Journal of Pyrotechnics

Issue 18, Winter 2003

Direct Editorial Concerns and Subscription Requests to:

Journal of Pyrotechnics, Inc.
Bonnie Kosanke, Publisher
1775 Blair Road
Whitewater, CO 81527, USA
(970) 245-0692 (Voice and FAX)
email: bonnie@jpyro.com

CAUTION

The experimentation with, and the use of, pyrotechnic materials can be dangerous; it is felt to be important for the reader to be duly cautioned. Without the required training and experience no one should ever experiment with or use pyrotechnic materials. Also, the amount of information presented in this Journal is not a substitute for necessary training and experience.

A major effort has been undertaken to review all articles for correctness. However, it is possible that errors remain. It is the responsibility of the reader to verify any information herein before applying that information in situations where death, injury, or property damage could result.

Table of Contents

Issue 18 Winter 2003

If you want to receive titles and/or abstracts for future issues by email, send a note to bonnie@jpyro.com. You will then receive this information about two weeks before the next issue is ready to mail.

Publication Frequency

The *Journal of Pyrotechnics* appears approximately twice annually, typically in mid-summer and mid-winter.

Subscriptions

Anyone purchasing a copy of the Journal will be given the opportunity to receive future issues on an approval basis. Any issue not desired may be returned in good condition and nothing will be owed. So long as issues are paid for, future issues will automatically be sent. In the event that no future issues are desired, this arrangement can be terminated at any time by informing the publisher. Additional discounts are available for payment in advance for issues of the *Journal of Pyrotechnics*. Contact the publisher for more information.

Back issues of the Journal will be kept in print permanently as reference material.

Color Values and Spectra of the Principal Emitters in Colored Flames

W. Meyerriecks* and K. L. Kosanke†

*702 Leisure Avenue, Tampa, FL 33613, USA

†PyroLabs, Inc., 1775 Blair Rd, Whitewater, CO 81527, USA

ABSTRACT

The emission spectra of many of the more important emitters in pyrotechnic flames were collected. For this purpose solutions and suspensions of sodium, potassium, calcium, strontium, barium and copper salts were aspirated into a propane gas flame as the excitation source. Performing instrument corrections and using appropriate data reduction strategies allowed the isolation of the individual spectra. Among these are the monochlorides and monohydroxides of strontium, calcium, barium and copper. The CIE color coordinates of the principal emitters were calculated from the isolated spectra. In addition, a table of normalized band and line intensities was produced for each of the successfully isolated emitting species.

Keywords: flame spectra, flame color, color emitter, color coordinate, monochloride, monohydroxide, barium, calcium, copper, strontium

Introduction

The desire to produce improved flame color has been an enduring goal of pyrotechnists. However, over the last century, much of the effort in that quest has not been guided by accurate spectral information. Two pioneers in quantifying this work were T. Shimizu[1] and B. E. Douda.[2–4] Most recently, with the introduction of relatively inexpensive computer-based spectrometers,[5] hard-data rather than subjective impressions are being more widely used to guide developments. However, to date, the lack of relatively complete and reliable information on the spectra and CIE color coordinates of the individual colored flame emitters remains as an impediment.

Shimizu, in his textbook,[6] was probably the first to address the assignment of a series of the principal colored flame emitters to their position in the chromaticity diagram. Nevertheless he made essentially no attempt to determine the composite chromaticity values (color coordinates) for emitters having more than one narrow spectral line such as sodium. Instead he made a series of somewhat expressionistic intensity assignments for the respective lines, such as for potassium, and assignment of the bands of the monochlorides and monohalides of the alkaline earth metals and copper.

Several reference texts are available with tables of wavelengths and peak intensities for atomic and molecular visible-light emitters.[7–11] Unfortunately they are somewhat incomplete and even contradictory. The intended use of these tables seems to be primarily geared towards analytical chemistry—for identifying the probable emitting atom or molecule for a given line or band present in a spectrum. (An extensive table, compiled from some of these sources, and including the authors' current work, has been appended to this paper.) Further, very few of the reference texts include actual spectra for the various emitters, and when they do, instrumentation effects have not been removed. What is generally presented are the "raw readings" directly from the instrument, which often includes many different emitting species.

No reference text that the authors have seen has presented isolated spectra for the various individual colored flame emitters. Having such data would allow the investigator to more accurately determine the emitting species present in the spectra of test compositions, and thus be better able to rapidly advance one's research goals. Also, having spectra, where instrumentation effects have been removed, allows for the

computation of standard CIE chromaticity coordinates, which collectively quantify the gamut of all practical colors that may be obtained in fireworks and related pyrotechnics. The authors conducted a series of spectroscopic experiments, isolated the spectra, and produced chromaticity coordinates for some of the most abundant emitters in common pyrotechnic flames.

Visible Light Flame Spectrometer

The energy source used to produce the spectra was a gas burner of the type typically used in an atomic absorption spectrometer. This type burner was well suited to the needs of a flame spectrometer for this project. Its aspirator provided a ready mechanism to introduce solutions (and fine suspensions) into the flame. The burner produced a fairly narrow, but 4-inch (100-mm) long flame. This provided a long optical path for the spectrometer, thereby increasing its efficiency. The burner and a specially fabricated gas handling system facilitated the use of various and mixed gas sources. At the heart of the system was an Ocean Optics[5] CHEM2000 spectrometer installed into a slot in a computer. The spectrometer was connected to a chimney and ambient light shield using a large (400 micron) diameter optical fiber, terminating in an adjustable light-collecting lens. Figure 1 is an illustration of the overall flame spectrometer as configured for this project.

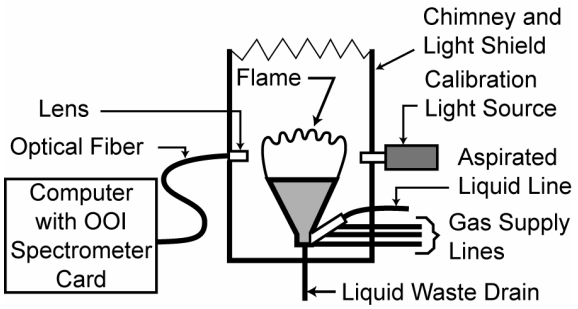


Figure 1. An illustration of the flame spectrometer as configured for this project.

Figure 2 is a diagram of the gas handling system for the spectrometer burner. In producing the spectra for this project, propane was the only fuel gas used. The supply of air (or air plus oxygen) to the flame was adjusted while aspirating pure water [or a mixture of carbon tetrachloride (CCl_4) and perchloroethylene (C_2Cl_4) for some of the measurements]. The relative proportion of oxidant supplied was only the amount sufficient to produce clean blue flame tips with a small distinct inner blue cone at the base of the flame. Figure 3 presents the spectrum of the flame and the classic C_2 (Swan) and CN band groups with perchloroethylene being aspirated into the flame. In each case, it is estimated that the temperature of the flame was approximately 1900 °C. This flame temperature is a little less than that of typical non-metal fueled pyrotechnic flames.[6] However, that is not thought to significantly alter the character of the isolated spectra reported in this article.

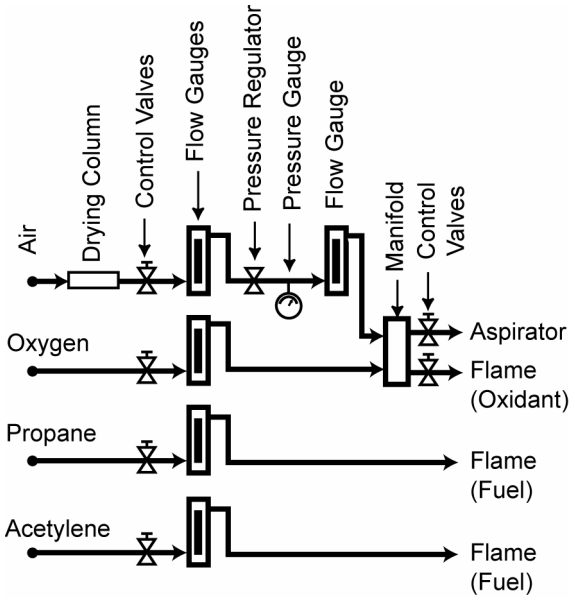


Figure 2. The diagram of the gas handling system for the spectrometer burner.

Instrument Calibration

The spectrometer was calibrated for wavelength by refining slightly the instrument calibration provided by the manufacturer. This was accomplished by fitting a simple linear equation to the actual and measured wavelengths for 15 sharp and clearly defined atomic peaks of the elements strontium, calcium, barium, potassium, sodium, mercury, and neon. This set of peaks ranged from 404.66 to 769.90 nm, which ade-

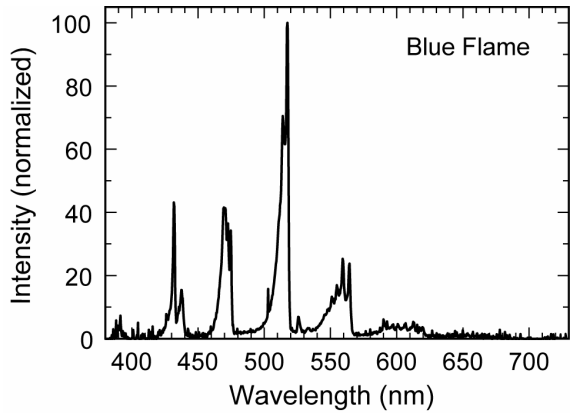


Figure 3. The spectrum of the blue flame with perchloroethylene aspirated into the flame.

quately covered the visible light range. (See Figure 4.) The goodness-of-fit parameter, r^2 (where unity is a perfect fit) was greater than 0.9999. The standard error was approximately 0.3 nm, which is less than the spectrometer's measured wavelength interval of approximately 0.4 nm. Note that the resolution of the spectrometer is 1.5 nm FWHM (full width half maximum).[5]

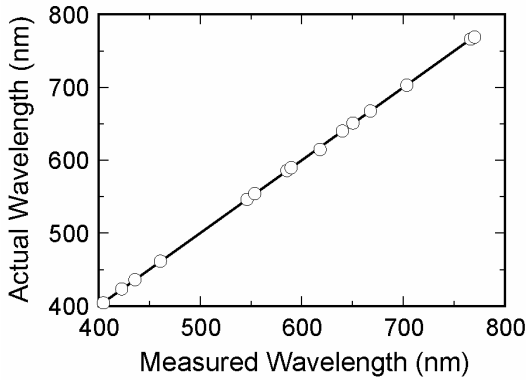


Figure 4. The wavelength calibration curve for the OOI spectrometer.

The optical path that a light ray follows into and through the spectrometer includes the collimating lens, optical fiber, a mirror, and a diffraction grating before it is dispersed onto a linear CCD (charge-coupled device) sensor that converts the light into an instrument-measurable electronic signal. Each of these components attenuates the incoming light by differing degrees at different wavelengths. The CHEM2000 spectrometer's diffraction grating exerts the greatest effect. It is designed with a blaze centered on approximately 555 nm[5]—the region of the spectrum where it is most efficient.

To calibrate for intensity, the spectrum of the supplied CHEM2000 tungsten-halogen bulb was taken, which is stated by the manufacturer to have a *color* temperature of 3100 K. A software application was developed to calculate the color temperature of tungsten at specified filament temperatures using Planck's Equation, and taking into account the temperature- and wavelength-dependent emissivity of tungsten. It was found that a *filament* temperature of 3035 K produced the closest match of chromaticity coordinates to those calculated for the stated *color* temperature of 3100 K. Both spectra—emissivity and measured—were normalized to unity at 555 nm, corresponding roughly with the blaze of the spectrometer. The corrected spectrum was then divided by the measured spectrum to obtain the required instrument intensity correction factors as a function of wavelength. Figure 5 presents the calibration curve that was required to remove the optical-path effects from the measured spectral data.

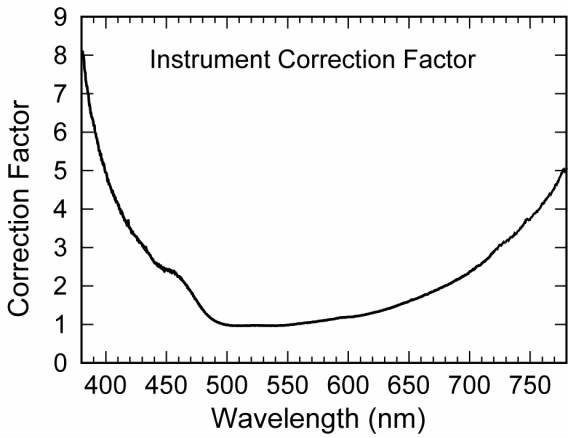


Figure 5. The intensity calibration curve for the OOI CHEM2000 spectrometer.

The CHEM2000 spectrometer is hardware programmable for sample integration time, ranging from as short as a few milliseconds to as long as two seconds per sample. The software acquisition mode used in this project is referred to as "Scope Mode"—a real-time function that

is similar to watching an oscilloscope. The output of this mode is raw spectrometer data, with intensities ranging from 0 to 4095. The CCD and 12-bit analog-to-digital converter both introduce noise into the measurements. It was found that integration times of less than approximately 250 ms resulted in a very good signal-to-noise ratio. For example, the spectrum of the blank (distilled water with no test emitter species present), integrated for 100 ms, accounted for an average intensity reading of 18 parts in 4096, or less than one-half of one percent of the full instrument range. Figure 6 shows the spectrum of a distilled water blank, where the peak at 589 nm is from a trace amount of sodium impurity. The spike at 502 nm is a single channel wide, and there is a lack of any identifiable source. It was concluded that it is probably a slightly noisy CCD detector well. The control software allows for samples to be repeatedly taken and averaged together, to effect additional noise reduction. This feature was utilized whenever the experimental setup permitted its usage.

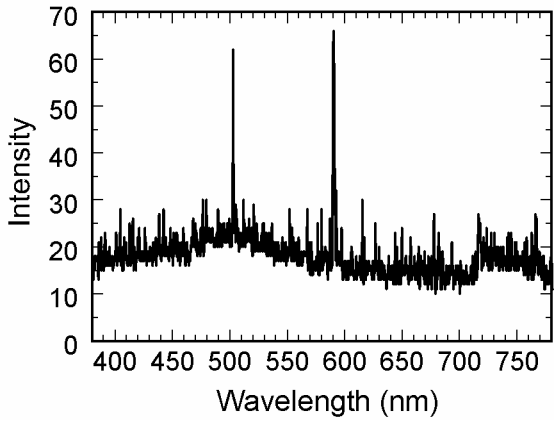


Figure 6. Spectrum produced using a blank sample (i.e., distilled water). (Intensity is in "scope units".)

Sample Preparation

The solutions for the production of the atomic spectra of sodium and potassium, and the molecular spectra of the monohydroxides of strontium, calcium, barium and copper were all prepared in the same way. These simply consisted of a set of fairly dilute aqueous solutions that were made using analytic reagent grade chemicals. The primary criteria used in selecting the chemicals were their availability in the chemical stocks of the laboratory and for their ability to produce the monohydroxide spectra, while avoiding halides or other species that might produce interferences. The nature of the aqueous solutions and their concentrations are reported in Table 1. These solutions were then aspirated into the propane-air flame of the spectrometer to produce the raw spectral data.

Table 1. Nature and Concentrations for Aqueous Solutions.

Chemical Name	Concentration (M)
Sodium hydroxide	0.10
Potassium nitrate	0.10
Strontium nitrate	0.20
Calcium nitrate	0.20
Barium hydroxide	0.10
Copper(II) nitrate	0.20

Samples for the production of the raw spectra for the monochlorides of strontium, calcium, barium and copper as the principal emitters were all made as suspensions. In each case, the appropriate metal chloride was thoroughly dried at 120 °C. While the sample was still hot, it was thoroughly crushed with a preheated mortar and pestle and transferred to a sealed flask for ball milling. The milling was accomplished using steel shot approximately 0.1 inch (2.5 mm) in diameter and using a sufficient amount of carbon tetrachloride (CCl_4) to cover the steel shot. The milling proceeded for 6 to 12 hours during which time the particle size was reduced to an average of approximately 1 micron (as determined using a scanning electron microscope). A magnet was used to remove any trace amount of iron that was worn from the steel shot during milling. To allow for successful aspiration of the suspensions into the spectrometer flame, they were diluted using perchloroethylene (C_2Cl_4) with a slight addition of the surfactant Neodol 23–5 (an alcohol ethoxylate, $C_{22}H_{46}O_6$). Further, during the time the suspensions were being aspirated into the flame, they were mechanically stirred. To produce a reasonably clean burning flame in the presence of the vaporized carbon tetrachloride and perchloroethylene, and to maintain a flame temperature estimated to be

approximately 1900 °C, the propane-air supply was augmented by supplying additional oxygen.

Data Reduction

After all of the spectra were taken and saved to the computer, they were initially processed to remove instrumentation effects. The method used was the same for all of the gathered spectra, and proceeded in the following order:

- The slight wavelength correction was applied.
- The spectrum was visually inspected:
  - For spectra where there were extensive regions that had no apparent features—flat and near-zero intensity (instrumentation noise only), such as that for potassium and sodium—an average value was taken of the background regions. This average value was then subtracted from the spectrum.
  - For spectra where most of the visible range included features of interest, the removal of the background was more complicated. The intensity values were divided by the integration time of the particular sample, thus converting the intensity from "scope units" into "scope-second units". A blank with a similar integration time was processed in the same manner, and the resulting spectrum was then subtracted from the spectrum being processed.
- The spectrum was rescaled using the instrument intensity correction factor.
- Any negative intensity values were set to zero.

Having removed instrumentation effects, peak identification and isolation was then performed. While the method varied as to the emitter, it was essentially a peak-by-peak subtraction of the individual species emissions from the composite spectrum, until only the sought-for emitter spectrum remained.

The various reference texts with tabulated wavelengths and emitting species materially helped in the identification of the individual peaks from the various emitting species, as did the few spectrographs found in some of the reference texts. Alkemade and Herrmann's work[12] proved valuable in identifying features in the spectra for calcium, barium, and the Swan series of the flame's blue cone. Another text,[13] edited by Mavrodineanu, proved very valuable for identifying copper and copper chloride spectra. Mavrodineanu and Boiteux's work[14] was useful for calcium, strontium, and barium. The work of Li et al.[15] helped in isolating gaseous barium oxide.

For complex spectra with numerous overlapping peaks of different emitters, the PeakFit software application[16] was utilized for peak isolation. Asymmetric peaks were placed at the correct wavelengths that correspond to the tabulated locations of the respective lines and bands for each probable emitter identified in the spectra. The individual peaks were interactively and iteratively adjusted for amplitude and asymmetry until the original spectrum was very closely approximated. In a few cases, an individual peak required a minor shift in wavelength from the tabulated value—on the order of 0.5 to 1.5 nm—to afford the best possible fit. The resulting sets of individual peaks were exported from the peak fitting application to a spreadsheet. The spreadsheet was used to isolate the approximated individual emitters.

Figure 7 illustrates this process: a small region of the measured spectrum of aqueous barium hydroxide is shown. Portions of four fitted peaks [three BaO peaks (centered at 481, 485, and

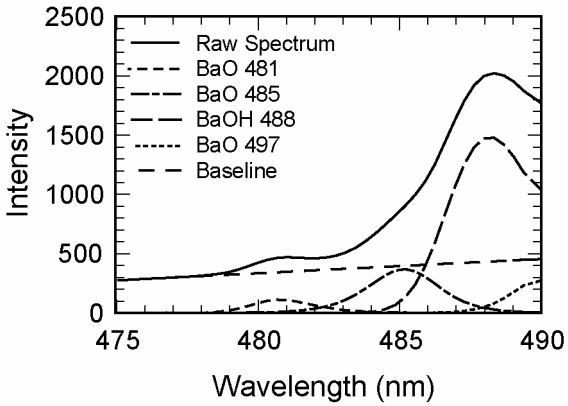


Figure 7. An example of the peak fitting method used to isolate the various contributions to a small portion of the raw barium monohydroxide spectrum.

497 nm) and BaOH centered at 488 nm] and a linear baseline are shown. Figure 8 presents the same portion of the spectrum, where the original spectrum has been plotted along with the fitted spectrum (offset by 100 intensity units for clarity). The close approximation of the peak fitting to the original spectrum is evident. Centered about the zero-point of the intensity axis is the residual spectrum, which has been scaled-up by a factor of five to improve its visibility in the graph.

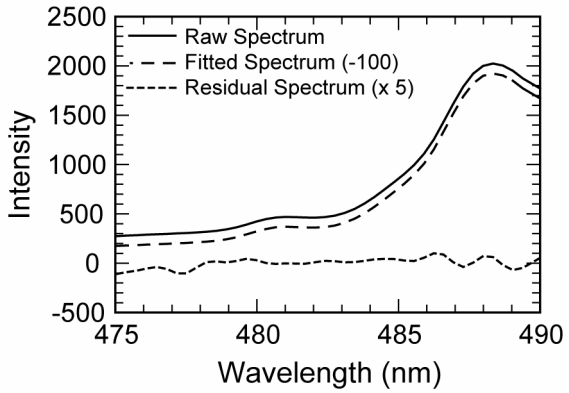


Figure 8. The result of peak isolation for the same spectral region shown in Figure 7. (Note that the fitted spectrum has been slightly offset from the raw spectrum, and the residual spectrum has been multiplied by 5.)

After the individual emitter spectra were isolated, a final "cleanup" was made to remove very minor amounts of unwanted, residual noise from the featureless regions of the graphs. This was followed by the calculation of 1931 CIE *xyz* chromaticity coordinates using the standard 2-degree, nanometer-increment, color matching functions.[17]

Each of the following spectra has been normalized such that the most intense peak equals 100 intensity units. Thus reported peak intensities can be compared within the same spectrum, but not between different spectra (emitter species).

The composite spectra and those of the various isolated components are presented and discussed below. (Table 2 later in this paper presents the normalized band and line intensities for the various emitting species.) Most of the spectra use a wavelength range of 380–730 nm, which represents the visible light range for most people. There are a few spectra that use the range 380–780 nm to allow inclusion of features in the near infrared. In the discussion of spectral features in the remainder of this text, wavelengths have been rounded to the nearest nanometer.

Sodium

The raw spectrum of the sodium hydroxide solution (NaOH in H_2O) had no measurable impurities. It is not shown, because it appeared fundamentally the same as the isolated spectrum of atomic sodium (Na), shown in Figure 9.

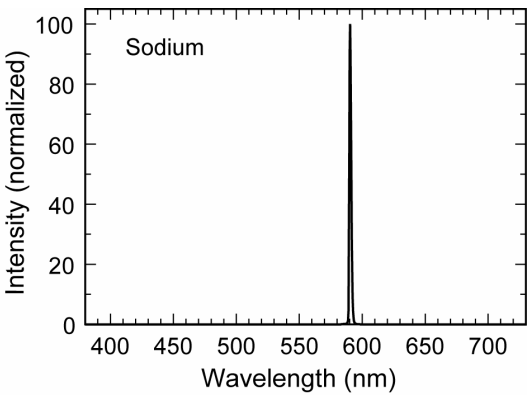


Figure 9. Spectrum of the isolated atomic sodium doublet peak.

Potassium

The spectrum of the potassium nitrate solution (KNO_3 in H_2O) included a small amount of sodium as an impurity, as is evidenced by the small peak at 589 nm in Figure 10a. (To make it easier to see, the region of the sodium impurity peak was multiplied by a factor of 10.) Also shown in this figure is the *very* small potassium peak at 404 nm, which has an intensity of 0.058. (To make it possible to see, the region of this peak has been multiplied by a factor of 100.) The sodium peak was removed to produce the pure atomic potassium (K) spectrum in Figure 10b. The peak at 767 nm is about 1700 times more intense than the one at 404 nm. This combination of peaks has a subtle but important effect on the perceived color of potassium flames, as described later. Note that these two graphs use a range of 380–780 nm.

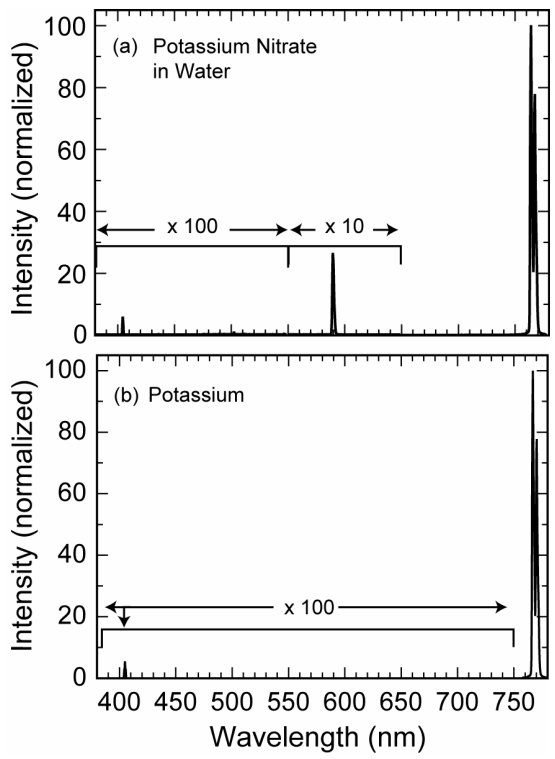
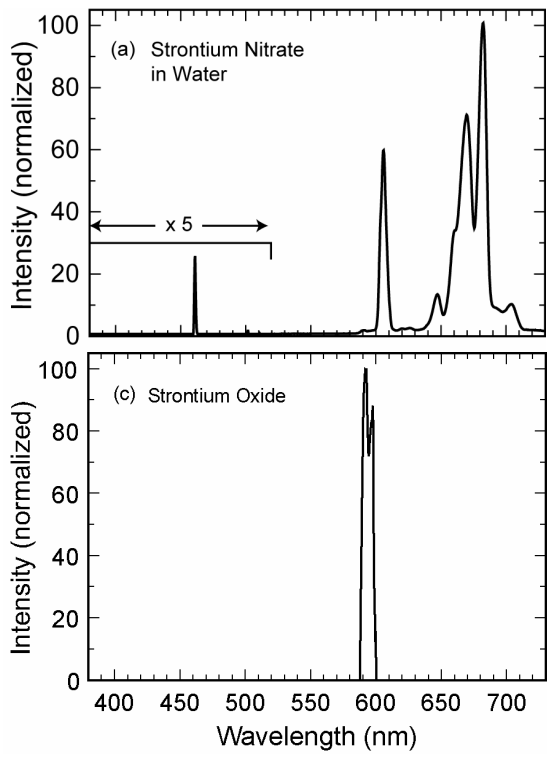


Figure 10. a) The spectrum of potassium nitrate dissolved in water. b) The isolated spectrum of atomic potassium.

