha-Eggert equation[20] [equation 5] gives the degree of ionization x_i of a given gaseous system.

$$\frac{x_I^2}{1-x_I^2} = 2\frac{Z_i}{Z_a}\left(\frac{2\pi m_e}{h^3}\right)^{\frac{3}{2}} \cdot \frac{E_I^{\frac{5}{2}}}{2p} \cdot \left(\frac{kT}{E_I}\right)^{\frac{5}{2}} \exp-\left(\frac{E_I}{kT}\right) \quad (5)$$

In the case of alkali metals, the partition functions Z_i and Z_a for the ion and the atom are

1 and 2, respectively, thus simplifying the equation to give

$$\frac{x_i^2 P_M}{(1-x_i)} = \left(\frac{2\pi m_e}{h^2}\right)^{\frac{3}{2}} \cdot (kT)^{\frac{5}{2}} \exp-\left(\frac{E_i}{kT}\right) \quad (6)$$

where h is Planck's constant [6.62608×10^{-34} J·s], E_I denotes the ionization energy of both Rb (4.177 eV) and Cs (3.894 eV), m_e denotes the mass of the electron [9.10939×10^{-31} kg], $P_M = p_a + p_i$, where p_a denotes the partial pressure of the atoms and where p_i denotes partial pressure of the ions, k denotes Boltzmann's constant
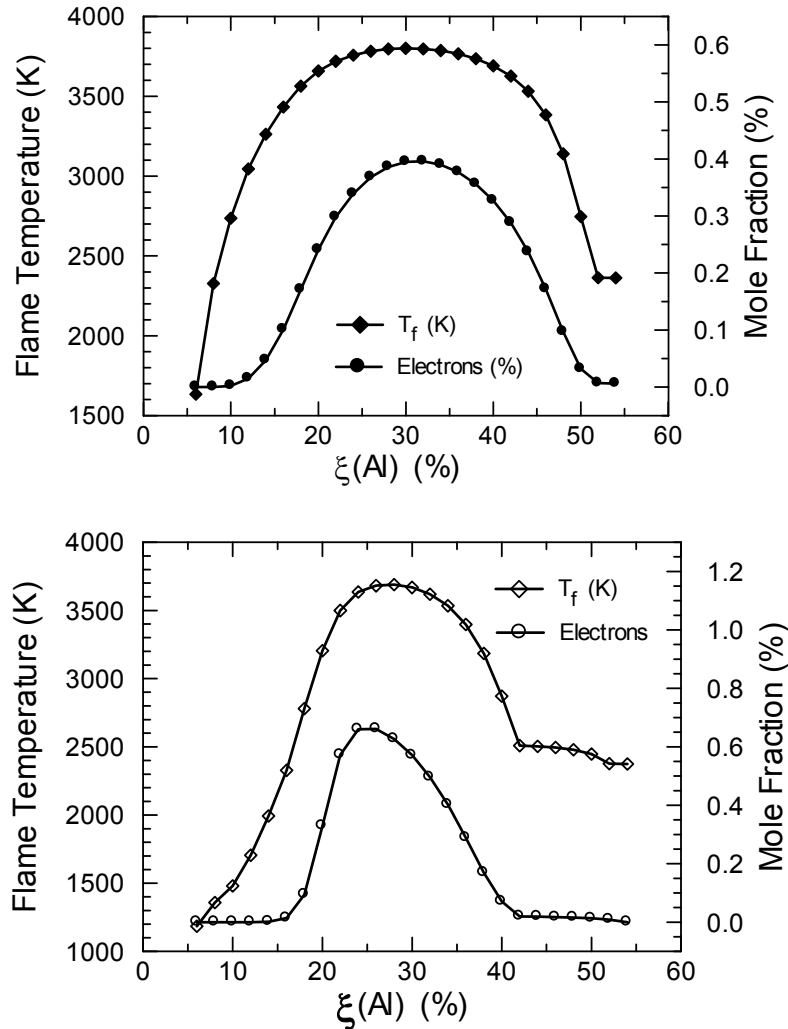
Figures 3a and 3b. The molar fraction of electrons as a function of ξ (Al) in RbClO₄/Al (upper) and RbNO₃/Al (lower) mixtures at 0.1 MPa pressure.[56]

$[1.38088 \times 10^{-23} \text{ J·K}^{-1}]$ and T denotes the absolute temperature of the system. Although T_f is higher for the CsClO₄/Al system (Figure 2a), the electron concentration is only about 50% of the CsNO₃/Al system (Figure 2b). This lower electron concentration is due to the formation of the Cl⁻ species, which scavenges the electrons in the case of the perchlorate system. In comparison, the rubidium systems, due to the higher ionization energy of Rb, yield lower electron concentrations but qualitatively show plots that are quite similar to the cæsium system.

Since cæsium plasmas have been considered as ideal working fluids for magnetohydrody-namic (MHD) electric power generation,[21] Flanagan[22] proposed to apply pyrotechnic compositions made of 65–75% dicæsium tetranitro-ethane [(CsC(NO₂)₂)₂], 15–20% energetic binder (e.g., Glycidyl Azide Polymer (GAP)), 15–20% metallic fuels (e.g., zirconium (Zr)) and ~5% CsNO₃ to generate a cæsium-containing plasma yielding electron densities of up to 2.25×10^{16} e⁻·cm⁻³. This composition looks quite similar to the system from Maček's older work[23] on energetics yielding high electron densities for seeding the upper atmosphere. Maček for this purpose applied stoichiometric compositions that were based on hexanitroethane (C₂N₆O₁₂), cæsium azide (CsN₃) and tetracyanoethylene

(C_6N_4). The equilibrium electron density was calculated as a function of $\xi(CsN_3)$ and was found to be maximum at the following stoichiometry:

$$5\ C_6N_4 + 3\ C_2N_6O_{12} + 2\ CsN_3$$
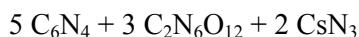
The composition was additionally investigated for thermal stability and was found to be stable when stored at a refrigerator temperature (+3 °C) and with exclusion of moisture. At ambient temperature and upon exposure to atmospheric moisture the composition would undergo rapid decomposition due to unstable hexanitroethane. Spontaneous ignition was found to occur between 100 and 110 °C. The stoichiometric mixture was calculated to burn at 3660 K. By the line-intensity-method, the combustion temperature was found be ~3520 K. The electron density was spectroscopically determined to be 6.5×10^{14} $e^-\cdot cm^{-3}$.

Similarly as in Maček's work, cæsium picrate ($CsO(C_6H_2N_3O_6)$) has been proposed as a monopropellant for MHD generators.[24]

Balwanz[25,26] investigated rocket exhaust plasmas based on combustion of stoichiometric $CsNO_3/Al$ and KNO_3/Al with the aim of understanding radio diffraction effects at either 10, 23.5, 35 or 70 MHz in rocket motor plumes. He showed that the electron concentration in plumes generated by $CsNO_3/Al$ payloads were depleted via electron attachment to aluminum oxide (Al_2O_3) particles, which is in accord with Maček's approach to exclude condensable species in a plasma generating mixture.

Another application using the ease of ionization of cæsium in pyrotechnic applications was given by Boettcher.[27] He proposed pyrotechnic compositions in the form of sheets that may be applied to the nose of missiles. Upon re-entry into the earth's atmosphere, these sheets would be ignited and would yield a high electron density. The sheets are composed of 19–38% cæsium chromate ($Cs_2Cr_2O_7$), 37–57% $CsNO_3$, 4–5% boron (B), 14–15% Al and ~5% binder. Other sheets in this invention comprise 50–82% $CsNO_3$, 14–47% Al, and 3–5% binder.