Strontium

The spectrum for the strontium nitrate solution ($Sr(NO_3)$ in H_2O) is presented in Figure 11a. (Note: the region of the atomic strontium peak was multiplied by a factor of 5 to make it easier to see.) After subtracting the minor sodium peak, isolating the individual spectra was straightforward since very few of the observed peaks of atomic strontium (Sr), strontium oxide (SrO), and strontium monohydroxide (SrOH) overlap. The isolated atomic strontium (Sr) peak is shown in Figure 11b. The two main strontium oxide peaks at 595 and 597 nm are barely visible, and the weaker ones—reported to be less than 1/20 the amplitude of the two main peaks—are lost in the intense strontium monohydroxide peaks. For this reason, the graph for strontium oxide (Figure 11c) is necessarily incomplete, but it does provide a useful reference for the two most prominent peaks. The isolated strontium monohydroxide spectrum is presented in Figure 11d.

Figure 11 ***[below].*** *a) The spectrum of strontium nitrate dissolved in water. b) The isolated spectrum of atomic strontium. c) The spectrum of the two strontium oxide peaks that could be cleanly isolated. d) The isolated spectrum of strontium monohydroxide.*



The spectrum for the strontium chloride suspension ($SrCl_2$ in CCl_4) is presented in Figure 12a. Subtracted from this spectrum were rescaled atomic strontium, strontium oxide and strontium monohydroxide spectra, resulting in an isolated strontium monochloride (SrCl) spectrum as seen in Figure 12b. It is interesting to note that none of the references in the Table in the appendix mention the two low-intensity peaks centered at about 687 and 700 nm. The character of the peaks—their spacing and width—suggest that they are a continuation of the strontium monochloride spectrum and are included as such.

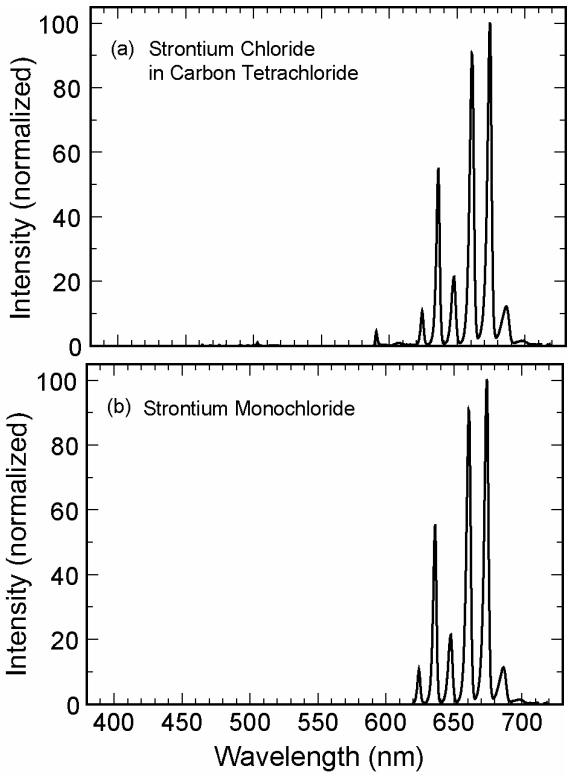


Figure 12. a) The spectrum of strontium chloride suspended in carbon tetrachloride. b) The isolated spectrum of strontium monochloride.

Calcium

The spectrum for the calcium nitrate solution ($Ca(NO_3)_2$ in H_2O) is presented in Figure 13a. The range for this figure extends from 380 to 780 nm so that the intense atomic potassium peaks, present as an impurity, may be clearly seen. After subtracting the potassium and sodium peaks, the isolation of the atomic calcium (Ca) peak (see Figure 13b) and the calcium monohydroxide (CaOH) peaks (see Figure 13c), were readily made. Unfortunately, calcium oxide (CaO) was not detected, and it cannot be reported in this work.

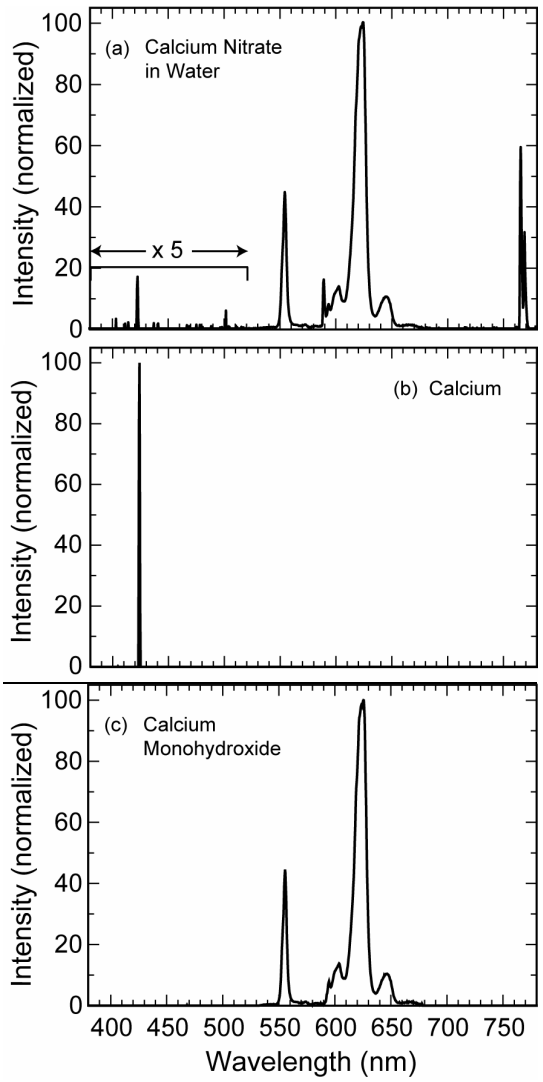


Figure 13. a) The spectrum of calcium nitrate dissolved in water. b) The isolated spectrum of atomic calcium. c) The isolated spectrum of calcium monohydroxide.

The spectrum for the calcium chloride suspension ($CaCl_2$ in C_2Cl_4) is presented in Figure 14a. Calcium monohydroxide was rescaled and subtracted from this spectrum, resulting in

the isolation of the calcium monochloride (CaCl) spectrum as seen in Figure 14b.

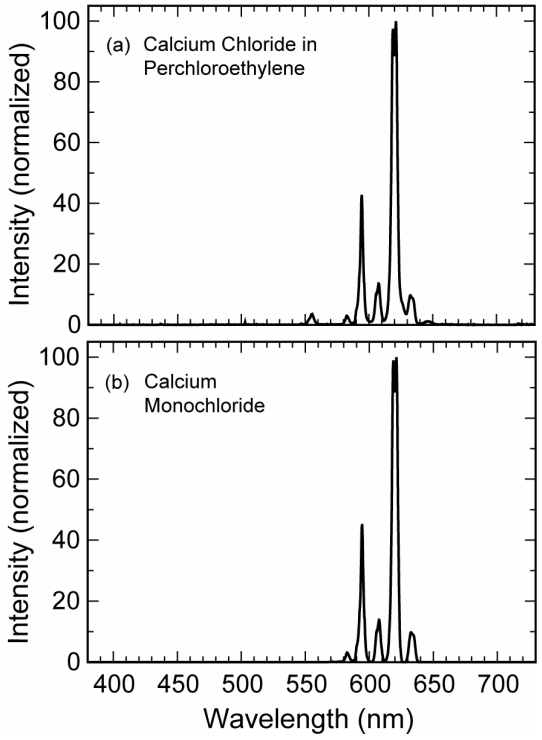


Figure 14. a) The spectrum of calcium chloride suspended in perchloroethylene. b) The isolated spectrum of calcium monochloride.

Barium

The spectrum for the barium hydroxide solution ($Ba(OH)_2$ in H_2O) is presented in Figure 15a. The range for this figure extends from 380 to 780 nm so that the prominent feature centered about 750 nm can be seen. Underlying this complex spectrum is a continuum that is produced by condensed-phase barium oxide (BaO).[6] The profile of this continuum (see Figure 15b) was approximated by fitting a curve to the local minima present in the raw spectrum. This continuum was then subtracted from the original spectrum, yielding an intermediate spectrum that represented the gas-phase emitters. Asymmetric peaks were then placed at the wavelengths corresponding to the tabulated locations for atomic barium (Ba), barium oxide (BaO), and barium monohydroxide (BaOH). The approximated barium monohydroxide peaks were thus isolated and are presented in Figure 15c. Likewise, the peak for atomic barium (Ba) was also isolated and appears in Figure 15d. Finally, the barium monohydroxide and atomic barium peaks were then subtracted from the intermediate spectrum, leaving gaseous barium oxide (see Figure 15e).

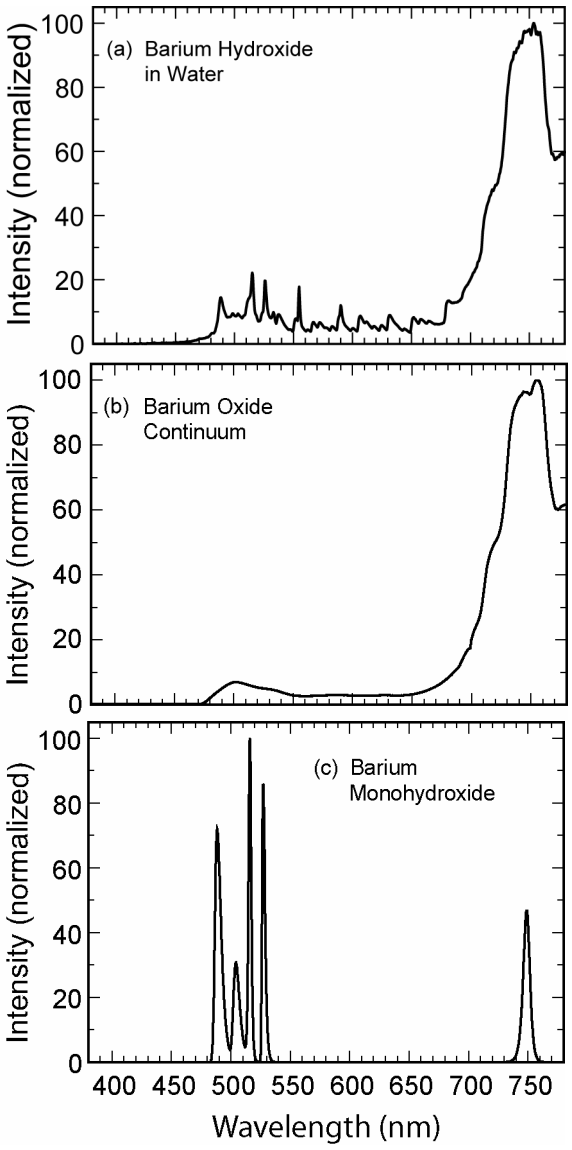


Figure 15. a) The spectrum of barium hydroxide dissolved in water. b) The spectrum of the condensed phase of barium oxide. c) The isolated spectrum of barium monohydroxide. [continued on next page]

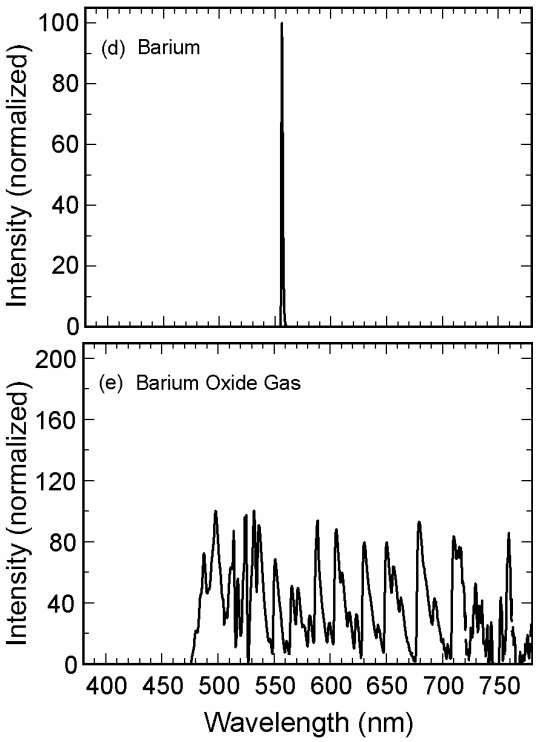


Figure 15. [continued] d) The isolated spectrum of atomic barium. e) The spectrum of vaporized barium oxide.

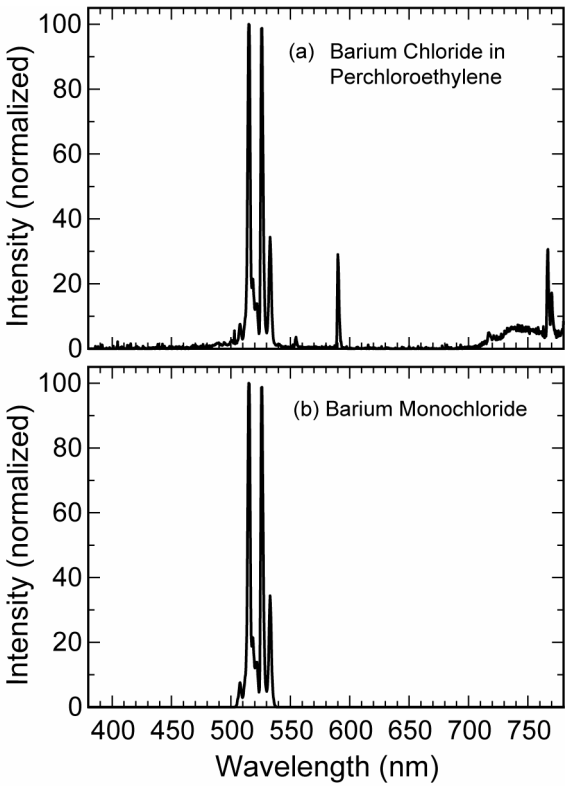


Figure 16. a) The spectrum of barium chloride suspended in perchloroethylene. b) The isolated spectrum of barium monochloride.

The spectrum for the barium chloride suspension ($BaCl_2$ in C_2Cl_4) is presented in Figure 16a. The range for this figure extends from 380 to 780 nm so that the peaks for atomic potassium impurities may be seen, as well as the low-intensity barium oxide continuum. Rescaled atomic sodium, potassium and barium, as well as barium oxide and barium monohydroxide spectra were subtracted, leaving an isolated barium monochloride (BaCl) spectrum, as seen in Figure 16b.

Copper

An attempt was made to acquire copper spectra by using copper nitrate dissolved in water, but the intensity of the peaks was so weak that it required an integration time of 2000 ms. This lead to excessive noise in the spectrum, making it impractical to resolve the individual and complex peaks for atomic copper (Cu), copper hydride (CuH), copper oxide (CuO), and copper monohydroxide (CuOH).

Copper(II) chloride in an aqueous solution ($CuCl_2$ in H_2O) was then tried, and this resulted in a reasonably intense and useful spectrum, as seen in Figure 17. Note that this figure is scaled from 380 to 780 nm, clearly showing the atomic potassium peaks, and also the atomic sodium peak at 589 nm that was so intense it was clipped by the spectrometer at the integration time used. This spectrum also includes low-intensity copper monochloride (CuCl) peaks, which further complicated peak identification and isolation. For this reason, a copper chloride suspension in perchloroethylene (discussed later) was processed first so that an isolated copper monochloride spectrum could be obtained, which was then rescaled and subtracted from the aqueous spectrum. This left an intermediate spectrum including peaks for atomic copper, copper oxide, copper monohydroxide, copper hydride, and impurities.

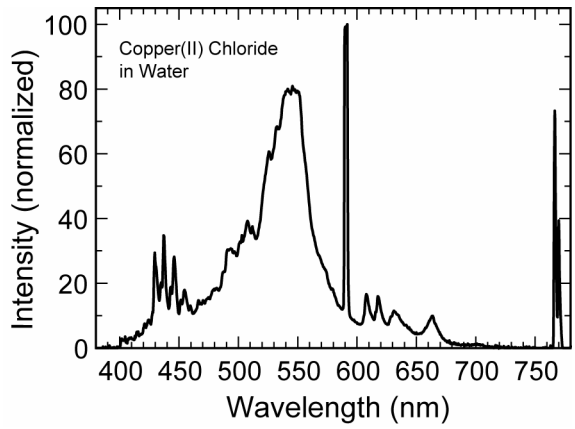


Figure 17. The spectrum of copper(II) chloride dissolved in water.

The copper monohydroxide peaks, located from approximately 490 to 540 nm, are the most prominent features seen in this figure. Copper hydride predominates towards the blue end of the spectrum, even riding up onto the shoulder of the first copper monohydroxide peak. Towards the red end of the spectrum copper oxide predominates, riding on the shoulder of the last copper monohydroxide peak. In a manner similar to that described above for barium hydroxide in water, the peaks for atomic sodium and potassium, copper hydride, copper monohydroxide, and copper oxide were manually placed and shaped using software, and then exported to a spreadsheet.

Interestingly, atomic copper peaks could not be positively identified despite there being a reported 18 peaks in the wavelength range from 380 to 750 nm. It is assumed that conditions were unfavorable for their formation in significant concentrations in the flame.

The atomic sodium and potassium peaks were subtracted from the intermediate spectrum. The individual copper monohydroxide peaks were summed, and this sum subtracted too, thereby eliminating the effect of the pronounced impact of the copper monohydroxide shoulders on copper hydride and copper oxide. The individual peaks for copper hydride and copper oxide were then isolated and cleaned up. Copper hydride and copper oxide are reported to overlap at 445, 446, and 464 nm, but none of these features could be positively discerned. Likewise, the reported (and low intensity) peaks of copper oxide at 583–584 nm could not be positively identified. Copper hydride and copper oxide spectra are presented in Figures 18a and b. The resulting clean copper hydride and copper oxide spectra were then subtracted from the intermediate spectrum, leaving the copper monohydroxide spectrum, which was then cleaned up and is presented in Figure 18c.

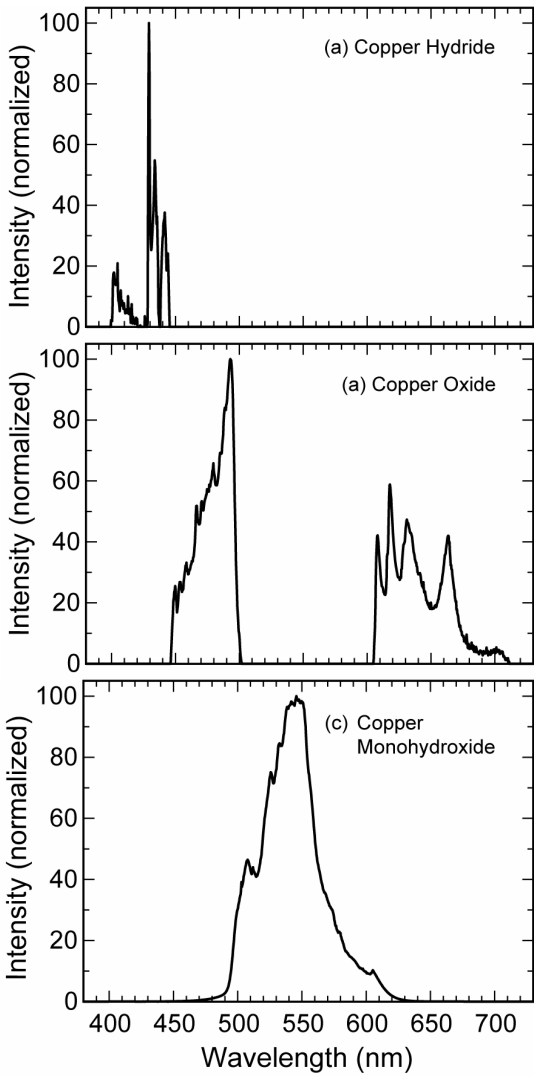


Figure 18. a) The isolated copper hydride spectrum. b) The isolated copper oxide spectrum. c) The isolated copper monohydroxide spectrum.

The spectrum for the copper chloride suspension ($CuCl_2$ in C_2Cl_4) is presented in Figure 19a. Virtually all of the features are associated with copper monochloride, which made isolation of the spectrum straightforward. This was rather fortunate in that it made the isolation of the other copper emitters present in an aqueous-based solution (discussed earlier) much easier. The isolated spectrum for copper monochloride is illustrated in Figure 19b.

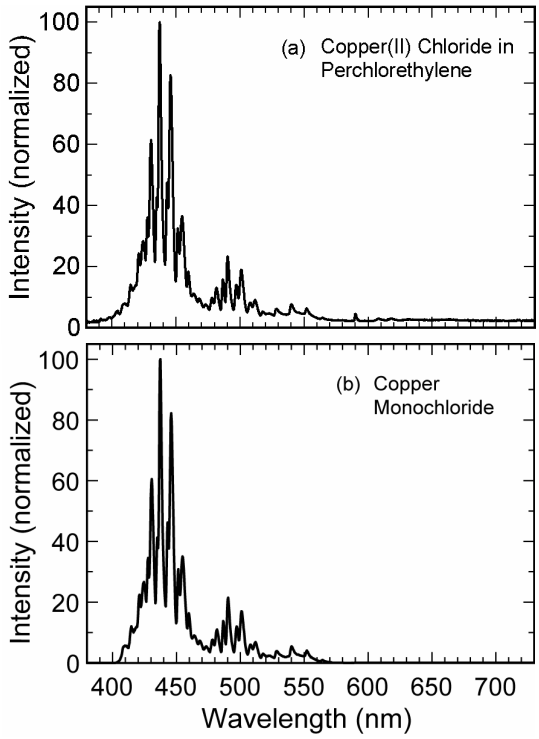


Figure 19. a) The spectrum of copper(II) chloride in perchloroethylene. b) The isolated spectrum of copper monochloride.

Results

The normalized (to 100 for the most intense peak) line and band intensities for the collection of principal colored flame emitters are presented in Table 2. (A presentation of some of the intensity data collected by others is included as a data table in the Appendix.) Table 3 presents the chromaticity coordinates for the principal emitters investigated in this study.

Table 2. Normalized Line and Band Intensities for the Principal Color Flame Emitters.

W. L.[a]	R. I.[b]	W. L.[a]	R. I.[b]
SrCl		**BaOH**	
624	11	488	72
636	55	502	30
648	21	513	100
661	90	524	86
674	100	745	47
687	11	**CuCl**	
700	1	412	6
SrOH		415	12
606	59	419	12
620	2	421	22
626	2	426	27
649	13	428	35
659	33	431	61
671	70	435	41
682	100	436	100
707	9	443	46
722	1	446	82
CaCl		449	31
581	3	452	35
593	45	460	16
605	11	465	9
608	14	469	7
619	99	476	5
621	100	479	7
633	9	482	11
635	8	485	13
CaOH		489	21
555	45	496	12
572	1	498	17
594	7	509	6
600	11	512	6
604	14	515	3
625	100	526	4
645	10	538	5
665	1	552	4
BaCl		**CuOH**	
507	8	505	46
514	100	512	44
517	21	524	75
521	14	533	84
524	99	546	100
532	34	605	10

a) W.L. = wavelength.

b) R.I. = relative intensity.

A normalized graph of the luminous sensitivity of the human visual system[17] is presented in Figure 20. The wavelength range corresponding to 1% or more of the maximum and extends from approximately 410 to 650 nm, with sensitivity approaching zero beyond this range. The intense potassium peaks at 767 nm (See Figure 10) are at what may be considered the edge of human visual perception and very near the infrared. However, due to its substantial intensity, the peaks at 767 nm produce a measurable shift in the perceived color of any flame that has potassium present in significant amounts. Chromaticity coordinates for the atomic potassium peaks at both 404 and 767 nm, for just the atomic potassium peak at 404 nm, and for just the pair of atomic potassium peaks at 767 nm have been included in Table 3 to demonstrate this effect. The influence of the near-infrared but intense 767 nm peaks is evident.

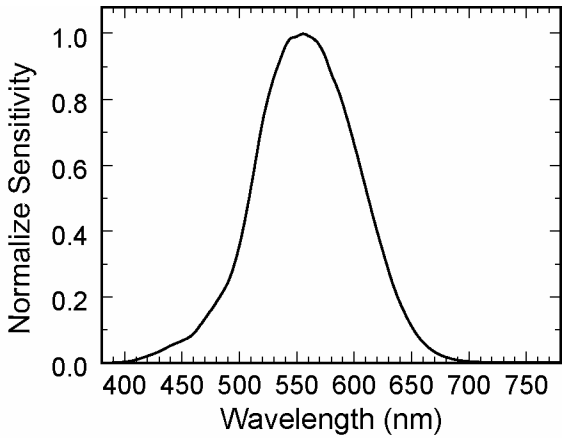


Figure 20. The luminous sensitivity of the human visual system, normalized to 1 at 555 nm.

The solutions produced for this work used reagent grade chemicals; even then the potassium peaks at 767 nm and the ubiquitous

Table 3. Chromaticity Color Coordinates for the Color Emitters Characterized in this Study.