Chemical tracer experiments have been carried out recently to obtain insight into the distribution of rocket exhaust effluents in higher atmosphere regions from the standpoint of environmental chemistry.[28] Pyrotechnic payloads

based on $CsNO_3$, Titanium (Ti) and B were used in these experiments. The chemicals in loose powder form were disseminated along the flight path of a missile. There again $CsNO_3$ served as both an oxidizer for Ti and B as well as an electron source.

For similar purposes, a pyrotechnic seeding pellet based on boron, nitrates, and magnesium aluminum alloy mixed with an unspecified cæsium source, was disclosed in reference 29. This pellet is supposed to be ejected in the wake of re-entering spacecraft to generate electrons for analytical purposes. In addition, the inventor claims this device also to be useful as a radar 'spoof' to decoy incoming radar-guided missiles.

As a combined distress signal Cornia[30] proposed a device to provide free electrons for detection by radar. This device employs a complex mixture of magnesium, ammonium perchlorate, cæsium nitrate, hexachlorobenzene, Viton and fluoroacrylic binder. Alternatively, cæsium perchlorate is proposed as a source of free electrons. The design of the device, which resembles a solid propellant rocket motor, provides oscillating combustion due to a pressure rise in the combustion chamber and the large pressure exponent of the composition. This in turn gives rise to a strobe-like behavior of the signals, which, in addition to the free electrons, provides smoke, and emissions in the visible and infrared region.[31]

Cohen[32] studied the velocity of ions present in plasma generated by a stoichiometric $CsNO_3/Zr$ mixture ($3\ CsNO_3 + 2\ Zr$) ($T_f \sim 3300$ K) to provide insight into the electrical perturbations due to charge collection on the outside of spacecrafts. He found the ion velocity, mainly based on the Cs^+-ion, to be ~1148 $m\cdot s^{-1}$.

From Wilson's 1911 cloud chamber experiments, it is known that ions serve as condensation nuclei for aerosols. Today, ion-induced nucleation is investigated with the aim of understanding their mechanisms[33] as well as the environmental consequence (e.g., associated with release of easily ionizable material from nuclear power plants and nuclear reprocessing plants[34]). In view of this, Weber,[35] in 1982 developed a series of pyrotechnic smoke formulations based on either rubidium or cæsium compounds to be used in smoke pots, hand gre-

Table 3a. IR-Smoke Formulations with Rb and Cs Compounds.

Ingredient	1	1a	1b	2	2a	2b	3	3a	3b
NH_4ClO_4	34	31.48	31.48	—	—	—	—	—	—
ZnO	30	27.78	27.78	17.78	14.55	14.55	—	—	—
Polybutadiene	26	27.07	27.07	4.45	3.64	3.64	1.79	1.31	1.31
NH_4Cl	10	9.26	9.26	—	—	—	—	—	—
$CsNO_3$	—	7.41	—	—	18.18	—	—	26.32	—
$RbNO_3$	—	—	7.41	—	—	18.18	—	—	26.32
Al	—	—	—	6.67	5.46	5.46	13.39	9.87	9.87
Si	—	—	—	8.89	7.27	7.27	—	—	—
C_2Cl_6 (HC)	—	—	—	55.56	45.46	45.46	—	—	—
B	—	—	—	6.67	5.46	5.46	—	—	—
$P_{(red)}$	—	—	—	—	—	—	58.04	42.76	42.76
Fe_2O_3	—	—	—	—	—	—	13.39	9.87	9.87
Mg	—	—	—	—	—	—	13.39	9.87	9.87

nades, vehicle discharge grenades or projectiles. Weber succeeded in modifying a wide variety of existing visible smoke formulations to be used as effective screening agents in the thermal infrared (Tables 3a and 3b). The screening effectiveness of compositions was determined in field trials using three white plates heated to 40 °C. The plates where positioned in a row 10 m apart. The plates were observed with electro optical (EO) sensors at 0.6, 3.5 and 10.6 μm from a distance of 100 m. After determination of the undisturbed contrast value, the smoke charges were ignited ~50 m from both the plates and the EO equipment and the contrast was evaluated again. As a footnote to Table 3b, (++) refers to 95–100% change in contrast, (+) refers to 80–95% contrast change, (–) refers to

Table 3b. Performance of IR-Smoke Formulations.