Emitter	CIE 1931 Color Coordinates		
	x	y	z
K (with both 404 & 767 nm peaks)	0.676	0.238	0.087
K (404 nm peak only)	0.173	0.005	0.822
K (767 nm peak only)	0.735	0.265	0.000
Na	0.576	0.423	0.001
Ba	0.344	0.653	0.003
BaO (Condensed)	0.380	0.520	0.101
BaO (Gas)	0.406	0.507	0.087
BaOH (approximated)	0.066	0.606	0.328
BaCl	0.094	0.811	0.094
Ca	0.171	0.006	0.824
CaO	NA	NA	NA
CaOH	0.630	0.369	0.001
CaCl	0.661	0.338	0.000
Sr	0.141	0.033	0.826
SrO (Incomplete)	0.593	0.406	0.001
SrOH	0.679	0.321	0.000
SrCl	0.720	0.280	0.000
Cu	NA	NA	NA
CuH	0.167	0.009	0.824
CuO	0.315	0.187	0.499
CuOH	0.290	0.666	0.044
CuCl	0.156	0.073	0.771
Blue Flame (with perchloroetylene)	0.218	0.395	0.387

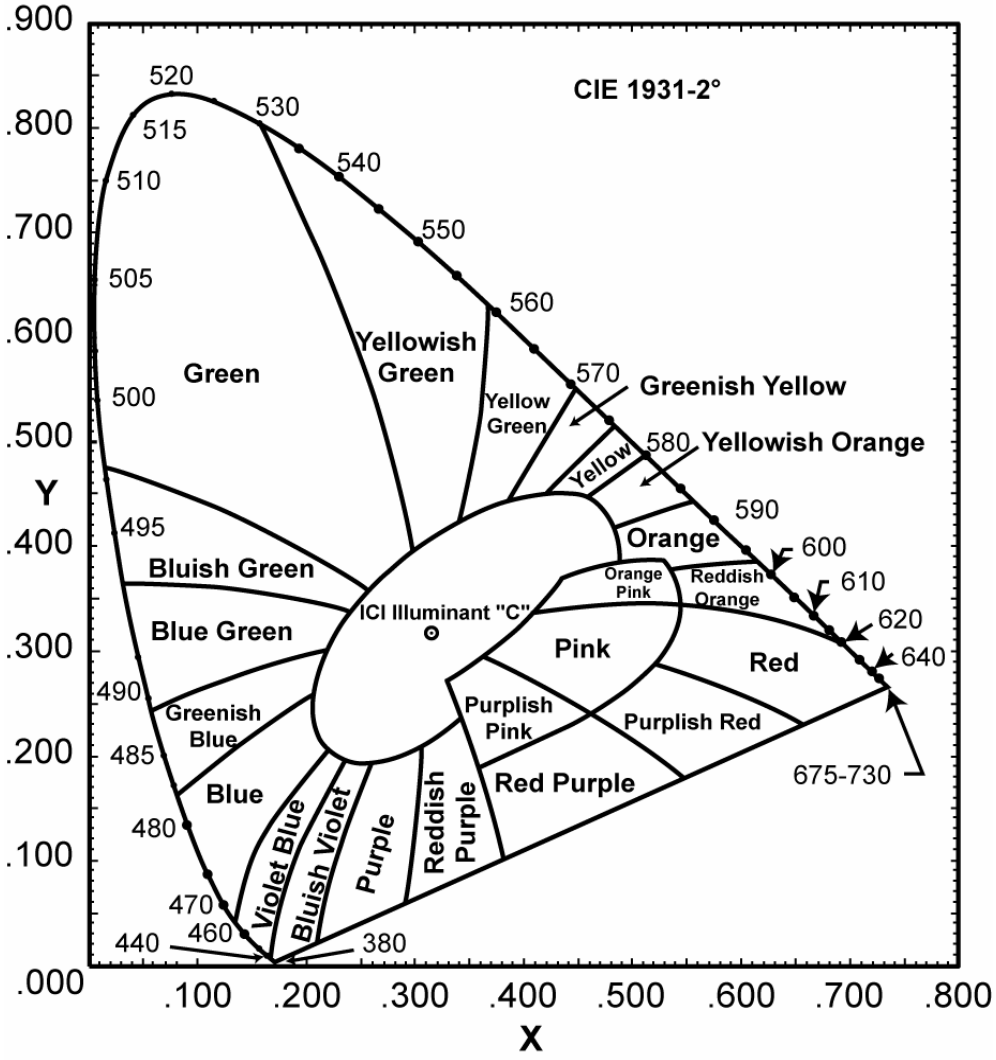


Figure 21. 1931 2° chromaticity diagram.

atomic sodium peak at 589 nm were very often intense. One may conclude that commercial grades of chemicals used in pyrotechnic applications will likely have greater concentrations of impurities such as these, with correspondingly greater interferences and perceived color shifts.

As an aid in interpreting the color point data in Table 3, Figure 21 has been included. This is a black and white rendition of the CIE 1931 2° Chromaticity Diagram. The color points determined in this work are plotted in Figure 22 on simplified versions of the chromaticity diagram of Figure 21. There are two chromaticity diagrams: the first (Figure 22a) displays the location of the color points for the principal colored flame emitters, and the second (Figure 22b) displays the location of the other color emitters studied.

In Figure 22b, some clarification is needed regarding the identification of some of the color points. The color point for potassium (K) is that including both the 404 and 767 peaks. Only a portion of the strontium oxide spectrum could be isolated from the more intense emitters and thus has not been included in Figure 22b. There are two color points for barium oxide, one corresponding to its emissions when vaporized, designated with the subscript (g), and one for its emissions when condensed, designated with the subscript (cond.).

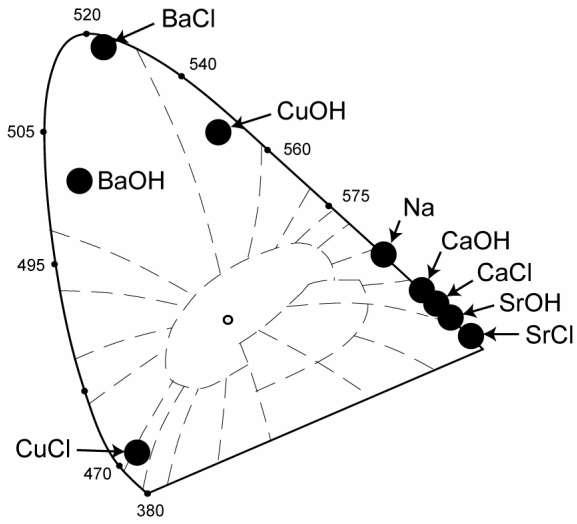


Figure 22a) chromaticity diagram showing the location of the color points for the principal colored flame emitters.

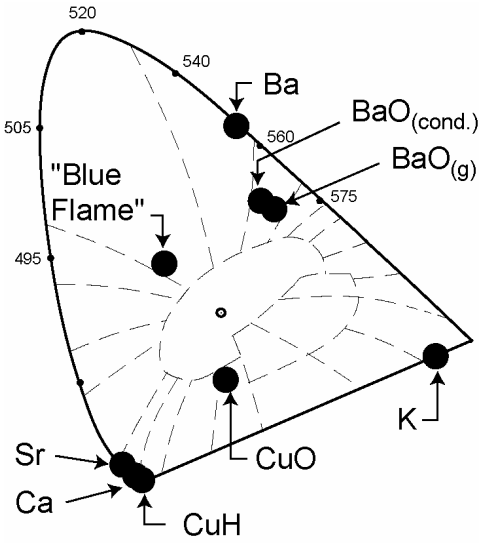


Figure 22b) chromaticity diagram showing the location of the other colored flame emitters studied.

Conclusions

With more complete and more detailed information regarding the spectral nature of the emitting species in pyrotechnic flames, work to improve flame color should be facilitated. For the most part, this project has been successful in producing that data (with another project anticipated to carry the work further). Upon considering the spectral data for the principal colored flame emitters, it does not appear that progress toward improved flame color will be easy.

Figure 23 summarizes the state of the art with respect to colored flame production, as well as identifying the probable limits of future improvements. The range of colors within the smallest of the quadrangles (shaded) represents the approximate limits of common high quality color formulations.[18,19] This covers a relatively small portion of the chromaticity diagram, and much of that consists of what would normally be described as shades of white. It is perhaps fortunate, that observers of fireworks displays do not have light sources producing bright and highly pure color available to them to compare with the colors of the fireworks, many of which would pale by comparison. The small size and central location of this color quadrangle for typical compositions probably also goes a long way toward explaining why photographs and video records of displays seem to reproduce the colors of the displays so poorly, unless the recorded colors are artificially enhanced.

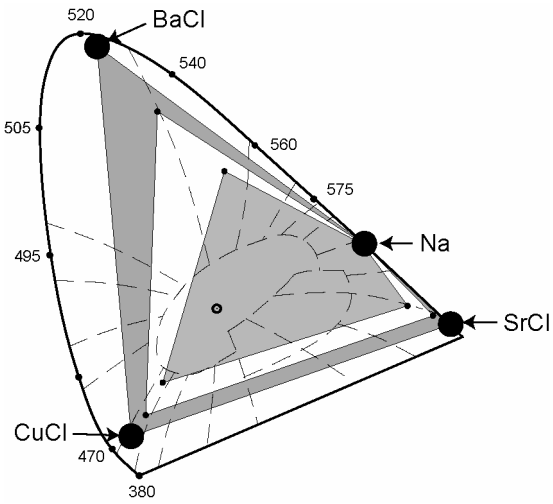


Figure 23. The state of the art for colored flame production. The smallest shaded quadrangle represents the limits of common high quality formulations. The mid-size un-shaded quadrangle demonstrates the very best color formulations reported to date. The largest shaded quadrangle is for the pure color species reported in this paper.

The next larger quadrangle (not shaded) demonstrates the approximate limits of the best color formulations reported to date.[18,20] These colors are quite impressive when viewed and are readily discernable as significantly better than even the best of the commonly produced colors. (Unfortunately, there are some limitations associated with the use of these formulations in terms of cost, non-color related performance, and convenience of manufacture.) Using any of the color mixing schemes to produce blended colors,[21–23] and even assuming the color formulations are perfectly compatible, one is constrained to produce colors no better than those inside this quadrangle.

Finally there is the outer quadrangle (shaded) formed by the color points of the most desirable color species (the monochlorides of strontium, barium and copper, plus atomic sodium). Unless other, even better color species can be found (and researchers have looked without significant success[2,24–27]), this is the ultimate limit of what is possible. In fact, given that flames generally consist of very many chemical species, of which many emit in the visible region, even reaching these limits will probably be impossible to achieve.

Acknowledgments

The authors gratefully acknowledge the work of all those who have added to the understanding of the chemistry of colored flame, most especially the pioneering work of T. Shimizu and B. Douda. The authors are also grateful to K. Hudson and especially to E.-C. Koch for their comments and suggestions on a draft of this paper.

References

1) T. Shimizu, *Selected Pyrotechnic Publications of Dr. Takeo Shimizu, Part 3, Studies on Fireworks Colored-Flame Compositions*, Journal of Pyrotechnics, 1999.

2) B. E. Douda, *Theory of Colored Flame Production*, RDTN No. 71, U.S. Naval Ammunition Depot Crane, IN, USA, 1964.

3) B. E. Douda, *Relationships Observed in Colored Flames*, RDTR No. 45, U.S. Naval Ammunition Depot Crane, In, USA, 1964.

4) B. E. Douda, "Emission Studies of Selected Pyrotechnic Flames", *J. Optical Soc. America*, Vol. 55 (1965) pp 787–793.

5) Ocean Optics, Inc., Dunedin, FL 34698, USA

6) T. Shimizu, *Feuerwerk vom physikalischen Standpunkt aus*, Hower Verlag, Hamburg, 1976. Reprinted and translated in four parts by Pyrotechnica Publications (1981 to 1989).

7) R. Herrmann and C. T. J. Alkemade, *Chemical Analysis by Flame Photometry*, Translated by Paul T. Gilbert, Interscience Publishers, 1963.

8) R. C. Weast, Ed. in Chief, *CRC Handbook of Chemistry and Physics*, 46th ed., Chemical Rubber Co., 1965.

9) M. L. Parsons and P. M. McElfresh, *Flame Spectroscopy: Atlas of Spectral Lines*, IFI/Plenum, 1971.

10) R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, 3rd ed., Chapman and Hall Ltd, 1963.

11) A. G. Gaydon, *The Spectroscopy of Flames*, 2nd ed., Chapman and Hall, John Wiley & Sons, 1974.

12) C. Th. J. Alkemade and R. Herrmann, *Fundamentals of Analytical Flame Spectroscopy*, translated from German by R. Auerbach and Paul T. Gilbert Jr., John Wiley & Sons, New York, 1979.

13) R. Mavrodineanu, Ed., Phillips Technical Library, *Analytical Flame Spectroscopy, Selected Topics*, Macmillan, 1970.

14) R. Mavrodineanu and H. Boiteux, *Flame Spectroscopy*, John Wiley & Sons, New York, 1965.

15) H. Li, C. Focsa, B. Pinchemel, R. J. Le Roy, P. F. Bernath, "Fourier Transform Spectroscopy of BaO: New Ground-State Constants from the $A^1\Sigma^+$-$X^1\Sigma^+$ Chemiluminescence*, Journal of Chemical Physics*, Vol. 113, No. 8 (2000) p 3030.

16) *PeakFit* Version 4.11, Systat, Richmond, CA, USA.

17) Color and Vision Research Laboratories, Institute of Ophthalmology, University College, London, and Visual PsychoPhysics, Tübingen Forschungsstelle für Experimentelle Ophthalmologie, University of Tübingen - http://cvrl.ioo.ucl.ac.uk/cvrl.htm

18) D. E. Chavez, M. A. Hiskey, and D. L. Naud, "High-Nitrogen Fuels for Low-Smoke Pyrotechnics", *Journal of Pyrotechnics*, No. 10 (1999).

19) B. V. Ingram, "Color Purity Measurements of Traditional Star Formulas", *Journal of Pyrotechnics*, No. 17 (2003).

20) S. Anderson, "Composite Color Stars", *Journal of Pyrotechnics*, No. 8 (1998).

21) R. Veline, *A Compatible Star Formula System for Color Mixing*, Self Published, 1989.

22) J. H. Baechle, *Pyrocolor Harmony – A Designer's Guide*, Self Published, 1989.

23) B. J. and K. L. Kosanke, "Lancework—Pictures in Fire", *Pyrotechnica* XV (1993). Reprinted in *Selected Pyrotechnic Publications of K. L. and B. J. Kosanke, Part 3 (1993–1994)*, Journal of Pyrotechnics, 1996.

24) C. Jennings-White, "Some Esoteric Firework Materials", *Pyrotechnica* XIII (1990).

25) B. T. Sturman, "The Rare Earths as Possible Flame Color Agents", *Journal of Pyrotechnics*, No. 9 (1999).

26) E.-C. Koch, "Evaluation of Lithium Compounds as Color Agents for Pyrotechnic Flames", *Journal of Pyrotechnics*, No. 13 (2001).

27) E.-C. Koch, "Special Materials in Pyrotechnics Part 2 – Application of Cesium and Rubidium Compounds in Pyrotechnics", *Journal of Pyrotechnics*, No. 15 (2002).

Appendix — Summary of the Reported Spectral Information for Colored Flame Emitters, Including the Results from this Study [See notes at end of Table.]

WL	Intensity							
(nm)	A	B	C	D	E	F	G	H
Ba								
552							6	
554	200	170		8.5			10	100
578							9	
602	4							
606	4							
611	12							
645	4							
648	4							
650	50							
653	25							
660	25							
706	4							
BaCl								
507	2				1			8
514	20				10			100
517	4				2			21
521					1			99
524	30				10			34
532	10				3			
BaO								
452	3							
454			vvW					
458	4		vvW					
462	7		vvW					
464	5		vvW					
466	3		vvW					
468	10		vvW		5			
472	5		vvW					
474	10		wM					
478			wM					
479	15							
483	10		wM					
485	50		wM		6			72
487			wM					
490			wM					
494			vvW					
497	30		vvW		3			100

WL	Intensity							
(nm)	A	B	C	D	E	F	G	H
BaO (cont.)								
501	10		vvW					
509	100		W		6			
514								87
521	70		vW		7			
526								97
533								100
535	90	80	vW	4	8	s		90
537			vW					
540			vvW					
542	5		vvW					
546	20							16
549	70	80	vvW	4	10	vs		
551	10		vvW					68
560	10							
564	40	80	vvW	4	9	vs		
566	5		vvW					
567	10		vvW					51
570	40	80		4	8	s		
571			vvW					
574								36
576	15		vvW					
577			vvW					
581	20		vvW		6	m		
582			vvW					
583			vvW					32
586	40		W	3.5	10	vs		
587		80						
588			W					
589	10		W					93
598	10		vvW		3	w		
604	50	70	W	3.5	9	vs		
608								88
610	20		W		5			
611	10		W					
612			W					59
616	10							
617			vvW		6			34
622			vW		6	m		

WL	Intensity							
(nm)	A	B	C	D	E	F	G	H
BaO (cont.)								
623	15							32
626								29
629	25		W		8	s		
632								79
636			vvW					
642	15		vW					26
649	25		wM		9	vs		
653								71
656	10		vW					57
663			vW					39
666								
670			vvW					
678	50		wM		8	s		
682								56
686	40		vW					33
693	60		vW					26
701			vW					10
710	80		vW		5			50
718			vW					46
725			vW					14
734			vW					32
744			vW					16
752			vW					26
755								
761			vW					41
BaOH								
487			wM					
488	120	100		5				72
497		80		4				
502	30	80		4				30
512			W					
513	140	150		7.5				100
524	80	80		4				86
745	45	50		2.5				47
Ca								
423	10k	250	vS	5				100
428	4							
430	15							
432	3							
444	10							
446	15							
459	8							

WL	Intensity							
(nm)	A	B	C	D	E	F	G	H
CaCl								
383	12							
388	13							
581	250							3
593	500							45
605					2			11
608					2			14
618					10			
619	500				5			99
621	500				10			100
622					5			
633					2			9
635					2			8
CaO								
385			vW					
386			vW					
387					2			
389			vvW					
392			vvW					
397					3			
408					5			
410					4			
413					3			
421					6			
422					5			
424					3			
435					5			
437					5			
438					6			
440					6			
443					3			
451					4			
452					3			
598					8			
600					8			
601					8			
604					3			
606					5			
607					7			
608					5			
609					6			
610					10			
618					6			
626					9			

WL	Intensity							
(nm)	A	B	C	D	E	F	G	H
CaO (cont.)								
628					4			
632					2			
634					4			
636					4			
731			vvW					
732			vvW					
733			vvW					
771			vW					
772			vW		6			
CaOH								
539			vW					
543	100		W					
546	100							
551	100							
552	200							
553	600							
554	1.2k	500			5			45
555	1k		vS	10	5			
556	400				2			
565	100							
570	100							
572	100	25		0.5				1
578			W					
581	100							
583			W					
594	100							7
597	200							
599	400							
600	400							11
601	600							
602	400	100						
603	400		[a]					
604			M	2				14
605	300							
607	200							
608	200							
609	200							
610	400							
612	200							
622		500		10				
623			vS					
625								100
644		70						

WL	Intensity							
(nm)	A	B	C	D	E	F	G	H
CaOH (cont.)								
645			M	1.4				10
665			W					1
683			vW					
698			vvW					
Cu [b]								
450					4			
455					7			
460					10			
461					8			
465					10			
471					5			
486					4			
487					4			
490					10			
492					8			
497					4			
498					8			
500					7			
511	50		vvW				4	
515							4	
522							5	
570	5							
578	10							
CuCl								
412					5			6
415								12
419	2				6	w		12
421	2				4	w		22
426	5				8	s		27
428	10				7	vs	9	35
433	10				10	vs		35
435	20				9	vs	10	41
436					5			100
441	7				6	s		
443	15				6	vs	9	46
446								82
449	4				4	m		31
452	5				1	m	5	35
460								16
465								9
469								7
476					5	vw	1	5
479					5	vw	2	7

WL	Intensity							
(nm)	A	B	C	D	E	F	G	H
CuCl (cont.)								
482								11
485					8	w	3	13
488	3				8	w	4	
489					6			21
495					4	vw	1	
496					5			12
498					4	vw	2	17
509								6
512								6
515					2	m	3	3
526					4	w	6	4
538					2			5
552								4
CuH								
401	5							18
407								12
413								10
416								7
428	30		vvW			vs		100
433	11					m		55
435	10							
436	9							
437	7							
438	9							
439	9							
440	9							
441	9							38
442	7							
443	8							
444	7							24
445	10							
446	11							
465	8							
CuO								
445					8			
446					7			
450								25
452					5			
453					5			27
458					6			33
464					6			
467								52
469					5			

WL	Intensity							
(nm)	A	B	C	D	E	F	G	H
CuO (cont.)								
470					5			
471					7			53
472					7			
477					6			57
480								66
483					4			
485					5			
486					5			69
488					5			83
492					5			100
583					2			
584					3			
605	10				9			
606	50				10			42
615	50				8			
616	50				9			59
628					1			
629					5			
632								47
638					2			
640					5			
643					3			
649					1			
CuOH								
493	60							
505	70	50		5				46
512								44
524	110	70	vvW	7				75
530	110		vvW					
512								84
537	120	100	vvW	10				
533								100
605								10
615-625			vvW					
	[c]	**K**						
404	500			0.03			5	0.06
405	250	30					4	
580	25							
694	40							
766	40k	10k		10			10	100
770	200k	10k		10			9	78

WL	Intensity							
(nm)	A	B	C	D	E	F	G	H
	[d]	**Na**						
568	40							
569	80							
589	800k	30k		10			10	100
590	400k			10			9	100
	[e]	**Sr**						
461	10k	500		1			10	100
483							5	
487							2	
496							3	
SrCl								
389	4							
392	4							
394	4							
396	4							
398	4							
401	4							
624							2	11
636	20						10	55
648							4	21
661	20						10	90
662							5	
674							5	100
675	10						5	
676							3	
687								11
700								1
SrO	[f]	[g]	[h]					
390			vvW					
392			vvW					
593								100
595		500	W	1				
597		500		1				88
608	25							
609	20							
610	10							
611	7							
750	5		vvW					
752	7		vvW					
754	10		vvW					
756	10							
787	20							
788	25							

WL	Intensity							
(nm)	A	B	C	D	E	F	G	H
SrOH								
604	3k							
605		5k		10			Str.	
606	7k					vs		59
608							10	
609							6	
610							4	
611							1	
620						vw		2
624	150							
626						vw		2
645		250		0.5				
646	700		M			m		
649								13
659	1.5k	500	W	1		w		13
666	5k	500		1				
671			vS			vs		70
672	4k							
680		250						
682	7k		vS	0.5		vs		100
704	500							
707			wM			m		9
722			W			w		1

Sources of Spectral Data

A) R. Herrmann and C. T. J. Alkemade, *Chemical Analysis by Flame Photometry*, Translated by Paul T. Gilbert, Interscience Publishers, 1963. [Note: Does not include peaks with an intensity of one.]

B) *CRC Handbook of Chemistry and Physics*, 46th ed., Robert C. Weast, Ed., Chemical Rubber Co., 1965. [Note: Only air-hydrogen flame values using aqueous solutions reported.]

C) R. Mavrodineanu and H. Boiteux, *Flame Spectroscopy*, John Wiley & Sons, Inc., 1965 [Note: Only acetylene-air, outer cone values reported.]

D) M. L. Parsons and P. M. McElfresh, *Flame Spectroscopy: Atlas of Spectral Lines*, IFI/Plenum, 1971. [Note: Only air-hydrogen values reported.]

E) R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, 3rd ed., Chapman and Hall LTD, 1963. [Note: Variety of sources, flame types, furnaces, and arcs reported.] NOTE: Looking at the more recent (4th) edition from 1975, there are obviously some deviations between the transitions listed in this table under **E**. At the time of writing, the authors did not have this edition available. In all probability – knowing the types of budgets that university libraries face – the older edition may be more readily found.

F) A. G. Gaydon, *The Spectroscopy of Flames* 2nd ed., Chapman and Hall, John Wiley & Sons, 1974.

G) B. E. Douda, *Theory of Colored Flame Production*, U.S. Naval Ammunition Depot, RDTN No. 71, 1964. [Note: Values from Gaydon are not reproduced for this column.]

H) This work.

Notes

Note: Some researchers used a non-numerical scale, such as *vvW* for Very Very Weak, *vs* for Very Strong, etc. No attempt was made to convert these to a numerical scale. In addition, there are discrepancies in wavelength assignments between the various sources. No attempt was made to reassign wavelengths.

a) 604–698 nm designated as "CaOH (?)" in the original text.

b) Designated as Cu_2, not Cu, in the original text.

c) Only values ≥ 25 are listed.

d) Only values ≥ 25 are listed.

e) Only values ≥ 25 are listed.

f) 595 and 597 nm are designated as possibly being Sr_2O_2 in the original text.

g) 595 nm is designated as Sr_2O_2 in the original text.

h) 595and 597 nm are designated as Sr_2O_2 in the original text.

Thermal Characterization of Smoke Composition

Z. Abdel-Qader, Q. S. M. Kwok, R. C. Fouchard, P. D. Lightfoot and D. E. G. Jones
Canadian Explosives Research Laboratory, 555 Booth Street, Ottawa, Ontario, K1A 0G1 Canada
email: djones@nrcan.gc.ca

ABSTRACT

The present work includes the thermal characterization of a smoke composition, the smoke components, as well as a potassium chlorate–lactose mixture using differential scanning calorimetry (DSC), thermogravimetry (TG), simultaneous thermogravimetry-differential thermal analysis-Fourier transform infrared spectrometry-mass spectrometry (TG-DTA-FTIR-MS), and accelerating rate calorimetry (ARC).

The DSC results for the smoke composition show a sharp exotherm at 140–210 °C, and the ARC results show one rapid exotherm with an onset temperature of 118 ± 5 °C. These exotherms result from the rapid and energetic reaction between lactose and potassium chlorate. Kinetic studies conducted separately in heat-wait-search and isothermal experiments in the ARC yielded substantially different results for the activation energy. Simultaneous TG-DTA-FTIR-MS was used to investigate the thermal behavior of the smoke composition and to analyze the evolved gases during the heating process. Carbon dioxide (CO_2), water vapour and carbon monoxide (CO) were detected with a significant intensity using FTIR-MS.

Further DSC and TG work was performed for 1-aminoanthraquinone (1-AAQ), a dye that is the main component of the smoke composition. DSC and TG results for the 1-AAQ dye are compared with those for a high purity 1-AAQ dye from a different source. The DSC and TG results indicate that the 1-AAQ dye sample had a significant nonvolatile residual mass compared to the high purity one.