Band	0.6 μm	3.5 μm	10 μm
1	+[(*)]	—	—
1a $CsNO_3$	++	+	+
1b $RbNO_3$	+	+	+
2	++	–	—
2a $CsNO_3$	++	++	++
2b $RbNO_3$	++	+	+
3	++	—	—
3a $CsNO_3$	++	++	++
3b $RbNO_3$	++	++	+

[(*)] for designation see text.

50–80% contrast change and (—) refers to change in contrast lower than 50%. In these smoke compositions, both Rb and Cs compounds become partially ionized and thus enhance the yield factor Y_f:

$$Y_f = \frac{m_s}{m_p} \qquad (7)$$

where m_s is the mass of smoke and m_p is the mass of the device, by enhancing the number of nuclei formed from the smoke reaction, as has been confirmed by measurements at ERDEC.[36]

Today the author's company (DIEHL Munitionssysteme GmbH & Co KG) manufactures smoke ammunition based on $CsNO_3$, $P_{(red)}$ and Zr. In the case of red phosphorus ($P_{(red)}$) as an aerosol source, reactions in the smoke plume cause extremely intense broadband infrared emissions that are the result of exothermic acid-base processes between cæsium hydroxide (CsOH) and phosphoric acid (H_3PO_4).[37] These broadband emissions result in lowered contrast and thus improved screening in both the 3–5 and 8–14 μm regions.

b) Devices Applying Infrared Emission

The $6p^2P_{1/2, 3/2} \rightarrow 6s^2S_{1/2}$ transition in cæsium produces two intense but invisible lines in the near infrared [894.3 and 852.1 nm]. This has led to the application of cæsium compounds in

Table 4. Emission Lines from MNO$_3$/Mg Flares where M is Rb or Cs. [40]

RbNO$_3$ nm	Series	CsNO$_3$ nm	Series
421.5	Main	455.5	Main
564.8	I. minor	459.3	Main
572.4	I. minor	566.4	I. minor
620.6	I. minor	584.5	I. minor
629.8	I. minor	601.0	I. minor
728.0	II. minor	621.3	I. minor
740.8	II. minor	621.7	I. minor
780.0	Main	697.3	I. minor
794.7	Main	698.3	I. minor
		722.8	Bergmann
		728.0	Bergmann
		801.5	Bergmann
		807.9	Bergmann
		852.1	Main
		876.1	I. minor
		894.3	Main

pyrotechnic compositions to provide convenient sources of near-infrared radiation for night vision devices. Perhaps surprisingly, in view of the attempts discussed previously to use rubidium to make red flames, the deep red rubidium lines have also been investigated for this purpose.

Night vision devices are widely used as electro-optical equipment for surveillance, searching and tracking in the near infrared (NIR) region of the electromagnetic spectrum. Since these devices, when operated in a passive manner, require only a small number of photons from both the visible and the near infrared, additional illumination is required under certain conditions such as the new moon and clouded skies at night. Although conventional illuminating rounds would achieve enhancement of illumination in the NIR, military tactics require concealed illumination. Thus NIR-illuminating sources must not be detectable in the visible range.

Lohkamp[38,39] was the first to address the problem and to propose a "Black Nite Flare", which combines both requirements such as illumination in the NIR as well as only slight emission in the visible. Lohkamp advises the use of flares based on either CsNO$_3$ or RbNO$_3$, hexamine, silicon and epoxy binder. This invention applies the strong emission behavior of both alkali metals in the NIR as has been measured by Douda.[40] Douda observed intense emission bands for CsNO$_3$ and RbNO$_3$ compositions (ξ(Mg) = 45% and 5% binder) as given in Table 4.

While yielding only 65 cd output in the visible range, Lohkamp's compositions (see Table 5) provide 14 W·sr^{-1} of radiation in the 0.7 to 1.0-µm range with a 40 mm cartridge flare.