Keywords: smoke composition, orange dye, aminoanthraquinone, thermal analysis, DSC, TG, DTA, FTIR, MS, ARC

Introduction

Pyrotechnic smokes have been widely used for signaling, screening and display. Coloured smokes are preferred, to assure contrast and to be distinct in the presence of clouds and ordinary smoke. The smoke compositions typically contain potassium chlorate as the oxidizer, lactose as the fuel, polyvinyl acetate as a binder, sodium bicarbonate as a neutralizer or cooling agent, and of course the organic dye for colour.[1] Anthraquinone dyes are commonly used in coloured dye mixes prepared for signal smoke grenades because of their resistance to decomposition by heat and their capacity to evaporate and recondense as a brilliant cloud or trail.[2]

A smoke composition containing 1-aminoanthraquinone (1-AAQ) dye (orange dye), supplied from Batch 0219 (B0219), was thermally analyzed. The thermal properties for the smoke composition, the 1-AAQ dye, as well as the potassium chlorate–lactose mixture were determined using various techniques, including differential scanning calorimetry (DSC), thermogravimetry (TG), simultaneous thermogravimetry-differential thermal analysis-Fourier transform infrared spectrometry-mass spectrometry (TG-DTA-FTIR-MS), and accelerating rate calorimetry (ARC). Since this particular smoke composition performs well in actual use, its thermal characteristics are a bench mark for future compositions containing components from new batches.

Experimental

Materials

A smoke composition containing: 1-AAQ dye from B0219 (55.0 %), potassium chlorate (21.9 %) and lactose (15.6 %) (the mass ratio of potassium chlorate to lactose is 1.4:1) and samples of each component were provided by Hands Fireworks. A sample of high purity 1-AAQ from Bayer Chemical Co. was also used. Also, a mixture of potassium chlorate and lactose was prepared in our laboratory in the ratio of 1.4:1, respectively.

DSC

A TA 5200 Thermal Analysis System with a DSC 2910 module was used for the thermal studies of smoke composition and the organic dyes in a nitrogen atmosphere. A heating rate of 5 °C min^{-1} up to 600 °C was applied to 3.0 mg of the organic dye samples as well as a 1.0 mg sample of the smoke composition. DSC measurements were conducted on dyes loaded into aluminum hermetic pans. The smoke composition was loaded into sealed glass microampoules, as described in the literature.[3]

TG

A TA 5200 Thermal Analysis System with a TG 2950 module was used to study the smoke composition sample as well as the 1-AAQ dyes (B0219 and Bayer). All samples were heated from room temperature to 1000 °C at 5 °C min^{-1}. A platinum pan containing 1.0 mg of the sample was used. The samples were purged with nitrogen or air at a flow rate of 40 cm^3 min^{-1} to the balance and 60 cm^3 min^{-1} to the furnace. A TG run with an empty platinum pan (i.e., no sample) showed a deviation from the baseline of approximately ± 40 μg up to 1000 °C.

TG-DTA-FTIR-MS

The simultaneous TG-DTA 2960 module interfaced to a Bomem MB100 Fourier Transform Infrared Spectrometer (FTIR), and a Balzers Thermostar GSD300 Quadrupole Mass Spectrometer (MS) was used to study the thermal behaviour and to identify the gases evolved during the heating of the smoke composition sample. Experiments were conducted in helium and air atmospheres purged at a flow rate of 50 cm^3 min^{-1}. Platinum foil was used as a reference material. Approximately 1.0 mg of smoke composition and 1.0 mg of potassium chlorate–lactose mixture were tested using the TG-DTA. An equivalent mass of the sample and a platinum foil were placed in separate alumina pans and heated at 20 °C min^{-1} up to 1400 °C. To confirm the baseline of the TG-DTA, an experiment using the same heating profile was performed on two empty alumina pans. The TG drift was ~33 μg (~3.3 % for a 1.0 mg sample) and the DTA curve fluctuated less than 0.15 °C over the entire temperature range.

ARC

The ARC is a commercial automated adiabatic calorimeter distributed by Arthur D. Little Inc. and is used for the purpose of assessing the thermal hazards of energetic materials.[4] About 0.5 g of the smoke composition was placed in a lightweight spherical titanium vessel, which formed part of a closed system including a pressure transducer. Experiments were started at ambient air pressure. The standard ARC procedure of "heat-wait-search" was used: the temperature of the system was raised from the initial temperature of 100 °C in 5 °C steps. The system was maintained adiabatic, both during periods of "wait" for dissipation of thermal transients and of "search" for an exotherm defined as a self heating rate exceeding 0.02 °C min^{-1}. The criteria set for the instrument to terminate a run were (i) a temperature maximum of 350 °C, (ii) a self-heating rate exceeding 2 °C min^{-1} or (iii) a pressure exceeding 7 MPa (1000 psi). Isothermal runs were performed on 0.5 g of the smoke composition sample and were carried out at 100, 105, 110 and 115 °C. The instrument was maintained isothermal for a period of time until onset and a runaway reaction was reached.

Results

Orange Dyes (1-AAQ)

The TG results for the 1-AAQ (B0219) dye and the sample from Bayer, both in nitrogen, are compared in Figure 1. The results indicate that B0219 dye has a significant nonvolatile residual mass (10 %), compared to about 1.3 % for Bayer, independent of the purge gas used in

the experiment. First step mass losses of about 90 % for B0219 and 98.7 % for Bayer were obtained between 150 and 250 °C, resulting from the sublimation of the 1-AAQ dyes. A second mass loss took place for B0219 dye at temperatures higher than 250 °C.

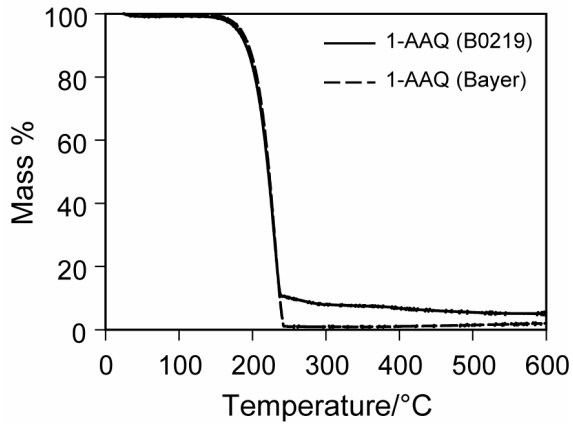


Figure 1. TG curves for two samples of 1-AAQ dye in N_2 at 5 °C min^{-1}.

The DSC results for the 1-AAQ dye (B0219) in an aluminum hermetic pan show one endotherm with an onset temperature of 251.6 ± 0.2 °C and $\Delta H = 106.9 \pm 0.3$ J g^{-1}, while the DSC results for the Bayer dye show one endotherm with an onset temperature of 253.0 ± 0.2 °C and $\Delta H = 112.9 \pm 0.1$ J g^{-1}. It was observed that the melting point of B0219 dye is a few degrees below that of the Bayer material, indicating the presence of impurities in B0219. For comparison, the reported melting point of 1-AAQ dye is 252 °C and its ΔH value is 127.0 ± 2.9 J g^{-1}.[5]

Potassium Chlorate–Lactose Mixture

Figure 2 shows the TG-DTA curves for the potassium chlorate-lactose mixture. The DTA curve shows a small endotherm with an onset temperature of about 145 °C, due to the dehydration of lactose monohydrate. The first broad exotherm shows multiple peaks with an onset temperature of about 196 °C. This exotherm may be due to a reaction between potassium chlorate and lactose as well as the exothermic decomposition of lactose.[6] The TG curve in Figure 2 shows a first-step mass loss of 3 % accompanying the small endotherm, followed by a second-step mass loss of about 52 % accompanying the first exotherm.

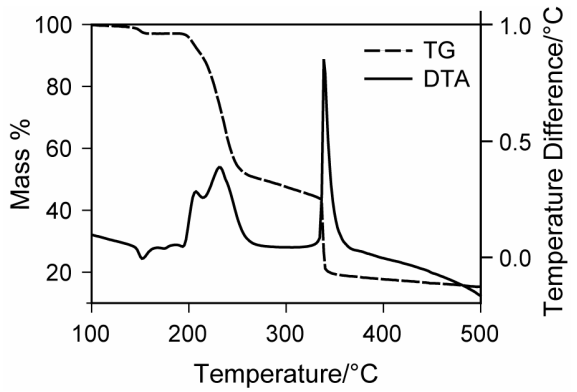


Figure 2. TG-DTA curves for 1.0 mg of potassium chlorate-lactose mixture in He at 20 °C min^{-1}.

A second, sharp exotherm in the DTA curve, with a smaller area than the first exotherm, started at about 336 °C, very close to the melting point of potassium chlorate. This exotherm may be due to further oxidation of residual carbon with potassium chlorate.[6] The mass loss accompanying this exotherm was about 33 %.

Smoke Composition

Figure 3 presents the DSC and TG results for the smoke composition. A mass loss of about 60 % occurred between 140 and 250 °C. By comparing the TG results for the 1-AAQ dye, the potassium chlorate-lactose mixture, and the smoke composition, this mass loss is believed to be due to the dehydration of lactose monohydrate, the lactose–potassium chlorate reaction and the sublimation of the 1-AAQ dye.

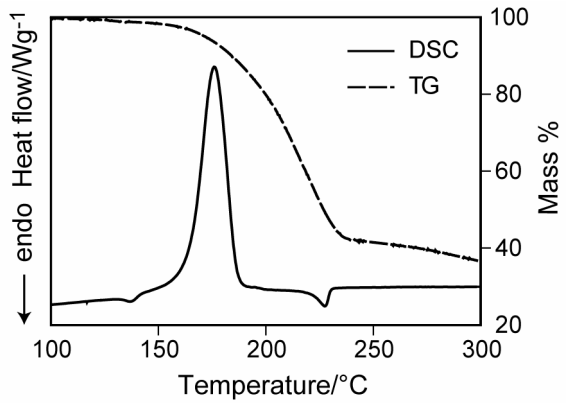


Figure 3. DSC (in ampoule) and TG (in open pan) curves for 1.0 mg of smoke composition in N_2 at 5 °C min^{-1}.

A small endotherm observed between 130 and 140 °C is due to the loss of one molecule of water of crystallization from the lactose molecule, which is in agreement with literature results.[6,7] Subsequently, a sharp exotherm was seen for the composition, due to the rapid and energetic reaction between lactose and potassium chlorate at 140–210 °C with an onset temperature of 142 ± 1 °C and ΔH = 3.2 ± 0.1 kJ g^{-1} (mass of potassium chlorate and lactose mixture). A small endotherm was observed between 212 and 235 °C resulting from the melting of the 1-AAQ dye.

The ARC results, showing the behaviour of the smoke composition in air, are presented in Figure 4. The smoke composition sample exhibited one exotherm with an onset temperature of 118 ± 5 °C. As shown in Figure 4, the smoke composition sample displayed continuous exothermic activity that was eventually terminated when it reached a self-heating rate of 2 °C min^{-1}.

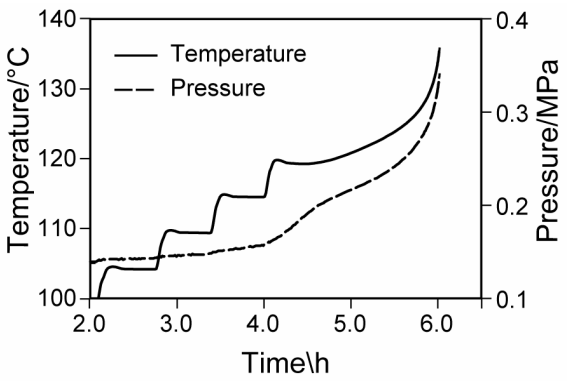


Figure 4. ARC results for 0.5 g of smoke composition in air at ambient pressure.

Figure 5 presents a plot of ln(Rate) versus reciprocal temperature for the heat-wait-search runs, from which the kinetic parameters of the smoke composition sample were determined. It was found that $E = 298 \pm 10$ kJ mol^{-1} and $\ln(Z/min^{-1}) = 88 \pm 1$, where E is the activation energy and Z is the pre-exponential factor in the Arrhenius equation. A value of –3.2 was obtained for $\ln(k/min^{-1})$ at 120 °C, where k is the reaction rate constant calculated using the kinetic parameters.

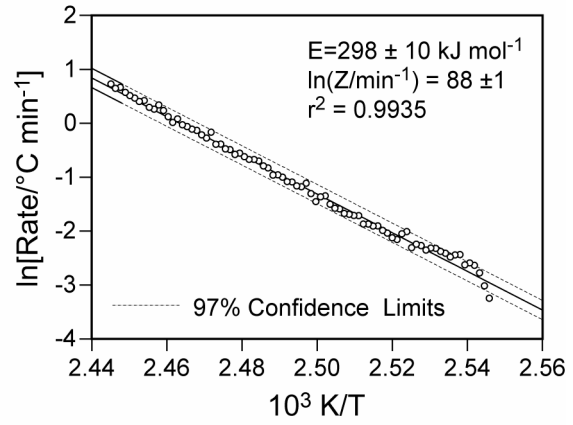


Figure 5. ARC results for 0.5 g of smoke composition in air (ln(Rate) vs. 1/T).

Isothermal ARC runs in air at 100, 105, 110 and 115 °C were also performed for the smoke composition. Figure 6 shows a plot of $\ln(\Delta t)$ against the isothermal temperatures, where Δt is calculated as the time taken to reach the maximum rate (2 °C min^{-1}). Assuming a zero order

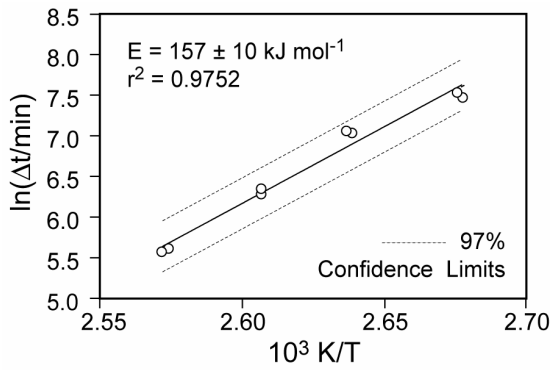


Figure 6. Kinetic results obtained from isothermal ARC data, Δt is time to Rate = 2 °C min^{-1}.

reaction, E = 157 ± 10 kJ mol^{-1} and ln(Z/min^{-1}) = 43 ± 3 were determined from Figure 6. A value of ln(k(120 °C)/min^{-1}) = –5.0 was obtained.

There is a significant difference between the rate constant and the kinetic parameters determined from the isothermal and heat-wait-search experiments. These differences may result from the invalidity of the assumption of a zero order reaction.

Figure 7 presents TG-DTA results for the smoke composition in both helium and air. In helium, the DTA curve shows a small endotherm between 130 and 170 °C, due to the loss of one molecule of water of crystallization from lactose monohydrate, followed by exothermic peaks obtained at onset temperatures of 190 and 300 °C, respectively. A small endotherm was observed between those two exotherms. The DTA curve in air shows broader multiple exotherms instead of the sharp one observed in helium. Some of these exotherms can be attributed to the oxidation of the organic dye and other smoke components as the evolution of CO_2 and some water accompanies them in both helium and air (as discussed later with reference to Figures 8 and 9).

A first-step mass loss of about 63 % in helium and 41.5 % in air ends at about 275 °C as shown in the TGA curve in Figure 7. It is possible that some oxidation causing mass increase occurs in the presence of air. Several mass loss steps follow at temperatures ≥ 275 °C, where a relatively high residual mass of smoke sample in air was detected compared with that observed in helium. The TGA baseline drift (3.3 %) can, at least in part, be attributed to the loss of moisture from the alumina pan.

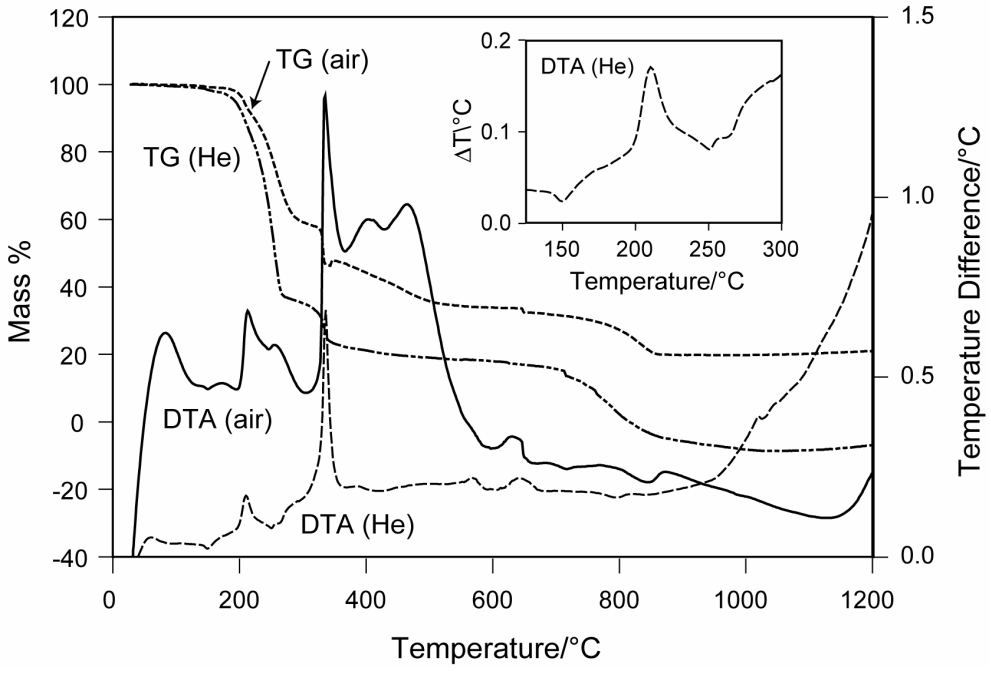


Figure 7. Comparison of TG-DTA results for 1.0 mg of smoke composition in He and in air at 20 °C min^{-1}.

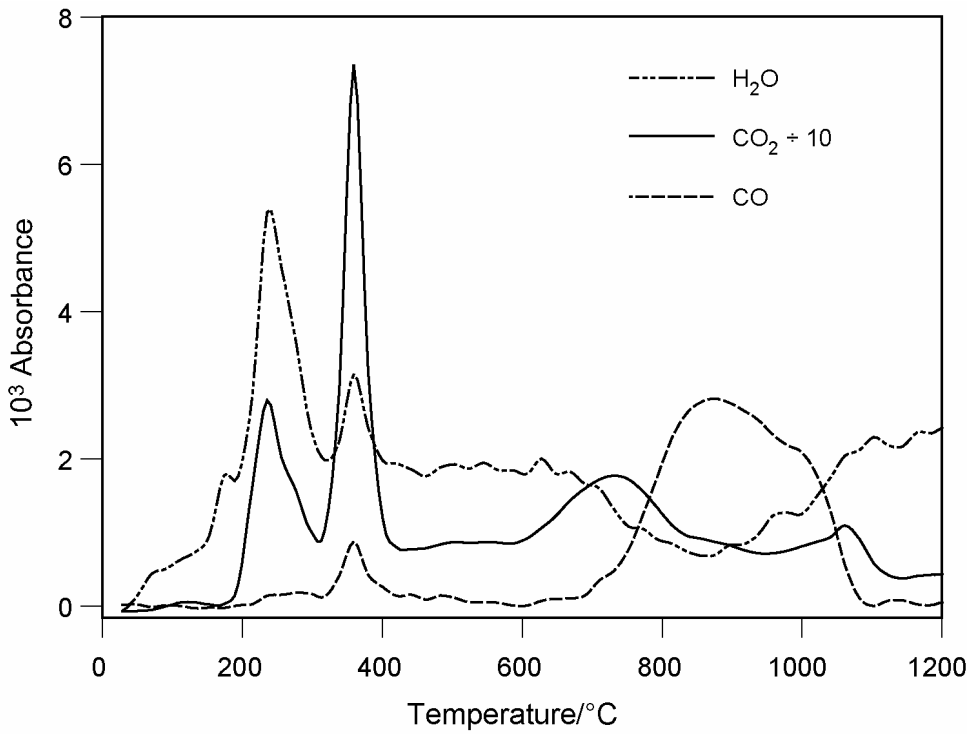


Figure 8. FTIR results for 1.0 g of smoke composition in He at 20 °C min^{-1}.

Figure 8 shows the major evolved gases for the smoke composition in helium. Traces of acetic acid, nitric acid, formic acid and ammonia were also identified by comparing the observed spectra with those provided in a product library.

The detected absorbances of CO_2 and CO were converted to concentration relative to CO_2 (as shown in Figure 9) using scaling factors provided in reference 8. Since the scaling factor for water was not available, its relative concentration was not estimated. The FTIR results in helium (Figure 9) showed that CO_2 was evolved in larger amounts than CO at temperatures below 700 °C, while CO was evolved in larger amounts than CO_2 above 700 °C. In air, CO_2 was evolved in larger amounts than CO over the entire temperature range.

Discussion of Results

Thermal analysis for the smoke composition, the 1-AAQ dyes (from B0219 and Bayer), and the potassium chlorate–lactose mixture was performed using TG, DSC, ARC, and TG-DTA-FTIR-MS. It was of interest to study the thermal behaviour of components in order to clarify the thermal behaviour of the smoke composition.

According to the TG and DSC results, 1-AAQ dye from B0219 contains a significant amount of nonvolatile impurities, much more than the sample from Bayer.

Heat generated by the reaction of potassium chlorate (oxidizer) and lactose (fuel) is responsible for volatilizing the organic dye in a smoke device.[1] The smoke composition sample studied in this report was claimed to have a ratio of 1.4:1 by mass (potassium chlorate:lactose). Thus, the potassium chlorate–lactose reaction can be represented by the stoichiometric reaction in equation 1

$$4\ KClO_3(s) + C_{12}H_{22}O_{11}(s) \rightarrow 4\ KCl(s) + 12\ CO(g) + 11\ H_2O(g) \quad (1)$$

The DSC, ARC and TG-DTA results show that the smoke composition sample exhibited a smooth and rapid exotherm resulting from the potassium chlorate–lactose reaction (eq 1). This reaction provides the energy that is necessary to cause the sublimation and partial decomposition

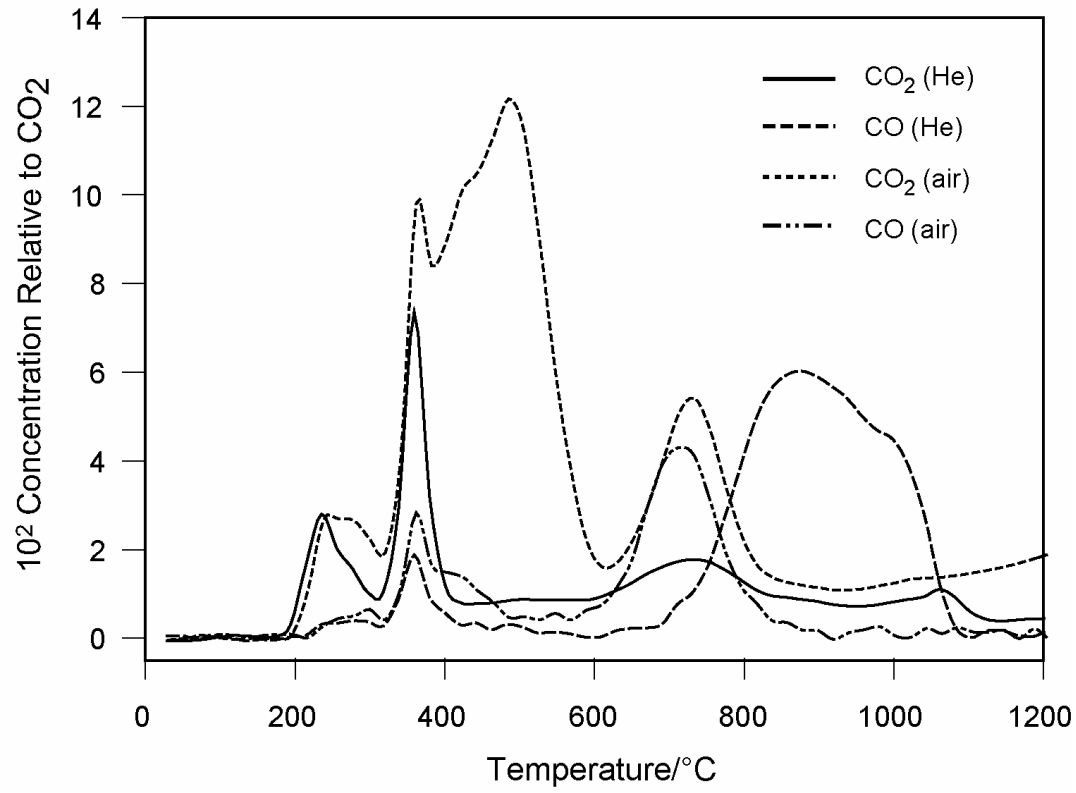


Figure 9. Comparison of FTIR results for smoke composition in He and in air at 20 °C min^{-1}.

(an undesirable event) of the organic dye. As shown in the balanced equation 1, CO would be the main product of the reaction. However, FTIR results showed that more CO_2 was evolved than CO for T < 700 °C (see Figure 9). The production of CO is only favoured above 700 °C as in equation 2:[9]

$$6\ C(s) + 6\ CO_2(g) \rightarrow 12CO(g) \qquad (2)$$

The DTA results suggest that the lactose monohydrate loses one molecule of water between 130 and 170 °C as shown by a small endotherm. Subsequently, a strong exothermic reaction took place at about 200 °C, during which some of the potassium chlorate was rapidly reduced to potassium chloride as shown in equation 1. This agrees with TG-DTA results for the potassium chlorate–lactose mixture presented in Figure 2. The temperature of the reaction coincides with that for the fusion of lactose. It may be reasonably surmised that this reaction was initiated by the partial solution of the potassium chlorate in liquid lactose, since potassium chlorate is very soluble in solvents containing hydroxyl groups.[6] It is likely that the reaction presented in equation 1 occurs simultaneously with the decomposition of lactose between 260 and 300 °C,[6] as shown by equation 3:

$$C_{12}H_{22}O_{11}(l) \rightarrow 12\ C(s) + 11\ H_2O(g) \qquad (3)$$

This assumption also explains the termination of the reaction before all the chlorate is decomposed, but there is no evidence for this phenomenon in Figure 7. Heat evolved from the reaction presented in equation 1 should be enough to enhance dye sublimation, as shown by a small endotherm at about 240 °C (Figure 7). However, it should be noted that the sample was subjected to a temperature ramp in the experiments and that sublimation of the dye would occur even in the absence of self-heating. The second sharp exotherm (Figure 7), similar to the second exotherm obtained from the potassium chlorate–lactose mixture (Figure 2), occurred between 300 and 370 °C, near the melting point of potassium chlorate and this may be initiated by this melting. This reaction is the oxidation of the carbonaceous residues by the remaining potassium chlorate[6] as presented in equation 4.

$$KClO_3(l) + 1.5\ C(s) \rightarrow KCl(s) + 1.5\ CO_2(g) \quad (4)$$

The carbonaceous residues might come from residual unsublimed dye, unreacted lactose, the decomposition of polyvinyl acetate or the decomposition of an impurity. In contrast with the first exotherm, less water was evolved (see Figure 8) and the main gaseous product of this reaction was CO_2 as determined by FTIR and MS. It should be noted that the vaporization of the dye occurs before the second stage of the process (200–250 °C) comprising the reactions represented by equations 1 and 4. Several decomposition steps of smoke components were present at temperatures above 500 °C, producing water, acetic acid, nitric acid, formic acid and ammonia as detected by FTIR (Figures 8 and 9). The presence of nitrogen-containing species indicates some decomposition of 1-AAQ. A relatively large amount of CO was produced above 700 °C apparently from the reaction of residual carbon with water (eq 5) or CO_2 (eq 2) or both

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \quad (5)$$

The TG-DTA results for the potassium chlorate–lactose mixture of 1.4:1 by mass ratio were compared with those obtained from the smoke composition in Table 1. The peak area (A) is used only for a qualitative comparison and is not an absolute value of enthalpy. The values of A for the smoke composition were calculated as per the mass of potassium chlorate–lactose present in the smoke composition according to the ratio mentioned earlier. In Table 1, the small endotherm is of similar area and onset temperature for the two samples. The first exothermic peak was larger for the potassium chlorate–lactose mixture than that for the smoke composition, which indicates that dye evaporation reduced the net exotherm. The lower value of A for the smoke composition reflects the fact that a significant amount of the 1-AAQ dye evaporated. The second exothermic peak (see Table 1) was larger for the smoke composition, which indicates the presence of more carbon to be oxidized by potassium chlorate. This carbon might have arisen from unreacted lactose or also from unevaporated dye or from both. The percentage contribution of the potassium chlorate–lactose reaction in the first-step mass loss in the smoke composition was estimated to be about 20 %, based on TG-DTA results for the potassium chlorate–lactose mixture. Assuming similar behaviour of potassium chlorate–lactose mixture in the smoke composition, this means that only 78 % of the dye content in the smoke composition will evaporate.

The smoke composition behaved differently in the TG-DTA and TG with respect to the residual mass content at the end of the runs. These differences may have resulted from the different experimental parameters used in the TG-DTA system compared with those used in the TG, or they may simply have been a result of a lack of homogeneity in the smoke composition sample. The lower residual mass content of the smoke sample obtained from the TG-DTA results in helium compared to that in air (Figure 7) indicates that, under these experimental conditions, the smoke composition contained some residues that were not oxidized in the presence of air.

The sharp exotherm for the smoke composition (Figure 3) suggests that the potassium chlorate and lactose reaction was essentially fast and complete. The impurities in B0219 are still of unknown composition. TG results showed that these impurities are of a nonvolatile nature. They might catalyze the potassium chlorate–lactose reaction, help to conduct heat into unreacted

Table 1. Comparison of TG-DTA Results in Helium.

	Endotherm		1st Exotherm		2nd Exotherm	
Sample	$\frac{T_{onset}}{°C}$	$\frac{A}{°C\ min\ mg^{-1}}$	$\frac{T_{onset}}{°C}$	$\frac{A}{°C\ min\ mg^{-1}}$	$\frac{T_{onset}}{°C}$	$\frac{A}{°C\ min\ mg^{-1}}$
Potassium chlorate-lactose mixture	147	0.037	196	0.84	336	0.51
Smoke containing B0219 dye	141	0.034	200	0.19	328	1.08

materials, react with chlorate and supply more heat to the process or some combination of these. An important factor that should be considered is the potassium chlorate to lactose ratio. Any change in this ratio will affect the amount of the dye sublimated due to changes in the heat evolved from the lactose oxidation reaction.

The heat evolved from the exothermic peak for the smoke composition sample of 3.2 ± 0.1 kJ g^{-1} (mass of potassium chlorate and lactose mixture), due to the potassium chlorate–lactose reaction, was compared with the literature value of 2.7 kJ g^{-1} for the reaction represented by equation 1. It should be mentioned that it is not expected to get exact ΔH values since the smoke composition is a complex mixture. Although the smoke composition containing B0219 dye functioned well in a smoke device and exhibited a sharp exotherm, it does not necessarily mean that the potassium chlorate–lactose reaction was complete. Smoke compositions are heterogeneous mixtures of a variety of components. Sampling of these mixtures at the milligram scale for DSC/DTA and TG measurements is always subject to uncertainties since these samples may not be representative of the composition on a bulk scale.[10]

Conclusions

Simple thermal analysis by DSC testing showed that the melting point of 1-AAQ dye from B0219 was lower than that of Bayer, and TG showed that B0219 has a substantial residual mass; both observations point to the presence of an impurity.

The smoke composition reacted smoothly in the DSC and TG-DTA (in helium) experiments showing rapid exotherms and also displaying a smooth, uninterrupted runaway reaction in the ARC.

References

1) *Encyclopedia of Explosives and Related Items*, Picatinny Arsenal, Part 2700, V8, Dover, NJ, USA, 1978.

2) A. Chin and L. Borer, "Identification of Combustion Products from Colored Smokes Containing Organic Dyes", *Propellants, Explosives, Pyrotechnics*, Vol. 8 (1983) pp 112–118.

3) D. E. G. Jones, R. A. Augsten, K. P. Murnaghan, Y. P. Handa and C. I. Ratcliffe, "Characterization of DMNB, a Detection Agent for Explosives, by Thermal Analysis and Solid State NMR", *J. Thermal Analysis*, Vol. 44 (1995) pp 547–561.

4) D. I. Townsend and J. C. Tou, "Thermal Hazards Evaluation by an Accelerating Rate Calorimeter", *Thermochimica Acta*, Vol. 37 (1980) pp 1–30.

5) G. Krien, "Thermoanalytische Untersuchungen an Rauchfarbstoffen", *Thermochimica Acta*, Vol. 81 (1984) pp 29–43.

6) F. S. Scanes, "Thermal Analysis of Pyrotechnic Compositions Containing Potassium Chlorate and Lactose", *Combustion and Flame*, Vol. 23 (1974) pp 363–371.

7) W. J. Sichina, *Characterization of Water of Hydration of Pharmaceutical Using the Pyris 6 DSC*, application note, PETech-54, Perkin Elmer Instruments, www.perkinelmer.com

8) T. B. Brill, H. Arisawa, P. J. Brush, P. E. Gongwer, and G. K. Williams, "Surface Chemistry of Burning Explosives and Propellants", *J. Phys. Chem.*, Vol. 99 (1995) pp 1384–1392.

9) *HSC Chemistry Software for Windows*, Ver. 4.0, Outokumpu, 1999.

10) P. D. Lightfoot, R. C. Fouchard, A.-M. Turcotte, Q. S. M. Kwok and D. E. G. Jones, "Thermal Techniques used in the Hazard Evaluation of Pyrotechnics", *Journal of Pyrotechnics*, No. 14 (2001) pp 15–26.

Assessing the Risks — Suggestions for a Consistent Semi-Quantified Approach

Tom Smith

Davas Limited, 8 Aragon Place, Kimbolton, Huntingdon, Cambs., PE28 0JD, United Kingdom

ABSTRACT

Assessing the risks of an operation, the operation of a whole factory, or the consequences of firing a firework display has become a way of life. Much modern legislation, certainly in the UK, is based less on "prescription" and more on "goal setting", which requires the risk creator to determine the nature of the risk and to allow him to control it adequately. Everyone involved in almost any activity, be it sport, driving, or managing a pyrotechnic production facility, has always assessed the risks—normally in their head and on the job. Modern legislation demands that these informal processes, accurate as they may have been, be documented, monitored and revised as appropriate, partly at least to "prove" in any post-accident enquiry that adequate steps had been taken to identify the particular circumstances that caused the accident. Failing to identify a particular risk is as negligent as failing to control a risk that had been identified.

Keywords: risk assessment, consequence, hazard management

What Does Assessing the Risks Mean?

Assessing the risk is not the same as "doing a risk assessment". The latter term has become devalued. In many cases it simply involves photocopying the last risk assessment! Assessing the risks is a serious task, and although in any operation, for instance a firework display, many factors remain constant, there are always site specific factors that must be addressed.

For instance constant factors may include:

- the range of fireworks used,
- the methods of erecting mortars, and
- the firing system.

Factors that change from site to site, and crucially from event to event include:

- local weather conditions,
- the physical site, for instance, can mortars be dug in, can angle irons be used, or does everything have to be supported by sandbags,
- constraints of the site, for example, where there is plenty of room for varying the firing position, the choice of fireworks may be made knowing that the site can be adapted with knowledge of likely wind conditions during the display—for instance, barges held by tugs may be moved to maximize the fallout area. On the other hand, where the site is fixed, the choice of fireworks may be conservative and dictated by the "worst case" scenario, and
- local hazards (e.g., gas cylinders in the fallout zone).

That is not to say that previous risk assessments are not valuable. Over time, previous risk assessments form a valuable resource, especially where they have been shown—as a result of a "near miss" or real incident—to be lacking. Revision and modification of existing risk assessments in the light of extended experience are probably the most valuable revisions possible.

Assessing the risks does not stop when a risk assessment is written. The process is iterative and risks are not adequately controlled if the process is stopped at any point. Old, out of date risk assessments are almost as useless as no risk

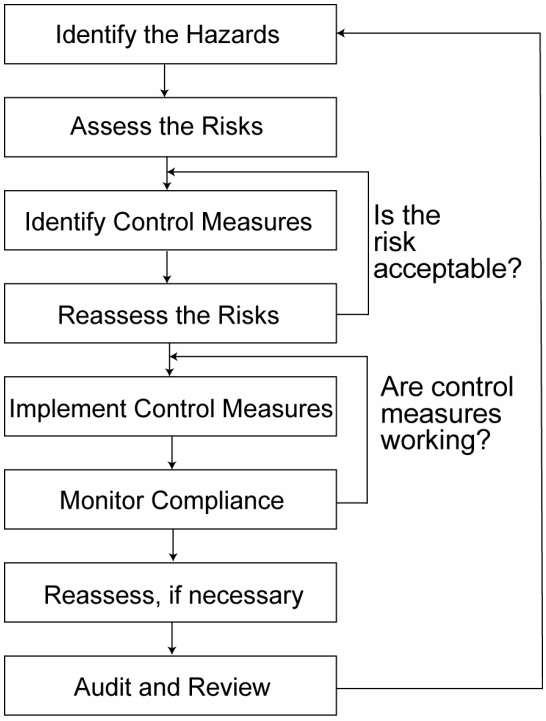


Figure 1. Flow chart for risk assessment.

assessment. Figure 1 presents a generalized flowchart for risk assessment.

Principles of Risk Assessment

Risk assessment is determining the risk posed by an operation. In its most general form the risk of an operation can be described as the product of the consequences of a particular identified incident and the frequency of the particular incident happening. Commonly this is described as

Risk = Hazard (H) × Frequency (F)

To determine the overall risk of an operation each identified risk is summed, for a variety of potential occurrences and thus consequences from a particular operation

$$\text{Total Risk} = H_1F_1 + H_2F_2 + H_3F_3 + \ldots + H_nF_n$$

For example, as a result of a fire (from whatever source) in a magazine containing solely 1.4G fireworks, which are packaged and stacked properly, the overall risk is comprised of the factors listed in Table 1.

Risk and Hazard

So what is meant by "Risk" and "Hazard" and why are the two so often confused?

The hazard of an event is the potential consequences of the event—however infrequently that event may occur. It is the intrinsic potential for harm, the consequence of an event. Synonyms for hazard include

- consequence and
- danger (a poor term and one with negative connotations)

The risk arising from that event considers both the intrinsic hazard of the identified event and the frequency of that event occurring.

Synonyms for frequency include

- likelihood,
- probability,
- incidence, and
- rate.

Table 1. Overall Risk from a Fire in a Magazine Containing Only 1.4G Fireworks.

Event	Hazard	Frequency
Rapid escalation leading to mass explosion	Building destruction, fragmentation, blast wave, "domino effects" to adjacent magazines	Very low
Projection of firework stars through open door	Burns, thermal effects, ignition of adjacent magazines, etc.	Probable
Smoke plume, deposition of heavy metal salts, etc.	Toxic hazard to fire fighters, environmental aspects, etc.	Probable
Effects confined entirely within magazine	No hazard to outside, however hazard during clean up, etc.	Low

Quantitative vs. Qualitative Risk Assessment

Quantitative Risk Assessment (sometimes referred to as "Quantified Risk Assessment"—but both Quantitative and Qualitative Risk Assessment are also referred to, ambiguously, as QRA) is the process of trying to determine the consequences of an event and the frequency of that event happening using "real" numbers. In this way an estimate of the overall risk may be obtained that is comparable with other risks that workers and the public face during normal activities. For example, in the UK a risk to a specified individual is considered broadly acceptable if it leads to a fatality at a frequency of 1 in 10^{-6} (i.e., about one in a million years). Fatalities more frequent than this may be acceptable provided they are "As low as is reasonably practical", so called ALARP, or they may be unacceptable. The upper end of the ALARP region in the UK is taken to be about 1×10^{-4} (or about one every ten thousand years) for members of the public. For workers, who may accept a greater level of risk as a consequence of working, the figure is taken to be 1×10^{-3} (or about one every thousand years).

ALARP implies that necessary steps should be taken to reduce the risk, provided that they are "reasonable". Ultimately therefore the measure of ALARP is often based on cost. Sometimes changes could be made that reduce risk slightly, but are cost prohibitive and therefore not practical. On the other hand, some risk control measures may be simple to achieve and also are cost effective.

Quantitative Risk Assessment is a very complicated and rather imprecise science. For instance, to assess the overall risk resulting from an explosion in a brick built magazine, the following facts (and many others) all need to be quantified:

1) Frequency of the event
   a) How often does an ignition occur?
   b) How often does this lead to a mass explosion?
2) The effect on workers and the public
   a) How far away are potential victims (e.g., do they lie in a debris zone, a blast zone or a fire zone)?
   b) How much time does each potential victim spend at that location?
   c) What is the effect of the incident on people in the open, or within buildings?
3) For people in the open
   a) How much time are they in the open?
   b) What fragments from the explosion are fatal to them?
4) For people in buildings
   a) What is the building construction?
   b) What is the effect of building collapse?
   c) What is the effect of window shatter?
5) What control measures are there
   a) Earth mounding?
   b) Directional effects?

It is obvious that this process is not simple!

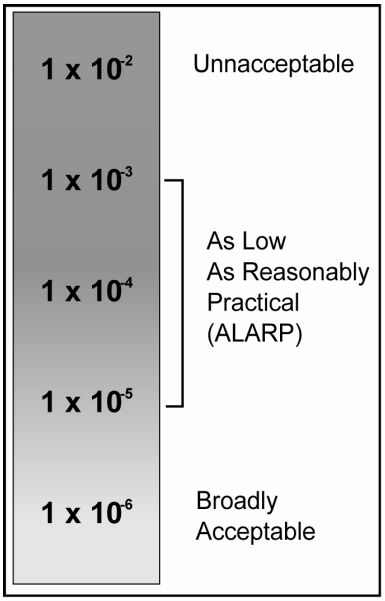


Figure 2. Individual risk.

Attempts have been made to quantify some of these variables. Merrifield and Moreton[1] conclude that accidents at licensed explosives sites occur at about 1×10^{-4} per building year—in other words, if there are 5000 licensed buildings

in the UK, they would expect an unintended ignition about once every other year. Their analysis concentrated on events that led to investigation and thus may actually under-report the frequency of unintentional ignitions. On the other hand, their own figures suggest that post 1974 (the introduction of new general Health and Safety regulations in the UK), the frequency dropped markedly.

Calculating a pure frequency for unintentional ignitions on a firework display site is much more difficult. In many cases a premature ignition may go unrecognized during a display; however, the consequences of such an ignition are usually negligible—providing that the firework continues to function normally. On the other hand, ignitions during rigging and testing have potentially severe consequences, and although the frequency remains low, good risk assessment and consequence control measures are needed to prevent accidents. For instance, responsible firework companies do not test electrical circuits with personnel in the firing area.

The consequences of an incident are also complex to determine. For instance the effect of debris on a person depends on:

- the trajectory of the debris,
- the area they present to debris (for low trajectory debris this is their frontal area, but for high trajectory debris this is their plan area),
- their distance from the explosion, and
- the amount and type of debris produced.

An extensive analysis of models used to predict consequences of an explosion was carried out in the recent review of UK explosives legislation.[2] A comprehensive paper detailing various consequence models available has also been produced by the UK's Advisory Committee on Dangerous Substances.[3] Both papers mainly consider the consequences of high explosive events, whether they are from blast wave or debris. Similar analysis of lower order events, especially those involving fireworks and pyrotechnics, is very rare.

Individual and Societal Risk

Not only does the risk need to be quantified as above, but the risk to two quite separate types of person must be considered. The two types are:

Individual, identified persons—for instance the operator of a particular process or the occupier of a particular dwelling that lies within an area likely to be affected by an incident.

Society as a whole—people passing by a factory on a busy road and the whole population surrounding a particular facility.

The assessment of the risks to these two separate types of person is termed "Individual Risk" and "Societal Risk".

Previously it was stated that the standard for acceptability of individual risk is taken to be 1×10^{-6}. The acceptability of a societal risk is much more complicated. In the most general terms, society's acceptance of a risk is inversely proportional to the number of people who may be affected by the risk. For instance, we all accept, although perhaps we shouldn't, that individuals are killed in road accidents every day of the year. These fatalities rarely make even local news reports; this risk has become a fact of life. However, if, a pile-up kills 10 people, we can be sure that the event will be reported widely in the locality and may even make national news. If hundreds of people are killed, the event will be reported internationally. If children are involved the event will get wider attention for smaller numbers of fatalities.

A plot of cumulative frequency of incidents (F) and number of fatalities (N), the F/N curve (Figure 3), is very reminiscent of the simple plot for individual risk and highlights the same three areas:

- where the risk is unacceptable,
- where risk reduction is required, and
- where the risk is considered negligible.

In practice the calculated societal risks resulting from an incident are normally laid over the acceptability chart above, and the overall acceptability of the risk (or otherwise) determined from where the points lie in relation to the areas above. Calculations may be made on

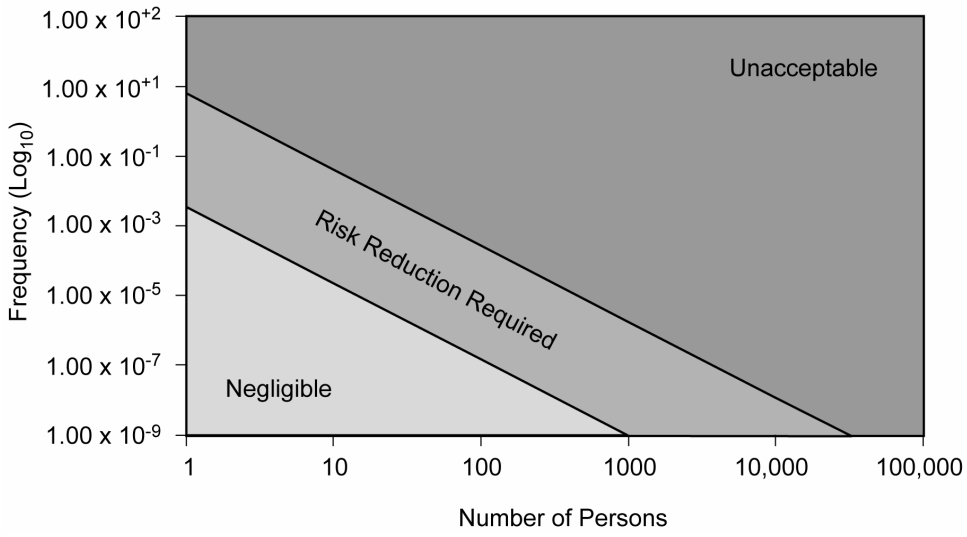


Figure 3. Generalised f/N curve.

the basis of hazard identification and mathematical modelling of consequence analysis.

This is not to say that we should necessarily equate acceptable societal risk with media perception, but the two run closely hand in hand!

Societal risk should be, but not always is, summed over an entire population—that is, in any one year, any event leading to multiple fatalities should be considered, and therefore the total risk should be calculated across all establishments that may pose that risk. It is unlikely that society would accept multiple incidents over a range of establishments during a relatively short time scale without rightly asking questions as to whether the risks were properly controlled across the entire industry.

Sadly, the public who thus determine the acceptable levels of societal risk are also the people who least understand the nature and mathematics of risk calculations. Indeed the public have little concept of frequency—otherwise why would so may indulge in the lottery!

As a result, most risk assessment is carried out on a qualitative or semi-quantitative basis. The remainder of this paper will concentrate on this approach.

Qualitative Risk Assessment Schemes

There are almost as many qualitative risk assessment schemes as there are people carrying out risk assessments—each may have had its merits, but we are now firmly convinced that a biased 0–10 rating system is the best. See Table 2.

Table 2. Comparison between Some Qualitative Risk Assessment Schemes.

Scheme	Ratings	Comments
Descriptive	Low, Medium, High	Too crude and too few divisions.
Simple 3 tier numeric	1,2,3	As above
Simple 6 tier numeric	1,2,3,4,5,6	Better - but need a “zero” entry
Simple 7 tier numeric with zero	0,1,2,3,4,5,6	Good
Biased 0–10 numeric	0,1,2,3,4,6,8,10	Good, puts greater weight on risks of high consequence or high frequency events

Potential Frequency Rating (PFR)

PFR	Description of Frequency	Approximate Frequency (per year)	Example
0	NEVER happens	$F = 0$	Firework debris falling 2 miles upwind
1	Very unlikely to happen	$F < 10^{-7}$	
2	Happens only rarely	$10^{-5} > F > 10^{-7}$	
3	Occasionally happens	$10^{-3} > F > 10^{-5}$	
4	Happens	$10^{-1} > F > 10^{-3}$	Firework fuse fails
6	Frequently happens	$1 > F > 10^{-1}$	
8	Almost always happens	$F > 1$	Lit firework debris landing in firing area
10	ALWAYS happens	$F > 10$	Firework debris landing on ground

Potential Severity Rating (PSR)

PSR	Description of Severity	Example
0	NOTHING of consequence	Ash on hand
1	Single trivial injury	Lit ash on hand causing very minor burn (e.g., from a sparkler)
2	Multiple trivial injuries	
3	Single minor injuries	Ash in eye
4	Multiple minor injuries	
5	Single major injury	Loss of limb
6	Multiple major injuries	
8	Single fatality	Death - immediate or as a result of injury
10	Multiple fatalities	

The advantages of a biased 0–10 scheme as indicated in the above chart are as follows:

- It includes a zero rating for both frequency and severity. This relates to risks that have no identified consequence or those that simply cannot happen. For example an explosives incident at an explosives factory cannot, by itself, affect a nuclear power station 10 miles away. An explosive incident at the same plant that resulted in release of a toxic gas could, on the other hand, affect the same power station as a result of wind drift and dispersion. Although many regulations (in the UK at least) require only the assessment of "significant risks", it is often better to document and dismiss a risk than not to document it at all!
- Although what follows rating of frequency and severity is just mathematics, the multiplication of the Hazard and Frequency components to evaluate Risk, biasing both ratings at the top end, the highest frequencies and highest consequences, allows risks where more than one group of people are affected to be rated higher than where only one group is affected, and frequently occurring risks to be rated higher than rare occurrences.
- The scheme has enough divisions to allow risks to be rated in a meaningful way and to allow risk control measures to have a real effect on the mathematics of the risk. For instance, a risk that potentially injured many people may be reduced to one that only caused minor injuries to many people once control measures are in place. Both these might be considered "medium" severities in a simple 3 tier scheme, so no risk reduction would be apparent.

Each potential identified risk should be assessed for both hazard and frequency and then rated for risk. In this way, each risk is related on a scale of 0–100 (Figure 4), and for multiple effects from the same event (e.g., both on-site

PFR/ PSR	0	1	2	3	4	5	6	8	10
0	0	0	0	0	0	0	0	0	0
1	0	1	2	3	4	5	6	8	10
2	0	2	4	6	8	10	12	16	20
3	0	3	6	9	12	15	18	24	30
4	0	4	8	12	16	20	24	32	40
5	0	5	10	15	20	25	30	40	50
6	0	6	12	18	24	30	36	48	60
8	0	8	16	24	32	40	48	64	80
10	0	10	20	30	40	50	60	80	100

	Broadly acceptable
	ALARP region
	Unacceptable region

Figure 4. Simple semi-quantified risk assessment.

and off-site fatalities), those events that pose the greatest risk are identified by simple addition. Figure 4 also identifies those areas where the resulting risk may be considered acceptable, often described by regulators as "broadly acceptable". This term acknowledges that the risk is not completely controlled and—once higher risks have been reduced—this area may merit revisiting to control the risk further. No enforcing authority will ever commit themselves to agreeing that a risk is fully and acceptably controlled and that it always will be. The remaining regions are those where the risk is unacceptable, and the vast majority where the risk is "ALARP". Again the plot resembles that for individual and societal risks.

In the ALARP band, steps should be taken to reduce the risks, but any such risk reduction measures must be proportionate with the effort required to achieve them, both practically and financially. Ultimately, therefore, risk reduction cannot be separated from cost expenditure. Every firework fired could be entirely safe to the operator if the operator is situated behind a 30 cm thick steel plate 2000 m from the firing area, but this is neither practical nor cost effective.