Table 5. IR Compositions Based on KNO$_3$, RbNO$_3$ or CsNO$_3$.[38]

Ingredient	1	2	3
KNO$_3$	70	—	—
RbNO$_3$	—	60.8	—
CsNO$_3$	—	—	78.7
Si	10	10	16.3
C$_6$H$_{12}$N$_4$	16	23.2	—
Epoxy binder	4	6	5
λ_{max} [nm]	760	790	800–900

Based on this knowledge, Nielson and Dillehay of Thiokol, improved these formulations, proposing either CsNO$_3$/KNO$_3$ blends[41] and CsNO$_3$/ammonium nitrate (NH$_4$NO$_3$) or RbNO$_3$/NH$_4$NO$_3$ blends.[42] In addition, in recent years much work has been done by Nielson in adaptation of these compositions to varying manufacturing processes such as casting[43] and pressing.[44]

Similar to these applications are small arms tracers, which can be tracked in the NIR with a suitable enhanced night vision device for special operations. Although NIR tracer compositions are known to use barium peroxide (BaO$_2$) as the oxidizer, because the gaseous combustion product barium oxide (BaO) provides intense emissions in the 800 to 900 nm range,[45] Nielson proposes the use of blends of both CsNO$_3$ and BaO$_2$ together with fuels such as boron and silicon with vinyl acetate-alcohol resins as nonsooting binders.[46] In addition, both the rubidium and cæsium salts of bitetrazole amines (BTA) are proposed as burn rate modifiers in these compositions. Unfortunately no information on performance is given.

Another application of both $CsNO_3$ and $RbNO_3$ to improve concealment in military applications is their use as muzzle flash suppressants as has been stated in reference 47a.

Similarly Vanpee[48] has investigated the inhibition of afterburning in rocket exhaust plumes by cæsium carbonate (Cs_2CO_3) and rubidium carbonate (Rb_2CO_3). Vanpee assumed that this inhibition is greatly dependent on the intermediate formation of the gaseous hydroxide of the respective metals in the combustion zone, which may suppress visible oxidative reactions via radical scavenging.

c) Miscellaneous Uses and Work

Aside from the above applications making use of inherent features of both cæsium and rubidium such as infrared emission and ionization, a series of other unspecific applications of both metals in pyrotechnics have been reported.

Spector[49] advises the use of cæsium nitrate among other oxidizers together with unspecified fuels in a "non-toxic smoke generator". Since the primary combustion products in this case are fed through a scrubber filled with unspecified coolant liquid, the ions, which contribute to the smoke performance in Weber's invention, may not account for the principle given here.

Burkardt[50] has proposed pyrotechnically generated nuclei based on mixed alkali-transition metal iodides as ice-forming agent for weather modification. He proposes compositions based on silver iodate ($AgIO_3$)/MIO_3/NH_4NO_3 and plasticized nitrocellulose (NC) where M = Li, Na, K, Rb, or Cs with stoichiometries of (5–15% /0.1–30%/5–45%/50–55%). Interestingly, Rb-based compositions provide higher nuclei yield than Cs-based compositions, the latter being even worse than pure silver iodide-based compositions. Contrary to Weber's findings mentioned above, the nucleus formation in this invention does not relate to ionization. The active species in causing ice formation are the microscopically dispersed complex iodides formed upon combustion.

In reference 47b, the $CsClO_4$/Al compositions are described as being suitable for incendiary payloads. In view of the flame temperatures in Figure 2a this is quite feasible but would make incendiaries much more expensive compared to those based on less expensive potassium perchlorate.

An application based on solid-state effects is mentioned in reference 51. According to this, $CsNO_3$ should be an effective phase stabilizer for ammonium nitrate, which is known to undergo phase changes at –170, –16, 32.1, 84.2 and 125.2 °C.