The challenge to industry is to be consistent in assessing both the hazard and frequency of any event in this simple, semi-quantitative, approach where definitions have been made in terms of, for instance, "happens" and "frequently happens". The virtue of using an extended 0–10 scale is that, in the light of experience, the frequency or hazard of an event may be reassessed when control measures are in place and the risk reassessed. For instance, shells discharging prematurely from stray sparks where the shell leaders are completely unprotected "happens". It is not a frequent event, nor is it an infrequent event. Covering each leader with tinfoil and protecting the mouth of each mortar with more tinfoil may reduce this to "happens only rarely"—a reduction in potential frequency rating (PFR) from 4 to 2. Assuming the consequences stay the same, this reduction in PFR reduces the overall risk from *this event* by half.

It is important to realize, however, that measures taken to reduce a particular risk to one set of individuals may actually increase the risk to others. The classic case here is electrical firing of racks of shells. Removing the operator from the firing point reduces the risk to him, but he may be so removed that he is unable to determine that the rack has been disrupted in some way and is now pointing horizontally towards the audience, thus greatly increasing the risk to them! All risk reduction measures must be such that the consequential risks to all parties are examined. The analysis may ultimately conclude that the measure is not effective. In the case of electrical firing of shells in mortar racks the

Example 1. Extracts from generalised risk assessment for a UK Firework Competition. Note that each competitor in the competition also has to provide a site specific risk assessment pertinent to the materials they are firing and their methods of rigging.

Risk Assessment — *Display*

Hazard & Effect	Details		Initial Risk	Minimise Risk By	Managed Risk
Unpacking display at site	Site/Process	Display Site	Hazard Index 10	*Good manual handling, monitoring etc*	Hazard Index 10
	Who Affected	Operator/Public	Frequency 2		Frequency 1
			Risk Index 20		Risk Index 10
Final assembly work (eg Lancework)	Site/Process	Display Site	Hazard Index 3	*Training*	Hazard Index 4
	Who Affected	Operator	Frequency 2		Frequency 1
			Risk Index 6		Risk Index 4
Manual handling of equipment	Site/Process	Display Site	Hazard Index 3	*Training*	Hazard Index 4
	Who Affected	Operator	Frequency 2		Frequency 1
			Risk Index 6		Risk Index 4
Hand firing of display	Site/Process	Display Site	Hazard Index 10	*Training, adequate fuse lengths etc*	Hazard Index 8
	Who Affected	Operator	Frequency 2		Frequency 1
			Risk Index 20		Risk Index 8
Electric firing of display (remote)	Site/Process	Display Site	Hazard Index 10	*Training*	Hazard Index 8
	Who Affected	Operator	Frequency 2		Frequency 1
			Risk Index 20		Risk Index 8
Misfired fireworks (not inc shells)	Site/Process	Display Site	Hazard Index 10	*Training, cool off period. Crowd control*	Hazard Index 6
	Who Affected	Operator/Public	Frequency 2		Frequency 1
			Risk Index 20		Risk Index 6

process will present a lower risk overall, only if adequate precautions have been taken to secure the mortar racks from disruption (e.g., adequate sandbagging, stakes, separation of tubes within the rack, etc.).

The Role of Risk Assessment in UK Pyrotechnic Operations

As noted above, UK law has gradually changed from one of "prescription" to one of "goal-setting". This change, brought about in essence by the publication of the Robens Report[4]—a fundamental review of UK Health and Safety legislation—has not been universally welcomed. Small businesses, which are predominant in the pyrotechnics sector—at least in the UK, would generally rather be told what they can and cannot do. Small businesses do not have the resources, time or staff to base their entire operations on even semi-quantified risk assessment. The Manufacture and Storage of Explosives Regulations (due for adoption in early 2004) recognize this and do lay out prescribed "Quantity/Distance" tables relating the permitted quantity allowed to be stored in a building to the "Hazard Type" of the material being stored, the construction of the building, and the proximity of inhabited buildings, major roads, etc.

Which Risks Are the Most Important To Address First?

Which risks are the most important to control effectively? It is tempting to conclude that high frequency risks are the most important, because they are the most easily dealt with. However, these risks should be of low consequence. (If they are high consequence *and* high frequency, then you are in the wrong business.) The most important risks to control are those of high consequence that occur infrequently. The plain truth is, we control these risks poorly. We assume they will not occur, and we don't quite know how to control them anyway.

Examples of both types of event can again be found in the firing of shells.

A high frequency, low hazard incident is the premature ignition of a shell from stray sparks, leading to the shell being ejected from the mortar in its normal manner, exploding normally in the air, and presenting the same risks from functioning as a shell fired deliberately.

A mortar tube that has been disrupted (i.e., displaced or tipped over by the malfunction of an adjacent tube) provides an example of a low frequency, high hazard incident. As described in Example 1, this example also illustrates the need to calculate the risk to both operator and audience. In this case remote electrical firing of the shell would almost certainly lead to lower risk to the operator, but if he is unable to witness the disruption of the mortar, and additional measures have not been put in place to prevent a shell discharging at a low trajectory towards the audience, and he then "presses the button", oblivious to the disruption of the mortar, a significant increase in risk to the audience may result.

Keeping Risks in Perspective

As previously noted, the public has little concept of risk. There is a danger with public information that "a little knowledge is a dangerous thing". The need for scientific education of the public is far beyond the scope of this paper, pressing though it may be, but the following points are important:

- The public (or legislators or event organisers) should not be misled into thinking risks are infinitesimally small when in reality accidents and incidents do occur.
- The public should be not bombarded with overly scientific information that they are unable to understand or to draw conclusions from.
- Information should be presented dispassionately, but concisely.

If risks in the ALARP region are controlled, they are infrequent, but the consequences may be relatively severe. This is why these risks are the most difficult to present to the public, and ironically they are the most difficult to control. How many times has the press been full of "We never knew the ... factory was there" or "I didn't know we were living next to a bomb ..."?

It is important to present the information at the appropriate level to the intended audience. Poorly documented risk assessment may be rejected by enforcers, and it is hoped that the methods presented here at least provide a degree of consistency of approach that makes the enforcers' task easier.

Presenting pages of detailed analysis to the public may convince them the operation is so "risky" that it is unacceptable. On the other hand, glib, "dumbed down" statements to the public may actually increase their suspicions and lead to the conclusion that proper risk assessment has not been carried out.

Documenting Risk Assessments

Like Risk Assessment methodology, there are as many ways of documenting the assessment of risks as there are people doing it. Risk assessments range from simple, single page, documents that generally lack detail and do not address all the risks, to multipage documents full of science that fail to highlight the most important risks, and the methods in place to control those risks. Example 1 presents a sample of the documentation we now adopt. Each row (each risk) is rated on the 0–10 system outlined above and details the identified hazards, the recipients of the hazard and the consequences and frequency of the risk occurring. It also details methods to control each identified risk. In essence therefore the column of control measures becomes an operating manual. If each of these measures is in place and is working effectively, then the risks are controlled to an acceptable level. Monitoring of the controls is paramount. The failure to implement a control measure may render a risk unacceptable. Data entry to this database is via a simple screen (Figure 5). Using a database is not, however, merely a means of regurgitating old documents, this would be hardly better than merely photocopying old risk assessment forms. Instead it encourages the user to re-examine old entries on the database pertinent to the tasks being examined, and to enter and quantify newly identified hazards, particularly site-specific hazards for pyrotechnic and firework displays. It does, however, provide examples on which to base the current risk assessment and outputs data in a concise manner.

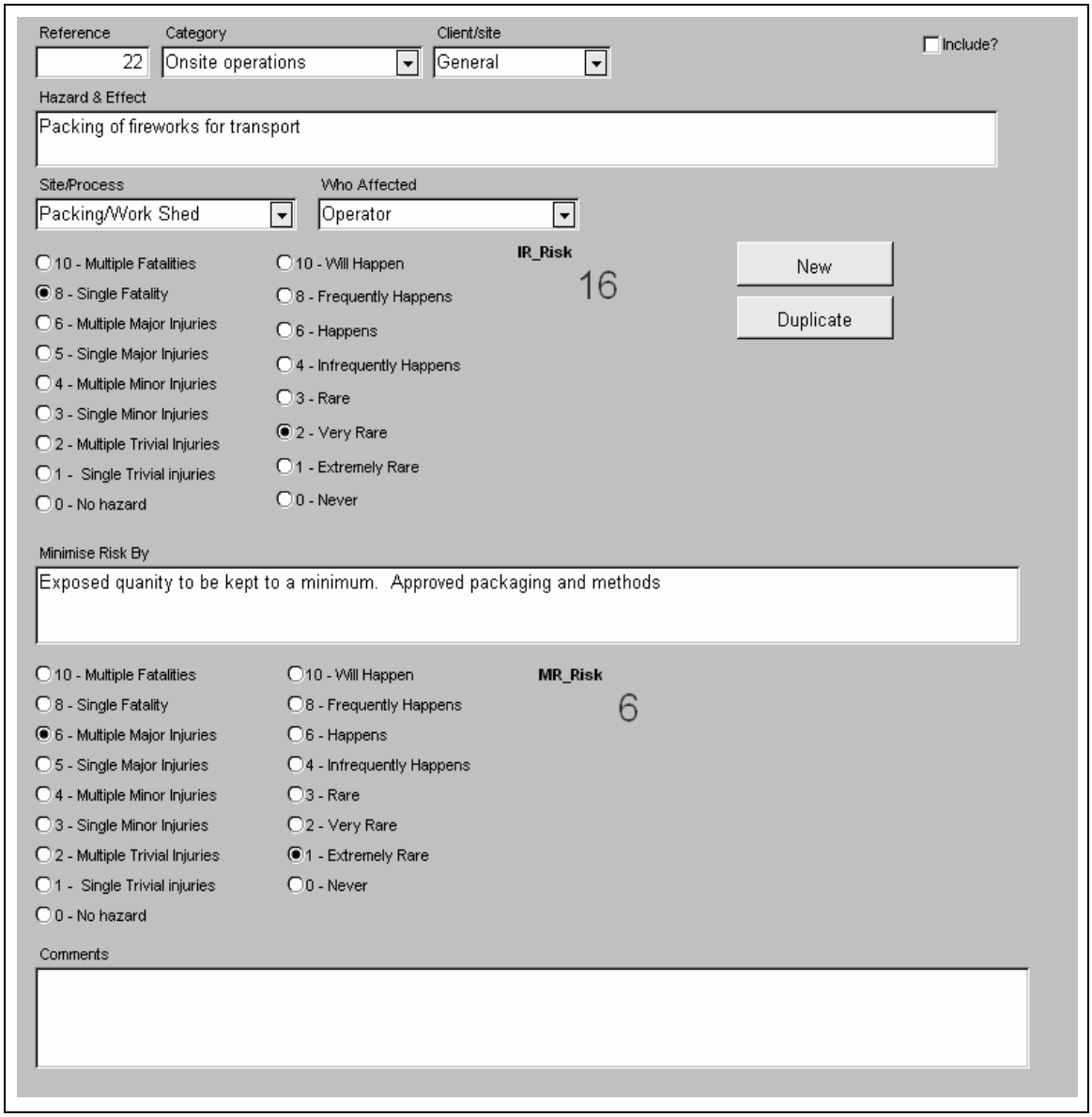


Figure 5. Data entry screen.

Conclusions

The process of assessing the risks from any operation, facility or event is a complex process, but one that ultimately not only helps quantify the risks involved but highlights, sometimes surprisingly, the highest risk operations.

Good analysis of risk also leads to identification of control measures, and thus the basis of operating procedures. However, the risk reductions achieved on paper only are meaningful if these operating procedures are adopted and monitored.

This paper presents a semi-quantified risk assessment protocol based on biased 0–10 scales for both hazard and frequency that we hope will find widespread use within the vast variety of operations throughout the pyrotechnic industry.

References

1) R. Merrifield and P. A. Moreton, "An Examination of the Major Accident Record for Explosives Manufacturing and Storage in the UK", *J. Hazardous Materials*, Vol. 63 (1998).

2) Controlling Risks around Explosive Stores — Review of the requirements on separation distances. Health & Safety Executive 3/02 http://www.hse.gov.uk/research/content/misc/qdwgrep.pdf

3) *Selection and Use of Explosion Effects and Consequence Models for Explosives* [ISBN 0-7176-1791-2].

4) Safety and Health at Work. The report of the Robens Committee, Cmnd 5034, Published June 1972. For a review on it's conclusions and impact see http://www.saxtonsmith.co.uk/robens.html

Bibliography

A Simple Problem to Explain and Clarify the Principles of Risk Calculation by Dennis C. Hendershot http://home.att.net/~d.c.hendershot/papers/pdfs/riskland.pdf

Environmental risk assessment: an Australian perspective by Tom Beer http://www.environment.gov.au/ssg/pubs/risk/risk1.html

Health & Safety Executive, *The Tolerability of Risk from Nuclear Power Stations*, 1988 (revised 1992) HMSO, London [ISBN 011 886368 1].

Health & Safety Executive, "Reducing Risks Protecting People", http://www.hse.gov.uk/dst/r2p2.pdf

Editorial Policy

Articles accepted for publication in the *Journal of Pyrotechnics* can be on any technical subject in pyrotechnics. However, a strong preference will be given to articles reporting on research (conducted by professionals or serious individual experimenters) and to review articles (either at an advanced or tutorial level). Both long and short articles will be gladly accepted. Also, responsible letters commenting on past Journal articles will be published, along with responses by the authors.

Control Systems for the Storage of Explosives, Including Fireworks

M. J. Bagley

Health and Safety Laboratory, Harpur Hill, Buxton, Derbyshire, SK17 9JN, United Kingdom

Disclaimer: The views expressed in this paper are those of the author and reflect his understanding of the information collected during a study carried out on behalf of the Ministry of Social Affairs and Employment in The Netherlands. As such, they should not necessarily be taken to be the views of the UK Health and Safety Executive.

ABSTRACT

This paper gives an account of the use of a questionnaire to obtain up-to-date information on control systems for the storage of fireworks and other types of explosives. The study showed that control systems for the storage of explosives based on quantity-distance schemes are used in many countries. In most of these schemes, fireworks are treated in the same way as other types of explosives.

The classification of fireworks is seen to be a particular problem because of the large number of different types that are on the market. There are also concerns about the accurate classification of fireworks stored in steel transport containers or in magazines constructed from brick or concrete. For the storage of mixed fireworks, several countries assign the fireworks to the same hazard division as the most hazardous type of firework in the store.

Keywords: explosives, storage, fireworks, control system

Introduction

This paper presents the results of a project to collect information on control systems for the storage of fireworks and other types of explosives. The project involved sending a questionnaire to organizations such as regulatory bodies, government departments and government laboratories around the world, and it was a part of a study of control systems for explosives that included a review of the literature.[1] For completeness, however, information obtained from the literature on the storage of fireworks is presented in the paper and is identified by a reference to the source material.

Development of the Questionnaire

The objective in developing a questionnaire on control systems for the storage of explosives was to obtain up-to-date information on the practices in use throughout the world. With this in mind, the control system employed in Great Britain was used to identify the issues of concern for inclusion in the questionnaire. Most of the questions had simple yes or no answers so as to obtain a good response from recipients, but a generous amount of space was left for comments or clarification of answers. To help users, guidance material included in the questionnaire was presented in a different format. Many of the recipients were known through professional contacts and others were identified from publications and from searches of the Internet.

The issues addressed in the first part of the questionnaire included the control of the hazards arising from accidental initiation of explosives, the classification of explosives for storage, the use of quantity-distance schemes, and the use of TNT-equivalence. Issues relating to the storage of fireworks were addressed in the second part of the questionnaire and included the role of packaging, the use of UN hazard divisions, storage of mixed fireworks and the type of store. An outline of the questionnaire is included as an Annex at the end of this paper.

The questionnaire was sent to recipients in 11 countries. Responses, which provided much use-

ful information, were obtained from Australia (Queensland and Western Australia), Sweden, France, Germany, Malta, Switzerland, Canada, and the United States.

Analysis of Responses to the Questionnaire

Types of Control System and Background Legislation

All of the countries responding to the questionnaire operate a control system for the storage of explosives that is separate from systems for the control of other dangerous substances. Great Britain also has a separate system for the control of explosives, and the main enabling legislation is the Health and Safety at Work, etc. (HSW) Act 1974.[2] The Explosives Acts of 1875 and 1923 and subordinate legislation are still important, but the earlier requirements are being modified or replaced by new sets of regulations made under the HSW Act. For example, at the time of writing, the public comment period on new regulations on the manufacture and storage of explosives (Manufacture and Storage of Explosives Regulations) had just ended.[3] With a few exceptions, the manufacture of explosives can only be carried out in a factory licensed by the Health and Safety Executive (HSE). Similarly, premises where more than 1800 kg of explosive are kept must also be licensed by HSE.[4] Other types of store are under the control of local authorities.[5]

In the United States, the Bureau of Alcohol, Tobacco, Firearms and Explosives (ATFE) in the Department of the Treasury regulates the storage of explosives for civil use. Explosives for military use are controlled by the US Department of Defense. In Germany, different authorities are responsible for regulating the handling of different groups of dangerous substances. In France, the relevant controls are French decree n°79-846 dated 28 September 1979, a French order dated 26 September 1980 and a French information circular dated 8 May 1981. In Sweden, the controls are the Act (1988:868) and Order (1988:1145) of Explosives and Flammables and Regulations of Explosives; the Act and Order contain fundamental provisions whereas the Regulations contain detailed provisions.

Queensland, Australia operates a licensing regime that has some similarities with the British system. The controls are the Queensland Explosives Act 1999 and associated regulations. Licenses are required for the storage of explosives including blasting explosives, fireworks, propellants and emulsions of UN Class 5.1. In effect, the Explosives Act calls up the national Australian Standard AS 2187 Part 1.[6] Western Australia operates a similar set of controls, and these are applied under the Explosives and Dangerous Goods Act 1961 and associated regulations. These controls also call up the national Australian Standard AS 2187 Part 1. In Canada, explosives are controlled under the Canada Explosives Act. Other classes of dangerous goods are not permitted in magazines.

In Malta, three types of explosives are in use—explosives for military purposes, explosives for the blasting of rock, and fireworks manufactured locally. The Armed Forces of Malta are responsible for controlling the storage of military and industrial explosives, whereas local authorities are responsible for the control of fireworks. The legislation on explosives includes the Manufacture and Storage of Explosives Regulations (1937)[7] and the Control of Fireworks and Other Explosives Regulations (1999).[8] The latter regulations define a "fireworks factory" as any premises where fireworks are manufactured or stored and include controls on the discharge of fireworks (both sites and operators).

Use of Quantity-Distance Schemes

The control systems in Great Britain, Australia (Queensland and Western Australia), Sweden, France, Germany, Malta, Canada and the United States are all based on a similar type of scheme (a quantity-distance scheme) in which the quantity of explosives permitted in an installation varies according to the distance from nearby buildings and other facilities. In Queensland, the distances are only guidelines; variations are made as appropriate (e.g., for underground magazines, magazines in mountains etc). In Great Britain, the safety distances may be refined by HSE in the light of the evidence accompanying an application for a license for a store or a factory. In these control systems, the separation distances vary with the type of ex-

plosive being stored and cover separation from other buildings on site as well as separation from buildings and facilities off site. However, in Malta this is only true of stored military and industrial explosives, not fireworks. Canada uses the British table of safety distances (for former categories of explosives X, Y, Z and ZZ).[9]

Switzerland also uses a quantity-distance scheme, but it differs in that the separation distances do not vary according to the hazard division or type of the explosive being stored. The separation distances cover separation from buildings on site as well as separation from buildings off site. Very large (unlimited) quantities of explosives are stored in magazines. Smaller quantities of explosives may be kept in a locker (up to 100 kg) or in a suitable container (up to 25 kg) but only in uninhabited ground floor rooms or in works-yards.

The sophistication of the quantity-distance schemes in terms of on-site and off-site separation distances varies from one country to another. The response from Queensland pointed out that the on-site separation distances are risk-based and include separation from magazines and associated facilities such as workshops. The off-site separation distances cover separation from protected works, Class A (e.g., roads); protected works, Class B (e.g., residences and schools) and vulnerable facilities (e.g., airports and high-rise, glass-fronted buildings). The definitions of protected works (set out in national Australian Standard AS 2187 Part 0[10]) are similar to those used in Great Britain.

In the United States, the tables of separation distances in the ATFE regulations include separation from inhabited buildings, public highways and passenger railways. An inhabited building is defined as any building regularly occupied, in whole or in part, as a habitation for human beings, or any church, schoolhouse, railroad station or other structure where people are accustomed to assemble, except any building occupied in connection with the manufacture, transportation, storage, or use of explosive materials. "The ATF regulations provide safety to the general public, not the persons working in a facility, which manufactures explosives. The US Office of Safety and Health Administration regulates worker safety." In Germany, the off-site separation distances take account of the number and vulnerability of people exposed to risk but not in a quantitative way.

Except in Sweden and Malta, small quantities of explosives may be stored in facilities outside the scope of the quantity-distance control system. In France, "small" means quantities less than 20 kg (e.g. stored in a supermarket). In Western Australia, storage outside the scope of the quantity-distance scheme is limited to 150 kg and must meet regulatory requirements and be approved by an inspector of explosives. In Queensland, such storage is limited to 5 kg of blasting explosives and 50 kg of fireworks, etc. The position in Canada and in the United States is similar. For example, the ATFE regulations in the United States permit limited storage indoors, but the building must not be a residence or dwelling. In Canada, there are magazines for storing small quantities of shop goods (consumer) fireworks, propellant powders and ammunition that are outside the scope of the quantity-distance scheme. In Great Britain, 7 kg of mixed explosives (including detonators) may be stored in a substantial lockable receptacle, used exclusively for explosives and held inside a shop, house, office or warehouse. The corresponding figures for shop goods and professional fireworks are 25 and 250 kg, respectively.[5] In Switzerland, fireworks for sale for the national festival on August 1st and for the celebrations on New Year's Eve are the only instances of the storage of explosives outside the scope of the quantity-distance scheme.

Control of the Hazards Arising from the Accidental Initiation of Explosives

The various control systems differ in the way that they take account of hazards arising from accidental initiation of explosives. The control systems in Great Britain, Germany, Switzerland, Queensland and Western Australia take account of blast, projected fragments from stored material, projected debris from an explosion within a building, thermal radiation and ground shock. The German system also takes account of fire jets, hazardous gases and self-propelling objects such as rockets. The French and Canadian control systems take account of the same hazards as the British system except ground shock, whereas the system in Malta takes account of the same hazards except ground shock and ther-

thermal radiation. The British control system is currently under review, partly because there are concerns that the existing separation distances may not always adequately take account of the hazard from projected debris resulting from a mass explosion in a building constructed from brick or concrete.

Blast overpressure is the main hazard taken into account in the control systems operating in the United States and Sweden. The United States quantity-distance tables for high explosives use a blast criterion with window breakage occurring at an overpressure of two pounds per square inch (13.8 kPa). The Swedish regulations are currently under review, and, at present, only partially address the hazards from projectiles and debris. However, the Act (1988:868) allows the licensing authority to ask for a risk analysis that takes into account debris and thermal radiation.

Use of the Concept of TNT-Equivalence

The concept of TNT-equivalence can be used to compare the performance of the same quantity of different explosives. In Great Britain and France, the TNT-equivalent of an explosive is determined as the mass of TNT that would yield the same peak overpressure at a given distance as the total mass of the material under consideration. The concept of TNT-equivalence is used only rarely in Germany and not at all in Malta, Sweden, Switzerland, Canada and the United States. In the Australian standards used in Queensland and Western Australia, the net explosive quantity (NEQ) in quantity-distance tables is given as the equivalent mass of TNT. The response from Queensland pointed out that this acts as a safety factor because most commercial explosives in use in Queensland are less powerful than TNT. If an explosive is more powerful than TNT, the NEQ is increased accordingly to determine satisfactory safety distances.

Classification of Explosives for Storage and the Effect of Packaging

Queensland, Western Australia, Canada and Sweden all classify explosives for storage using the UN transport classifications, modified as necessary in the light of test data, experience or historical data and by analogy. For example, Queensland accepts the ingredients of emulsion explosives as Class 5.1 for transport but storage has to be licensed. Sweden pointed out that the UN scheme is only designed for the classification of packaged articles and for individual unpacked articles. Storage in freight containers may change the classification because of the quantity or because of self-confinement. In Canada, the classifications for storage are set out in the Canada Explosives Act.

Switzerland also classifies explosives for storage using the UN transport classifications, modified as necessary in the light of test data or by analogy, but at present, the control system does not differentiate between the various hazard divisions within Class 1.

The German scheme for the classification of explosives for storage is essentially the same as the UN scheme except that it does not have the Hazard Divisions 1.5 and 1.6. The differences from the UN scheme reflect the history of the legislation on explosives in Germany. In France, explosives are given a new classification for storage based on the UN compatibility group. However, this can be changed in the light of test data.

Neither the United States, Great Britain nor Malta use UN transport classifications for classification of explosives for storage. In Malta, industrial and military explosives are stored according to their hazard division and compatibility group. There are no classifications for fireworks. In the United States, ATFE classifies explosives for storage as high explosives, low explosives or blasting agents:[11]

a) **High Explosives.** Explosive materials which can be caused to detonate by means of a blasting cap when unconfined (e.g., dynamite, flash powders and bulk salutes).

b) **Low Explosives.** Explosive materials which can be caused to deflagrate when confined (e.g., Black Powder, safety fuses, igniters, igniter cords, fuse lighters and "display fireworks" classified as UN0333, UN0334 or UN0335 by the Department of Transportation (DOT).

c) **Blasting Agents.** (e.g., ammonium nitrate-fuel oil and certain water gels).

The storage of explosives is regulated in the United States to protect the public and to secure

explosives against theft. ATFE regulations differ from the transport requirements "because, once the explosives arrive at their final destination they may be stored with larger or mixed quantities of explosives and/or removed from the shipping container, which changes the designation". The ATFE regulations do take account of the nature of the packaging, but only in a limited number of circumstances. For example, high explosive detonators may be stored as low explosives provided that they are packaged so that they do not present a mass explosion hazard.

In Great Britain, HSE uses a system of hazard types to classify explosives for storage.[4] The hazard types were developed because there are certain conditions of storage (and manufacture) where a different hazard may be presented from that recognized in the UN classification for transport. The four hazard types use descriptions similar to those used in the UN scheme:

Hazard Type 1: having a mass explosion hazard;

Hazard Type 2: having a serious projection hazard but not a mass explosion hazard;

Hazard Type 3: having a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard;

Hazard Type 4: having a fire or slight explosion hazard or both, with only local effect.

Some of the control systems based on the UN Scheme (Queensland, Western Australia, Sweden and Germany) take account of the nature of the packaging. In Canada, there is no relaxation of the classification on the grounds of packaging. Queensland does not have confidence in the UN classification of large metal containers filled with bulk product such as emulsions. All emulsions are considered to be explosives even if not allocated to Class 1 when tested.

Effect of the Type of Storage Building

With the exception of the French control system, all the control systems take account of the type of storage building in some way. In Sweden, this is most likely to be done if a risk assessment is carried out on the facility. Germany, Queensland, Western Australia and the United States have specific requirements for the construction of magazines and other storage facilities. For example, in the United States, high explosives must be stored in a Type I or Type II magazine, which provides protection against penetration by bullets. In Queensland, magazines have to be of robust construction in order to secure the stored explosives against theft. Such magazines are considered to be a source of debris and shrapnel in the event of an incident.

The national Australian Standard AS 2187 Part 1 used in Queensland and Western Australia contains specific requirements for the construction of magazines, including separation distances, lighting, lightning protection and the use of holding-down bolts to secure certain portable and re-locatable magazines.

In Canada, there are specific stacking requirements for large stacks of propellants that have been classified for transport as Hazard Division 1.3C.

Impact on the Environment

The control systems in Queensland, Sweden, Switzerland and Germany take account of effects on the environment, although in Sweden, there are no specific regulations. The situation in Queensland and Western Australia is similar to that in Great Britain. For example, in Queensland, any local authority concerned about effects on the environment can add environmental requirements to the controls in the Explosives Act 1999. In the United States, the ATFE regulations do not contain specific requirements to protect the environment, but before a manufacturing or storage site is approved by ATFE, the site must meet all federal, state and local regulations.

Use of Quantitative Risk Assessment

Quantitative risk assessment (QRA) is used in Great Britain, France, Switzerland, Queensland and the United States. In Switzerland, the control system relies entirely on the use of quantitative risk assessment with a target level of residual risk. In Sweden, the use of QRA with respect to storage facilities is under discussion. However QRA is used for refining separation distances at manufacturing sites. In the United States, QRA is used to estimate the risk to members of the public. It is also used exten-

sively at fireworks manufacturing sites where loose, dry explosive powders and/or explosive materials are present during various stages of the fireworks assembly process. In Queensland, the Chief Inspector of Explosives can over-ride the quantity-distance tables on the basis of a competent QRA. QRA is also used to provide the basis for exemptions from the regulations and during consideration of the safe handling of explosives at ports.

Storage of Fireworks and Use of the Net Explosive Quantity (NEQ)

Queensland, Western Australia, Sweden, France, Germany and the United States all treat fireworks in the same way as other explosives. In Malta, fireworks are only used by professionals. The storage of fireworks in Malta is not controlled using a quantity-distance scheme; instead, fireworks are stored in licensed "fireworks factories". As long as a factory is situated at least 200 m away from inhabited areas, there is no restriction on the quantity of explosives stored in that factory. The regulations in Malta prohibit the use of high explosives in the manufacture of fireworks. In Queensland and in Western Australia, the use of fireworks by the general public is prohibited. The prohibition came into effect in Western Australia in 1967. Fireworks may only be used by trained, licensed operators at public displays.

The storage of fireworks in Canada differs from the storage of other explosives in that different standards for magazines are applied. In Switzerland, storage of fireworks differs from the storage of other types of explosive in that up to 300 kg may be kept in living areas.

In the United States, consumer (small) fireworks are outside the scope of the ATFE storage regulations. However, each state or municipality can make its own regulations in addition to the ATFE regulations. Federal explosive manufacturing and storage regulations must be enforced as the minimum requirements. (Note: the ATFE regulations include a simple quantity-distance table for the storage of display fireworks except bulk salutes. Bulk salutes are stored using the quantity-distance scheme for high explosives.) In France, fireworks are brought into the quantity-distance scheme by means of their TNT-equivalence.

With the exception of Switzerland, all countries responding to the questionnaire use the net quantity of explosive (NEQ) to determine the quantity of both consumer and professional fireworks permitted in storage. In Canada, separation distances for magazines use the NEQ but the licensed quantity is the gross weight. In France, Queensland and the United States, the gross weight may be used if the net weight is unknown. As noted above, in the United States, the ATFE regulations only cover professional fireworks. According to ATFE, packaging does not directly influence the storage of fireworks in the United States, but use is made of the NEQ. In guidelines established in 1991 in conjunction with experts from industry, the approximate weight of explosive materials in display fireworks is calculated for storage as 50% of the weight of the completed fireworks, unless the actual weight of the explosive material can be determined. For example if a display shell has a mass of 500 g, the net mass of pyrotechnic compositions, explosive materials and fuses would be 250 g. According to ATFE, these values are approximate industry averages, and should be within 10% of the actual mass. The estimate reflects the average composition found in both domestic and imported aerial shells. For fireworks stored loose in bins, the proprietor has to supply the mass of each shell before the mass of explosive materials can be estimated. For fireworks such as "cakes" (batteries) etc., a 25% mass calculation is sometimes applied.

In Great Britain, the gross mass rather than the net mass is used to determine inventories of manufactured fireworks in storage. Another way in which fireworks are treated differently from other types of explosive is that HSE has introduced a scheme whereby a default UN transport classification of fireworks may be claimed under the Classification and Labeling of Explosives Regulations 1983 (CLER).[12] The default system has been agreed upon by HSE and the British fireworks industry and was introduced to cope with the large number of different types and sizes of firework currently on the market or about to be placed on the market. The system provides a list of classifications according to the type of firework. Some examples of the types identified are two sizes of rocket (with or without sticks), two types of Roman candle, report shells (not in mortars) and shells (in mortar).

The publishing of the default list does not replace the requirement for HSE to classify all individual fireworks and is not intended to be used as a basis for applicants to classify fireworks themselves. Classification by the default route may be claimed where test results are not available or where no satisfactory documentary evidence of classification in the country of manufacture can be obtained.

Hazard Classification of Stored Fireworks

In most countries (France, Germany, Queensland, Western Australia, Canada and Sweden) the maximum permitted quantity of stored fireworks does depend on the UN hazard division of the stored fireworks. In France, fireworks are divided into four groups according to their mass and according to the distance that material is projected from the burning fireworks. A quantity-distance scheme is used for the storage of fireworks and is organized according to the UN transport classification of the fireworks. In Germany, fireworks are also divided into four classes according to their mass, with very small fireworks in Class 1 and large fireworks in Class 4. As in France, a quantity-distance scheme is used for the storage of fireworks and is organized according to the UN transport classification of the fireworks.

In Great Britain, the maximum permitted quantity of stored fireworks depends on the hazard type mentioned earlier. In Sweden, fireworks sold to the public are usually assigned to Hazard Division 1.3. When fireworks are stored in shops, the packaging (cardboard box) is often removed. The regulations only take mass explosion hazards into account. As noted earlier, in the United States, ATFE does not use UN transport classifications for the storage of explosives. However ATFE does distinguish between consumer fireworks defined by the US Consumer Product Safety Commission, display fireworks (defined as low explosives) and aerial salutes which contain flash compositions. Flash compositions, whether in the raw state or in a finished salute, are stored as high explosives. According to ATFE, consumer fireworks are equivalent to Hazard Division 1.4 and low explosives are equivalent to Hazard Division 1.3.

In Switzerland, the maximum permitted quantity of stored fireworks depends on the gross mass of the type of firework involved and also on the type (only for the short-term storage of professional fireworks).

France and Canada were the only countries responding to the questionnaire to confirm that the assignment of fireworks to hazard divisions for storage depends on the confinement provided by the type of store. In France, this is especially true for assignment to Hazard Divisions 1.1 and 1.2. Experience in Sweden has also shown that the type of store is important. Queensland shares British concerns about the accurate classification of fireworks stored in steel transport containers or in magazines constructed from brick or concrete. Against a background of accidents involving stored fireworks at places such as Uffculme, United Kingdom (1998)[12] and Enschede, The Netherlands (2000),[13] HSE has commissioned the Health and Safety Laboratory to undertake research on the effects of confinement on fires involving stored fireworks. Recently a bid for research in this area has been accepted as a part of the European Union's Fifth Framework Programme and involves partners in the United Kingdom, The Netherlands and Germany. Pending the results of the research, HSE has issued interim guidance on the assignment of fireworks stored in steel magazines to Hazard Types. For example, the fireworks assigned to Hazard Type 1 are all sizes and types of shell in a mortar, report shells and aerial maroons with a diameter greater than 75 mm and any items classified UN Hazard Division 1.1 by HSE under CLER. It is worth noting that these concerns are also recognized in the recent UN Recommendations on the Transport of Dangerous Goods, Model Regulations.[14] Paragraph 2.1.3.2.3 states that "The scheme of assessment is only designed for the classification of packaged substances and articles and individual unpacked articles. Transport in freight containers, road vehicles and rail wagons may require special tests which take into consideration the quantity (self-confinement) and kind of substance and the container for the substance".

In Canada, magazines for the storage of fireworks are usually of light construction. Inspectors consider the suitability of the construction of a magazine when making decisions on the maximum quantity of fireworks that may be stored.

Mixed Storage of Fireworks

In Great Britain, France, Germany, Queensland and Western Australia, mixed fireworks are assigned to the same hazard type or hazard division as the most hazardous type of firework in the store. In Sweden, shops selling fireworks to the public are permitted to store up to 100 kg of fireworks.

In the United States, aerial salutes are considered to be high explosives. However when they are mixed 50/50 with aerial shells, their classification is reduced to low explosive. In Canada, display fireworks are normally classified as Hazard Division 1.3 and this classification is used even though a small quantity of report shells classified as Hazard Division 1.1 may be present.

Conclusions

Control systems for the storage of explosives based on quantity-distance schemes are used in many countries. In most of these schemes, fireworks are treated in the same way as other types of explosives. In addition, the maximum permitted quantity of stored explosives generally depends on the hazard division or a modified form of the hazard division within Class 1 of the United Nations scheme for classifying explosives for transport.

The classification of fireworks is seen to be a particular problem because of the large number of different types that are on the market. However, a default classification scheme can help in this respect as can the use of generic definitions.

There are also concerns about the storage of fireworks in steel transport containers or in magazines constructed from brick or concrete. The confinement provided by the store may affect the classification of the fireworks. Until the problem of classification for storage is resolved, the practice of assigning fireworks that are on a borderline to the more hazardous group should provide a margin of safety.

Acknowledgements

I should like to thank the Ministry of Social Affairs and Employment in The Netherlands for funding the work described in this paper and for encouraging its publication. I should also like to thank the specialists in Queensland, Western Australia, Sweden, France, Germany, Malta, Switzerland, Canada and the United States who responded to the questionnaire.

References

1) M. J. Bagley, "A Review of Controls for the Storage of Explosives", *Propellants, Explosives, Pyrotechnics*, paper in preparation.

2) P. G. Jones, "The Law and Explosives", *Explosives Engineering*, Vol. 2, No. 4 (1988) pp 1–9.

3) Health and Safety Commission, *Proposals for New Regulations on the Manufacture and Storage of Explosives*, Consultative Document CD174, HSE Books, 2002, 296 pp.

4) Health and Safety Executive, *Guidance for Applicants for an Explosives Factory or Magazine*, Health and Safety Executive, 1999, 16 pp plus appendices.

5) Health and Safety Executive, *Summary of the Acts concerning Sale of Explosives*, Health and Safety Executive, 1986, 14 pp [ISBN 0 7176 02478].

6) Standards Australia, *Australian Standard AS 2187.1-1998: Explosives-Storage, Transport and Use-Storage*, Standards Australia, 1998 [ISBN 0 7337 1782 9].

7) Government of Malta, *Subsidiary Legislation 33.01, Manufacture and Storage of Explosives Regulations*, http://justice.magnet.mt/Documents/ENGLISH.

8) Government of Malta, *Subsidiary Legislation 33.03, Control of Fireworks and Other Explosives Regulations*, http://justice.magnet.mt/Documents/ENGLISH.

9) J. H. Thomson, *Guide to the Explosive Act 1875*, Her Majesty's Stationery Office, 1962, 297 pp.

10) Standards Australia, *Australian Standard AS 2187.0-1998: Explosives-Storage, Transport and Use-Terminology*, Standards Australia, 1998 [ISBN 0 7337 1781 0].

11) U.S. Department of the Treasury, Bureau of Alcohol, Tobacco and Firearms, *Federal Explosives Law and Regulations*, ATF P 5400.7 (09/00).

12) R. Merrifield, "Hazards Associated with the Storage of Fireworks", *Journal of Pyrotechnics*, No. 14 (2001) pp 1–14.

13) C. P. Weeth, "Enschede: Lessons to Relearn", *Proceedings of the 6th International Symposium on Fireworks*, Walt Disney World Resort, Lake Buena Vista, FL, USA (2001) pp 367–383.

14) *Recommendations on the Transport of Dangerous Goods, Model Regulations*, 11th rev. ed., ST/SG/AC.10/1/rev. 11, United Nations, New York and Geneva, 1999.

Annex

Outline of Questionnaire on Controls for the Storage of Explosives Including Fireworks

1) In your country, do you operate a control system for the storage of explosives that is separate from systems for the control of other dangerous substances?

2) Does the control system for the storage of explosives take account of the following hazards arising from accidental initiation:
   a) blast;
   b) projected fragments from stored material;
   c) projected debris resulting from an explosion within a storage building;
   d) thermal radiation;
   e) ground shock?

3) Does the control system for the storage of explosives take account of any other hazards arising from accidental initiation? If yes, please state the hazards.

4) Does the control system for the storage of explosives require the classification of different types of explosive according to the hazard (e.g., mass explosion hazard, projection hazard, etc.)?

5) Does the control system for the storage of explosives take account of the nature of the packaging or containment vessel? If the answer is yes, please say how this is done.

6) Does the control system for the storage of explosives take account of the nature of the storage facility/building? If the answer is yes, please say how this is done.

7) Are explosives classified for storage using their UN transport classifications?

8) (.1) If changes are made to the UN transport classifications, are these made on the basis of:
   a) test data;
   b) analogy;
   c) other information (please state)?

   (.2) If explosives are not classified for storage using their UN or modified UN transport classifications, what system is used?

9) Does the control system make use of the concept of TNT-equivalence for determining inventories of stored explosives?

10) If the answer to Question 9 is yes, how is the TNT-equivalence determined? For example, is a correction factor used?

11) Is the control system for the storage of explosives based on fixed quantity-distances? If the answer is no, please go to Question 17.

12) Do the separation distances vary according to the hazard division or type of the explosive being stored?

13) Do the separation distances cover separation from other buildings on site as well as separation from buildings and facilities off site?

14) For buildings and facilities on site, does the separation distance vary with:
    a) the type of building/facility;
    b) the number of people exposed to risk;
    c) the vulnerability of people exposed to risk?

15) For buildings and facilities off site, does the separation distance vary with:
    a) the type of building/facility;
    b) the number of people exposed to risk;
    c) the vulnerability of people exposed to risk?

16) Are there any explosives stores that are not covered by the quantity-distance control system (e.g., shops storing fireworks, stores at a quarry)?

17) Does the control system take any account of the impact on the environment (e.g., sites of special scientific interest, endangered species, etc.)?

18) Does the control system permit the use of quantitative risk assessment to estimate the risk to workers and/or members of the public?

19) Does the control system rely entirely on the use of quantitative risk assessment with a target level of residual risk?

20) (.1) If the answer to Question 19 is no, is quantitative risk assessment used to refine or reduce the separation distances in a quantity-distance scheme?

    (.2) What other use is made of the risk estimates?

Please Note: some of the following questions on fireworks make a distinction between fireworks sold in shops (consumer fireworks) and fireworks usually used only by professional operators. Consumer fireworks are of the type assigned to UN hazard divisions 1.4G and 1.4S for transport, whereas fireworks used by professional operators are of the type assigned to UN hazard divisions 1.3 (mainly), 1.2 and 1.1 for transport.

21) Does the control system for the storage of explosives treat the storage of fireworks differently from the storage of other types of explosives?

22) Because of the possible role of packaging in respect of the hazards posed by the storage of fireworks, is the net quantity of explosive (NEQ) used to determine the quantity of the following types of fireworks permitted in storage:
    d) consumer fireworks;
    e) fireworks used by professionals?

23) If the answer to all or part of Question 22 is no, is the gross weight of fireworks used to determine the quantity of the following types of fireworks permitted in storage:
    f) consumer fireworks;
    g) fireworks used by professionals?

24) Is the maximum permitted quantity of stored fireworks dependent on the UN hazard division of the fireworks?

25) If the maximum permitted quantity of stored fireworks is not dependent on the UN hazard division, are fireworks divided into different categories for storage by:
    a) size;
    b) gross weight;
    c) type (e.g., shop goods fireworks and fireworks used by professional operators);
    d) another system (please state)?

26) Does the assignment of fireworks to hazard divisions for storage depend on the confinement provided by the type of store (e.g., steel container)?

27) Does the control system for the storage of explosives set maximum permitted quantities for the mixed storage of different types of fireworks?

28) If the answer to Question 27 is yes, are the mixed fireworks assigned to the same hazard division as the most hazardous type of firework in the store?

Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures — Part 5: Application of Self-Heating Theory to the Prediction of Ignition Temperatures

J. E. Fletcher

Health and Safety Laboratory, Harpur Hill, Buxton, Derbyshire, SK17 9JN, United Kingdom

ABSTRACT

The self-heating models of Frank-Kamenetskii and Thomas have been applied to predict self-ignition temperatures for sulfur-chlorate mixtures in spherical and cylindrical geometries of varying size. The models were validated by comparison to experimental cardboard tube test data previously reported. It was found that the Frank-Kamenetskii model, combined with kinetic data from differential scanning calorimetry, gave the best agreement with the experimental results. However, careful selection of the kinetic parameters proved critical and, in this study, DSC data provided more relevant predictions than ARC data. By appropriate selection of size and geometry, the models could be further applied to predict self-ignition temperatures for other mixtures and geometries or systems that can be related to actual fireworks.

Keywords: sulfur, chlorate, fireworks, thermal stability, self-heating, Frank-Kamenetskii, Thomas

Introduction

Previously reported work in this series[1–4] has examined the thermal stability of sulfur/potassium chlorate mixtures in cardboard tubes when heated using a heated-block apparatus. The test samples were either heated at a constant rate or held at a constant elevated temperature until an ignition was observed. The thermal stability of the mixtures was reported in terms of the lowest temperature at which spontaneous ignition was observed, referred to as the (self) ignition temperature. Sulfur-chlorate mixtures have been shown to have low thermal stability and ignition temperatures as low as 383 K have been reported[2] for stoichiometric mixtures held in cardboard tubes.

The self-ignition temperature of a material depends upon the rate at which heat is generated inside the material through internal chemical reaction balanced against the rate at which heat is dissipated to the surroundings. If the rate of heat generation exceeds the rate of heat loss, then the material will self-heat and spontaneous ignition may occur. The self-ignition temperature is defined as the lowest temperature, to which a sample must be heated, under prescribed conditions, for self heating, leading to spontaneous ignition, to occur. Under bulk conditions or conditions favourable to heat retention, sulfur/chlorate mixtures are liable to self-heating, giving rise to spontaneous ignitions.

Part 5 of this series applies the self-heating theories of Frank-Kamenetskii and Thomas to predict the ignition temperatures of sulfur/chlorate mixtures. The predicted temperatures are compared to those observed in previously reported experiments.

Self-Heating Theory

Theoretical models of self-heating are based upon the mathematical interpretation of the balance between the rates of heat generation and heat dissipation. For a system in thermal equilibrium the temperature distribution, T, as a function of time, t, can be described by

$$\rho_b c \frac{\partial T}{\partial t} = \lambda \nabla^2 T + Q \rho_b A \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where

ρ_b = density,

c = heat capacity of the material,

λ = thermal conductivity of the material,
Q = heat of reaction per unit mass,
A = Arrhenius pre-exponential factor,
E = activation energy,
R = universal gas constant (8.314 J mol^{-1} K^{-1}), and
∇^2 = Laplacian operator.

A zero-order Arrhenius type rate of heat generation is assumed and heat transfer is by conduction only.

A general solution to equation 1 would include two constants of integration derived from the boundary or storage conditions under consideration. Because of the exponential term, an exact analytical solution of the heat balance equation has so far not been achieved. However, models for self-heating have been proposed that find approximate solutions for the heat balance equation and differ from each other only in the assumptions made.

Semenov[5] proposed a solution where the temperature distribution of the reacting body is uniform and resistance to heat transfer occurs solely through thermal resistance at its boundary (i.e., the wall of the containment vessel). This model is most readily applied to gases and turbulent liquids, where the principal heat transfer mechanism is convection, and is of less relevance to solids, where other models are more appropriate.

Frank-Kamenetskii[6] proposed a solution in which all the resistance to heat transfer is within the reacting mass and that its boundary acts as an isothermal heat sink (i.e., remains at the same temperature as the environment). This model is most suited to solid systems, in contrast to Semenov's model. Frank-Kamenetskii gives an approximate solution to the heat balance equation, describing the steady-state temperature distribution in a reacting body in terms of the Frank-Kamenetskii (FK) parameter, δ, defined as

$$\delta = \frac{Er^2 Q \rho_b}{\lambda R T_a^2} A \exp\left(-\frac{E}{RT_a}\right) \qquad (2)$$

where

T_a = environment temperature and
r = characteristic length of a geometric shape: half-thickness of a slab or radius of a sphere or cylinder.

Frank-Kamenetskii showed that solutions of the heat-balance equation (eq. 1), for a steady-state temperature distribution, are possible only when the FK parameter δ, is less than or equal to a critical value, δ_c. If $\delta > \delta_c$, no stationary state temperature distribution exists, and the sample temperature will continue to rise, by self-heating, resulting in a thermal explosion. Frank-Kamenetskii calculated δ_c for $m = 0$ (an infinite slab) analytically and for $m = 1$ (an infinitely long cylinder) and $m = 2$ (a sphere) numerically. The calculated values of δ_c are given in Table 1 for each shape factor m.

Table 1. Critical Values of δ_c Derived by Frank-Kamenetskii.

Shape Factor, m	δ_c
0, infinite slab	0.88
1, infinite cylinder	2
2, sphere	3.32

Thomas[7] refined the Frank-Kamenetskii model by allowing for thermal resistance and dissipation of heat through the boundary, effectively amalgamating the Semenov and Frank-Kamenetskii models. Thomas proposed an approximate solution to equation 1 that allowed for Newtonian cooling through a finite heat transfer co-efficient, H, at the interface between the reacting mass and its surroundings (the self-heating material may be contained within a vessel or may be enclosed in a second solid material of different thermal properties, generating no heat).

Thomas defined the Biot number, α, as:

$$\alpha = \frac{H \times r}{\lambda} \qquad (3)$$

where

α = Biot number,
r = the length parameter, and
H = overall heat transfer co-efficient.

For each of the three geometries in Table 1, Thomas calculated the critical parameter δ_c in

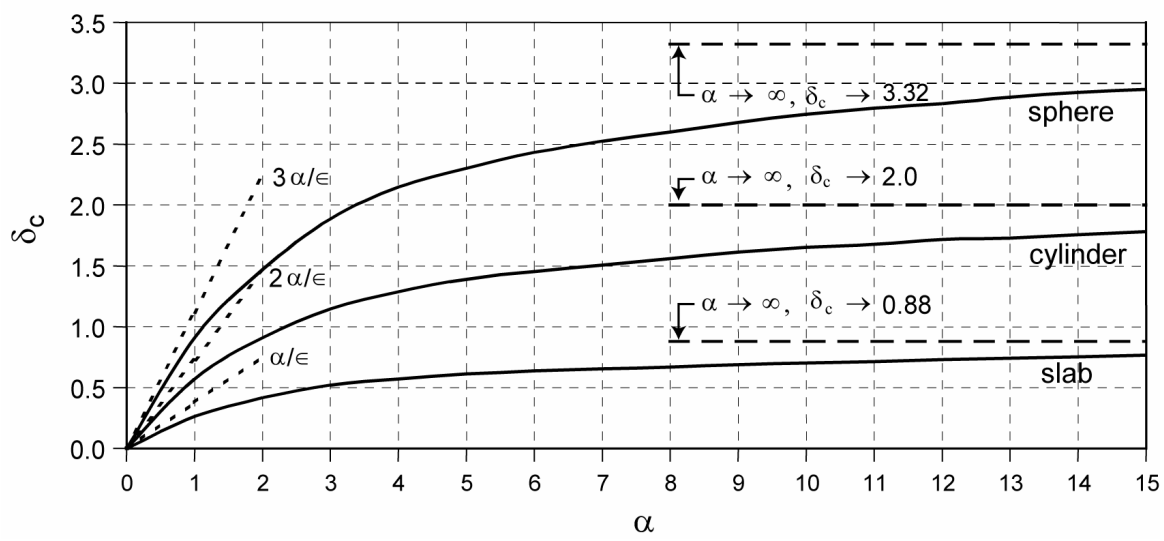


Figure 1. δ_c as a function of α for a slab, cylinder and sphere.

terms of α. The plot in Figure 1 shows calculated values for δ_c.

It can be seen from Figure 1 that as $\alpha \to \infty$, the values of δ_c for a slab, cylinder and sphere approach the limiting values calculated by Frank-Kamenetskii (0.88, 2 and 3.32 respectively). As $\alpha \to 0$, δ_c approaches limiting values given by $(m + 1)\ \alpha/\varepsilon$, which is in fact the Semenov condition.[5] Therefore, the Thomas model successfully combines the Semenov and Frank-Kamenetskii models giving the same results as these models at the extreme limits of α.

The existence of a critical value of δ, for a given system, infers that there is also a critical (environment) temperature T_c, above which the system is thermally unstable and will undergo self-heating.