In addition, $CsNO_3$ and $RbNO_3$ are known to provide a series of low-melting eutectics with some alkali nitrates. $RbNO_3$ forms a double salt with $LiNO_3$. The eutectic mixture, which is 35 mol-% $RbNO_3$ + 65 mol-% $LiNO_3 \cdot RbNO_3$, melts at 179.5 °C. With $NaNO_3$, the eutectic mixture (178.5 °C) is found at 55 mol-% $RbNO_3$. With KNO_3, the eutectic mixture (291 °C) is found at 70 mol-% $RbNO_3$. The eutectic mixture of $CsNO_3$/$LiNO_3$ is at 43 mol-% $CsNO_3$ and melts at 174 °C. With KNO_3, the eutectic mixture (200 °C) is found between 50 and 67 mol-% $CsNO_3$. All information is from references 5 and 8.

Dodecahydrododecaborate methanolate $Cs_2(B_{12}H_{12} \cdot CH_3OH)$ has been described as an additive to propellants and pyrotechnics to enhance ignition and burning rate.[52] In addition, $Cs_2(B_{12}H_{12} \cdot CH_3OH)$ is proposed as fuel for a gas generant composition.[53]

Recently Berger[54] investigated $CsClO_4$/Ti compositions as possible sources for near infrared radiation. Although $CsClO_4$ compositions, as mentioned above, would certainly give rise to cæsium chloride (CsCl) formation which exclusively radiates in the UV,[9b] titanium might serve as a chlorine scavenger due to the higher bond dissociation energy of titanium chloride (TiCl) (494 kJ·mol^{-1}) compared to CsCl (448 kJ·mol^{-1}) as has been discussed recently for the lithium perchlorate ($LiClO_4$)/Al system.[55] Because the authors did not present thermochemical calculation on the investigated stoichiometries, this has now been done in Figure 4 for adiabatic flame temperature, electron, cæsium, and cæsium chloride concentrations.[56]

Since there is no advantage of the $CsClO_4$/Ti compositions over existing "concealed" NIR payloads because of the intense visible emission of TiO as has been shown in reference 57,
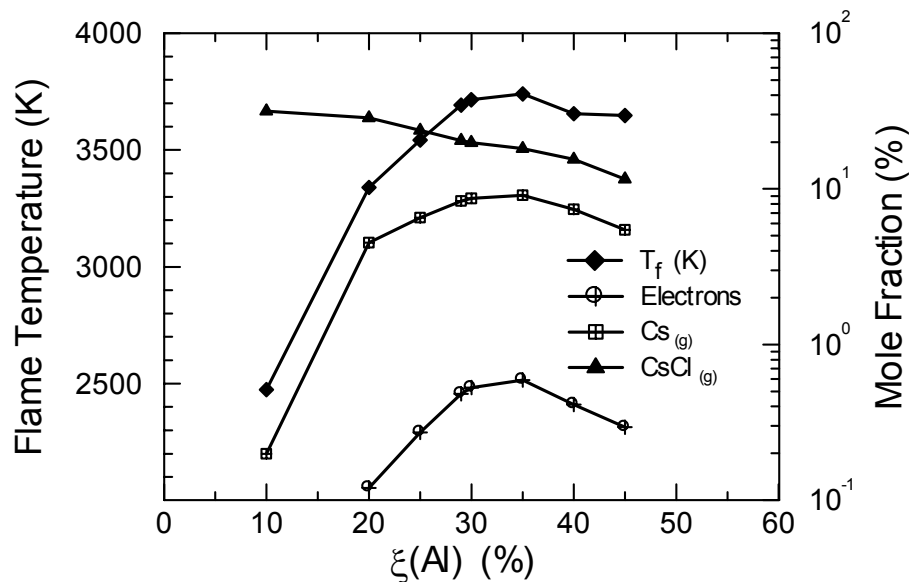
Figure 4. Molar fraction of electrons, Cs and CsCl as function of ξ(Ti) in CsClO₄/Ti at 0.1 MPa.

it seems that these payloads may be more suitable for tracking flares in either surface-to-air or anti-tank missiles.

Berger's work also provides details of the combustion mechanism, burn rate and heat of combustion as well as safety information on the CsClO₄/Ti mixtures. It was observed by differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetry (TGA) measurements that CsClO₄ forms an eutectic mixture with the primary decomposition product CsCl at ~400–500 °C wherein oxidation of the solid Ti particles occurs. The burn rate *u* increases almost linearly between ξ(Ti) 20 and 60% from 3 to 127 cm·s⁻¹, whereas the highest heat of combustion (5080 J·g⁻¹) is attained at ξ(Ti) of 40%. The highest sensitivity towards electrostatic discharges occurs at ξ(Ti) > 40% with ignition energy values ranging from 0.56 to 1 mJ. Sensitivity towards friction is highest at ξ(Ti) = 20% (19 J) and maximum friction sensitivity is found between ξ(Ti) = 35–50% (120 N) according to BAM procedures.

The spectra of several CsNO₃ and RbNO₃ / magnesium compositions in both the visible and NIR have been investigated by Douda.[40] Douda[58] also tested the effect of minor amounts of both RbNO₃ and CsNO₃ on the spectral per-

formance of lithium nitrate (LiNO₃)/Mg flare compositions.

Thermochemical Properties of Rb and Cs Compounds

To conclude this review, the following reliable data on the nitrate and perchlorate of Rb and Cs are summarized in Table 6. For comparison, values for the potassium salts are also included. In general, reaction mechanisms of the nitrates and perchlorates of Rb and Cs are identical to those of the corresponding potassium salt.

The thermochemical behavior of both Rb and Cs dinitramide (M-N(NO₂)₂) compounds, which in general can be seen as high density oxidizers, has been studied in detail by Cliff.[64,65] He could show, that the decomposition of the dinitramide salts occurs via metal nitrate and dinitrogen oxide formation according to equation 8.

$$M - N(NO_2)_2 \xrightarrow{\Delta} M\,NO_3 + N_2O$$

(8)
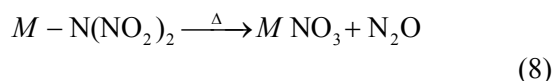
which is valid where M is Na, K, Rb, or Cs.

Table 6. Properties of K, Rb and Cs Nitrates and Perchlorates.

Parameter	Unit	KNO_3	$RbNO_3$	$CsNO_3$	$KClO_4$	$RbClO_4$	$CsClO_4$
CAS-Nr.		7757-79-1	13126-12-0	7789-18-6	7778-74-7	13510-42-4	13454-84-7
m_r	$g \cdot mol^{-1}$	101.103	147.473	194.91	138.549	184.918	232.356
mp	°C	333[62]	310[62]	414[62]	580[60]	597[60]	577[60]
crystal density	$g \cdot cm^{-3}$	2.109	3.11	3.685	2.52	2.8	3.327
phase transition	°C	128[61]	167[63]	160[61]	299[59]	280[59]	222[59]
type		rh→tg[#]	tg→c(*CsCl*)	h→c	rh→c	rh→c	rh→c
phase transition	°C	–	188[63]	–	–	–	–
type		–	*C(CsCl)*→h	–	–	–	–
phase transition	°C	–	278[63]	–	–	–	–
type		–	h→c(*NaCl*)	–	–	–	–
dec.p [*]	°C	533[62]	548[62]	584[62]	580[60]	597[60]	577[60]
ΔH_f^{298}	$kJ \cdot mol^{-1}$	494.63	495.05	505.97	432.79	437.19	434.72
Oxygen content	wt-%	39.56	27.12	20.52	46.19	34.61	27.54
Price index	KNO_3=1 ~0.5 \$/kg	1	~4000	70	5	~3000	150

[*] dec.p designates the temperature at which $p(O_2)$ over the molten salt equals 0.1 MPa.

[#] crystal lattices designations: rh = rhombic, tg = trigonal, c = cubic, CsCl, NaCl, h = hexagonal.

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