To calculate T_c, it is first necessary to calculate the Biot number, α, for the geometry under consideration (eq. 3). Once α is known, the critical value of the Frank-Kamenetskii number δ_c can be calculated either mathematically from the equations of Thomas or graphically from Figure 1. For a purely Frank-Kamenetskii approach ($H = \infty$ and hence $\alpha = \infty$) values for δ_c can be taken from Figure 1. The critical temperature, T_c, can then be determined from equation 2, provided the necessary parameters are known. Alternatively, a critical value for the characteristic length of the required geometry can be calculated, for a given environment temperature.

For this work on sulfur/chlorate mixtures, where the onset of self-heating leads rapidly to spontaneous ignition of the material, the theoretical critical temperatures predicted by the Frank-Kamenetskii and Thomas models are considered to be equivalent to the experimentally determined (self) ignition temperature of the mixtures.

While the infinite slab geometry is of limited practical use, the cylindrical and spherical geometric models can be applied to fireworks. The spherical geometry could be used to predict T_c for individual fireworks components such as stars, typically of 10 to 20 mm diameter. On a larger scale, the Frank-Kamenetskii and Thomas models (with an appropriate value for H), could be applied to a complete firework such as a simple shell typically with diameters up to 300 mm, although 75 to 150 mm is more common. Although this is an over-simplification, since variations in internal compositions or components would need to be ignored, it would give a worst-case situation.

Similarly, the infinitely long cylinder geometry could be used to model a fountain type firework, provided its length was much greater than its radius. This latter situation could be

applied to the previous thermal studies for compositions contained within cardboard fireworks tubes.

Experimental

Application of the Frank-Kamenetskii and Thomas models requires knowledge of certain properties of the material and system being studied. These properties fall into three categories; the chemical thermodynamic and kinetic properties (E, A, Q), physical properties (c, λ, ρ_b) and geometric properties (m, r, H). Where possible, values for these parameters were obtained from the literature. In the absence of suitable literature data, values were determined by experiment.

Previous work has examined many mixtures with widely varying compositions. However, for this study, it was decided to focus on three specific mixtures; the compositions are listed in Table 2. Mixture 1 is an approximately stoichiometric composition according to Tanner's equation[8] and has been previously extensively studied. Mixture 2 was chosen because previous work[3] identified the 5:95 mixtures as the least stable (i.e., having the lowest ignition temperature). Mixture 3, more representative of a typical fireworks composition, was obtained by replacing half of the sulfur in Mixture 1 with charcoal.

Table 2. Composition of Test Mixtures.

Component	Mixture		
	1	2	3
Flowers of sulfur	30	5	15
Potassium chlorate (AnalaR)	70	95	70
Charcoal	0	0	15

Chemical Properties

Literature data[9] for sulfur/chlorate mixtures were limited and there was insufficient or incomplete information available for the three selected mixtures. In addition, the acidity of the sulfur, in mixtures where data were reported, differs from that of the sulfur used here. Since previous work in this series has shown sulfur acidity to have an effect on thermal stability, such literature data are not applicable for this work. Therefore, thermodynamic and kinetic data were obtained for the three mixtures by experiment. The techniques of differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC) were employed to determine values for the parameters E, A and Q.

DSC data were obtained using a Mettler-Toledo TA4000/DSC25 heat-flux calorimeter following the procedure described in ASTM Test Method No. E698-79.[10] Isothermal ageing tests were performed, following the same procedure, to check the validity of the calculated kinetic parameters.

ARC data were obtained using a Columbia Scientific ARC2000 calorimeter. Kinetic data were calculated using ArcWin computer software V1.5, following the methodology described by Townsend and Tou.[11]

The thermodynamic and kinetic data obtained are listed in Table 3.

Physical Properties

The heat capacities of the three mixtures were derived from the fractional sum of the heat capacities of the components in the mixture. Heat capacity data for the components were obtained from the literature[12] and showed little variation over the temperature range of interest, from ambient (293 K) up to typical ignition temperatures of 393 K.

Thermal conductivity of the mixtures was determined by experiment, using an electrical version of the Lee's disk method.[13] Disks of each test material were made by compressing 8 g of loose material in a hand-operated hydraulic press, to a pressure of 1000 kg (1 tonne). By applying 7, 8 and 9 volts, the thermal conductivity of each disk was determined over a range of temperatures. However, little difference was seen as a function of temperature and the reported results are averaged over the three voltage settings.

Table 3. Thermo-Kinetic Parameters Determined by DSC and ARC.

Method/Parameter (units)	Mixture 1 30% sulfur (flowers) 70% potassium chlorate	Mixture 2 5% sulfur (flowers) 95% potassium chlorate	Mixture 3 15% sulfur (flowers) 15% charcoal 70% potassium chlorate
DSC			
Activation energy, E ($J\ mol^{-1}$)	1.47×10^5	1.40×10^5	4.40×10^5
Arrhenius factor, A (s^{-1})	1.67×10^{16}	1.33×10^{15}	1.67×10^{50}
Heat of reaction, Q ($J\ g^{-1}$)	2350	1410	2380
Isothermal Ageing			
Half life/temperature	63 min. @ 380 K	62 min. @ 386 K	68 min. @ 423 K
Heat of reaction of aged sample ($J\ g^{-1}$)	1319	1080	No exotherm observed
ARC			
Activation energy, E ($J\ mol^{-1}$)	2.32×10^5	1.66×10^5	5.73×10^5
Arrhenius factor, A (s^{-1})	6.7×10^{36}	6.5×10^{20}	3.7×10^{70}
Heat of reaction, Q ($J\ g^{-1}$)	1055	807	1595

Bulk density data, obtained from the physical measurement of each disk, were in the range of 1.4–1.69 g cm^{-3}. Previously reported work in this series examining the thermal stability of mixtures pressed into the shape of cylindrical stars (diameter 9 mm, length 10 mm and mass 1.0 g) gave a density of 1.6 g cm^{-3}. The physical properties of the three mixtures are summarised in Table 4.

Geometric Parameters

The physical dimensions of ten cardboard tubes identical to those used in previous work were measured and average values obtained.

Length = 140 ± 0.2 mm
Internal diameter = 10.0 ± 0.2 mm
External diameter = 14 ± 0.1 mm
Mass = 6.4 ± 0.1 g

The overall heat transfer coefficient, H, of the system (material inside the cardboard tubes) was evaluated[14,15] by recording a cooling curve for a cardboard tube—closed at one end with a clay plug—filled with boiling water and closed at the upper end with a tissue plug. Over the period of the measurements, the sealed tubes remained intact; no absorption of water into the cardboard was observed and the appearance of the outer surface of the tubes remained dry. A plot of $\ln (T - T_a)$ versus time should be linear, allowing H to be calculated from the gradient (the reciprocal of the gradient gives the Newtonian cooling time, $t_N = Vc_\rho/SH$, where V = volume and S = surface area).

Table 4. Physical Properties of Sulfur/Chlorate Mixtures.

Parameter (units)	Mixture 1 30% sulfur (flowers) 70% potassium chlorate	Mixture 2 5% sulfur (flowers) 95% potassium chlorate	Mixture 3 15% sulfur (flowers) 15% charcoal 70% potassium chlorate
Heat capacity, c ($J\ g^{-1}\ K^{-1}$)	0.84	0.88	0.88
Thermal conductivity, λ ($W\ m^{-1}\ K^{-1}$)	0.337	0.402	0.292
Bulk density, ρ_b ($g\ cm^{-3}$)	1.50	1.69	1.40

The average overall heat transfer coefficient of four tubes was calculated to be:

$H = 16.8 \pm 1.0$ W m^{-2} K^{-1}

Application of Models

The data obtained for the three mixtures were used in the Frank-Kamenetskii model. Theoretical (self) ignition temperatures were calculated for an infinitely long cylinder and a sphere for a range of characteristic lengths (radii). The results are given in Tables 5 and 6 and shown graphically in Figure 2. Critical temperatures were calculated twice, using thermodynamic and kinetic data from both the DSC and the ARC.

Table 5. Ignition Temperature of an Infinitely Long Cylinder of Sulfur/Chlorate Mixture, Calculated as a Function of its Characteristic Length (Radius), Using the F-K Model.

Characteristic Length: Radius of infinite cylinder (mm)	Ignition Temperature (K)					
	Mixture 1 30% sulfur (flowers) 70% potassium chlorate		Mixture 2 5% sulfur (flowers) 95% potassium chlorate		Mixture 3 15% sulfur (flowers) 15% charcoal 70% potassium chlorate	
	DSC	ARC	DSC	ARC	DSC	ARC
5	376	295	384	352	419	398
10	365	291	372	343	414	395
20	354	286	360	335	410	392
50	341	281	346	325	404	387
100	332	276	336	317	400	385
200	323	273	327	310	396	382

Table 6. Ignition Temperature of a Sphere of Sulfur/Chlorate Mixture, Calculated as a Function of its Characteristic Length (Radius), Using the F-K Model.

Characteristic Length: Radius of sphere (mm)	Ignition Temperature (K)					
	Mixture 1 30% sulfur (flowers) 70% potassium chlorate		Mixture 2 5% sulfur (flowers) 95% potassium chlorate		Mixture 3 15% sulfur (flowers) 15% charcoal 70% potassium chlorate	
	DSC	ARC	DSC	ARC	DSC	ARC
5	380	296	389	355	421	400
10	369	292	376	346	416	396
20	358	288	365	338	411	393
50	344	282	350	327	406	389
100	335	278	339	320	401	386
200	326	275	330	313	397	383

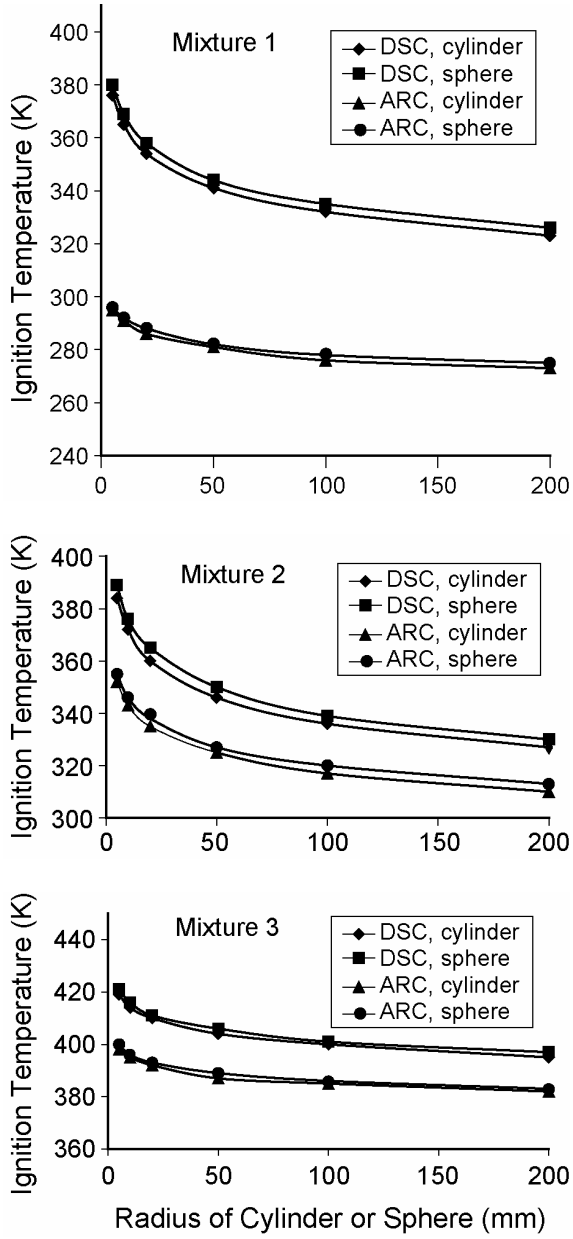


Figure 2. Predicted ignition temperatures for Mixtures 1 to 3 calculated using the F-K model.

The characteristic lengths for which the ignition temperatures were calculated were chosen to be representative of typical sizes of fireworks and/or firework components. The larger lengths (20, 50 and 100 mm) relate to typical sizes of firework shells that are commonly available, while the smaller lengths (5 and 10 mm) are typical of individual fireworks components (e.g., stars). The 5 mm characteristic length, combined with infinitely long cylinder geometry, approximately describes the experimental arrangement of cardboard fireworks tubes used in previous work.

The collected parameters were applied to the Thomas model, using the cylinder geometry with a radius of 5 mm, to predict ignition temperatures of cardboard firework tubes containing test mixtures. The data used and the calculated results are given in Table 7.

Comparison with Experimental Tube Test Data

Mixture 1. The calculated ignition temperatures, following Frank-Kamenetskii, for Mixture 1 contained in 5 mm radius, infinitely long cylinders are 376 K using DSC derived kinetic parameters and 295 K using ARC derived data. The equivalent values, following Thomas, are 357 and 287 K for DSC and ARC, respectively. The Thomas values are lower than their equivalent Frank-Kamenetskii values, which is to be expected since Thomas allows for thermal resistance at the boundary (insulation) so more heat is retained in the system. Stoichiometric mixtures of flowers of sulfur with AnalaR potassium chlorate, equivalent to Mixture 1, have been studied isothermally, within 5 mm radius

Table 7. Ignition Temperatures (T_c) of Sulfur/Chlorate Mixtures Contained within Cardboard Firework Tubes, Calculated from DSC and ARC Data Using the Thomas Model.

Parameter	Mixture 1	Mixture 2	Mixture 3
H	16.8 W m^{-2} K^{-1}	16.8 W m^{-2} K^{-1}	16.8 W m^{-2} K^{-1}
r	5 mm	5 mm	5 mm
λ	0.337 W m^{-1} K^{-1}	0.402 W m^{-1} K^{-1}	0.292 W m^{-1} K^{-1}
α ($H \times r/\lambda$)	0.249	0.209	0.287
δ_c	0.18	0.15	0.21
T_c (ARC)	287 K	336 K	393 K
T_c (DSC)	357 K	362 K	412 K

cardboard firework tubes, under conditions of elevated temperature. It was found that at a temperature of 383 K, mixtures ignited after 250–260 minutes, while, at 373 K, no ignitions were observed after 23 days. This suggests that the critical temperature lies within the range 373–383 K. The ignition temperature, calculated using the DSC data (376 K), gives good agreement with the experimental results when the Frank-Kamenetskii model is used. With the Thomas model however, the calculated value is lower (by 15–20 K) than that observed by experiment. This difference may be due to the time period of the tube experiments (i.e., an exotherm, leading to ignition, may occur at lower temperatures than actually observed, if the induction or observation period was much longer) or it may be attributed to an incorrect choice for the overall heat transfer coefficient for the experimental conditions. The ignition temperatures calculated using ARC data (295 K, Frank-Kamenetskii) are significantly lower than actually observed and are approaching typical ambient temperatures.

Mixture 2. Calculated ignition temperatures, for a cylinder with a 5 mm radius, using the Frank-Kamenetskii model, are 384 K with DSC data and 352 K with ARC data. Applying the Thomas model, the calculated ignition temperatures are 362 and 336 K with DSC and ARC data, respectively. Experimental tube test data indicated that the ignition temperature was in the range of 373–383 K (ignitions as low as 383.7 K, after 330 minutes, were observed). For this mixture, as with Mixture 1, the ignition temperature predicted by the Frank-Kamenetskii model, combined with DSC data, most closely resembles the experimental results, giving a good correlation. Calculated values using ARC data and/or the Thomas model were again significantly lower than that observed by experiment.

Mixture 3. Calculated ignition temperatures are 419 and 398 K by Frank-Kamenetskii with DSC and ARC data, respectively and, 412 and 393 K by Thomas with DSC and ARC data. Again, experimental tube tests gave ignitions as low as 383 K (after 365 minutes). None of the models predicted an ignition temperature in agreement with the experimental results.

Discussion

From the information above, it can be seen that the Frank-Kamenetskii model, combined with DSC chemical data, correctly predicts, to a reasonable degree of certainty, the ignition temperatures of Mixtures 1 and 2. Predictions with the same model, using ARC data, are consistently lower than are actually observed and approach typical ambient temperatures. For example, the predicted ignition temperature for Mixture 1, in a 5 mm radius infinitely long cylinder, using the Frank-Kamenetskii model with ARC data is 295 K. This difference between ARC and DSC can be explained in terms of how the kinetic parameters are derived by each technique.

The ASTM method used for the DSC, calculates kinetic data by measuring the temperature at which the reaction maximum occurs. Therefore, it is influenced mainly by the actual ignition reaction of the bulk material. The 'fine detail' of the reaction (i.e., the early reaction stages) is of less significance. In contrast, the pseudo-rate constant analysis used by the ARC considers the finer detail, and kinetic parameters are calculated primarily with data from the early stages of the reaction. In the case of sulfur/chlorate mixtures, the ARC identifies small pre-ignition exotherms which, in the adiabatic environment of the ARC, lead to ignition of the bulk material. The calculated kinetic parameters (and hence predicted ignition temperatures) are influenced mainly by these early exotherms. In practice, however, sulfur/chlorate mixtures in cardboard tubes are not adiabatic, heat is lost to the environment and the small exotherms do not cause ignition, which occurs at much higher temperatures. The ignition temperatures predicted using ARC kinetic data are therefore lower than actually observed. The ignition temperatures predicted using DSC kinetic parameters give better agreement with experimental data since the kinetic parameters better reflect the behaviour of the bulk material in a non-adiabatic environment.

The failure of the Frank-Kamenetskii model for Mixture 3 may be attributed to an incorrect choice for the kinetic parameters. This is confirmed for DSC data by the failure of the isothermal ageing test. For Mixture 3, the iso-aged

sample showed no reaction suggesting that it had ignited during the ageing process and that the calculated kinetic values are too high. This is reflected in the calculated ignition temperatures, which are much higher than the experimental ignition temperatures.

The failure of ARC and DSC to obtain correct kinetic data for Mixture 3 may be because of the complex nature of the chemical reaction. The ARC pseudo-rate constant analysis and DSC ASTM method are applicable to reactions whose behaviour can be described by the Arrhenius equation and the general rate law. They are not applicable to reactions that are partially inhibited or processes that include simultaneous or step reactions, and may not be applicable to materials that undergo phase transitions if the reaction rate is significant at the transition temperature. It has been suggested that the ignition of a sulfur/chlorate mixture may be triggered by the generation of sulfur dioxide. In the case of Mixture 3, the charcoal present in the mixture would tend to absorb any sulfur dioxide present, thus inhibiting the reaction.

It is already known that the addition of certain materials has a stabilising effect on the sulfur/chlorate mixture. Robertson[6] found that the addition of kieselguhr (diatomite), charcoal and calcium chloride dihydrate increased thermal stability while sodium sulfate decahydrate had no effect. In general, any material that has the ability to absorb either the active species (sulfur dioxide) or water or to prevent formation of acidic species will have a stabilising effect on the mixture.

The predicted ignition temperatures calculated by the F-K models have been compared to, and show agreement with, a single experimental data point (i.e., a long cylinder of diameter 5 mm). The trends predicted by the model have not been verified since the collection of additional experimental data points was outside the scope of this study. Verification would require data points for larger diameter geometries (e.g., 20, 50 or even 100 mm). However, with larger diameters there is an increase in hazard potential.

Conclusions

The Frank-Kamenetskii model has been shown to give the best agreement with the experimental results, predicting, to a reasonable degree of certainty, the ignition temperatures of sulfur/chlorate mixtures in cardboard tubes. However, careful selection of the kinetic parameters is critical and, in this study, DSC data provided more relevant predictions than ARC data. This model could be further applied to predict ignition temperatures for other mixtures and geometries or systems that can be related to actual fireworks.

When a third component is added to the mixture, the predicted results differ from those measured due to the complexity of the reaction. The experimental techniques used to derive kinetic data for the model assume standard Arrhenius kinetics. The failure of the model to correctly describe a sulfur/chlorate composition containing charcoal is attributed to experimental problems of obtaining accurate chemical kinetic data.

References

1) D. Chapman, R. K. Wharton and G. E. Williamson, “Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixture Part 1: Introduction”, *Journal of Pyrotechnics*, No. 6 (1997) pp 30–35.

2) D. Chapman, R. K. Wharton, J. E. Fletcher and G. E. Williamson, “Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 2: Stoichiometric Mixtures”, *Journal of Pyrotechnics*, No. 7 (1998) pp 51–57.

3) D. Chapman, R. K. Wharton, J. E. Fletcher and A. E. Webb, “Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 3: The Effect of Stoichiometry, Particle Size and Added Materials”, *Journal of Pyrotechnics*, No. 11 (2000) pp 16–24.

4) D. Chapman, R. K. Wharton and J. E. Fletcher, “Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 4: Firework Compositions and Investigation of the Sulfur/Chlorate Initia-

tion Reaction", *Journal of Pyrotechnics*, No. 12 (2000) pp 43–51.

5) N. N. Semenov, "Thermal Theory of Combustion and Explosion", *Uspekhi Fiziceskih Nauk*, Vol. 23 (1940) pp 251–292.

6) D. A. Frank-Kamenetskii, *Diffusion and Heat Exchange in Chemical Kinetics*, 2nd ed. (Translated J. P. Appleton), Plenum Press, 1969.

7) P. H. Thomas, "Thermal-Conduction Equation for Self-heating Materials with Surface Cooling", *Transactions of the Faraday Society*, Vol. 54 (1958) pp 60–65.

8) H. G. Tanner, "Instability of Sulfur–Potassium Chlorate Mixture", *Journal of Chemical Education*, Vol. 36 (1959) pp 58–60.

9) J. Robertson, "The Reaction of Sulphur with Calcium and Potassium Chlorates", R.A.R.D.E. Branch Memorandum, 12/76 (EM2) 1976.

10) American Society for Testing Materials, *Arrhenius Kinetic Constants for Thermally Unstable Materials*, ASTM E698-79, Committee E-27, SCE27.02, 1979.

11) D. I. Townsend and J. C. Tou, "Thermal Hazard Evaluation by an Accelerating Rate Calorimeter", *Thermochimica Acta*, Vol. 37 (1980) pp 1–30.

12) R. H. Perry and C. H. Chilton, *Chemical Engineers' Handbook*, 5th ed., McGraw-Hill, 1973, pp 3/123–3/124.

13) O. M. White, *Essentials of Heat*, 1st ed., Cleaver-Hulme Press Limited, 1961, pp 146–147.

14) T. J. Snee and J. A. Hare, "Development and Application of a Pilot Scale Facility for Studying Runaway Exothermic Reactions", *J. Loss Prev. Process Ind.*, Vol. 5 (1992) pp 46–54.

15) *Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, "Test Series H", 3rd rev. ed. United Nations, New York and Geneva, 1999.

Particle Size Effect in Pyrotechnic Compositions Containing Potassium Chlorate

M. Fathollahi, S. G. Hosseini, S. M. Pourmortazavi, and F. Farahani

Material and Chemical Engineering Excellency Ctr.,
Malek Ashtar University of Technology,
PO Box 16765-3454, Tehran, Iran

ABSTRACT

In this research, the effect of potassium chlorate particle size on the heat of reaction and the ignition temperature was studied. Potassium chlorate of known particle size was prepared by crystallizing saturated solutions of potassium chlorate at various cooling rates and then isolating crystals of the desired particle size by sieving. The heat of reaction was measured using a bomb calorimeter. The ignition temperature was determined by thermal analysis.

The results indicate the heat of reaction increases non-linearly as the particle size decreases. The maximum change, however, was only about 4%.

The experimental results indicate that 100 to 250 microns is the best range of particle sizes for potassium chlorate intended for use in pyrotechnic compositions for vaporizing organic materials.

Keywords: potassium chlorate, particle size, heat of reaction, ignition temperature

Introduction

The particle size effect is universal and affects all reactive systems: fuels, oxidizers, propellants, pyrotechnics, and explosives. The reactive systems can be powders, slurries, or solid or liquid dispersions in a gas. In the case of liquids, the droplet size must be taken into consideration. For solids, whether the particles are nearly spherical or jagged, the particle size is very important. From a more fundamental point of view, it is the surface area, expressed as surface-to-mass ratio, that must be considered.[1] In this paper, it is assumed that reference to particle size refers to the diameter of a hypothetical spherical particle.

Most effort has been expended in the investigation of particle size effects with regard to liquid fuels, monopropellants and explosives. At first glance, the results of these investigations[1] do not seem to be consistent. On the one hand, it is well known[2] that atomization of a fuel greatly aids in decreasing its auto ignition delay. On the other hand, it has also been shown[3,4] that each fuel, under otherwise identical conditions, has an optimum particle size that results in minimum ignition delay; whereas larger particles evidently are not heated sufficiently fast. Another investigation has demonstrated that the auto ignition temperature for a particle increases with decreasing particle size.[5]

These effects, however, are not actually inconsistent but are the result of various physical and chemical processes that occur concomitantly and, in many instances, competitively. This is particularly true where an endothermic phase change absorbs some of the exothermic combustion energy.[6]

Heat of reaction is an important parameter of pyrotechnic compositions, being one of the factors that controls the maximum temperature attained during combustion. This is especially important for pyrotechnic compositions that are used to vaporize organic material, such as a smoke dye. The organic material decomposes at relatively low temperatures; the combustion temperature must therefore be high enough to vaporize the material, but low enough to ensure that the material is not destroyed.

In this paper, we will present the effect of potassium chlorate particle size on heat evolved and ignition temperature of a mixture containing potassium chlorate and lactose.

Experiments

Apparatus

Bomb Calorimeter

An IKA adiabatic/quasi-adiabatic calorimeter system C 4000 thermometer was used in the determinations of heat of reaction. This calorimeter has the advantage that it contains a sensitive control and an integrated heating and cooling system. It consists of a stainless steel bomb, an inner chromium-plated copper calorimeter, an outer water jacket and an adiabatic jacket, a measuring sensor in the calorimeter water, and controls for making adjustments. It was calibrated in the normal way using standard thermochemical benzoic acid pellets, ignited with platinum wire and cotton under 30 atmospheres of oxygen.

DTA/TG Apparatus

A Stanton Model TR-01 thermobalance, with a sensitivity of 0.1 mg, with a Stanton 780 differential thermal analysis (DTA) attachment, was used for the ignition temperature study.

Materials

The potassium chlorate was laboratory reagent grade material from Merck Chemical Ltd.

The lactose used as fuel was laboratory reagent grade material from Merck Chemical Ltd. (sieved to pass a 72 BS sieve).

Procedure

Preparation of Potassium Chlorate Particle Size

The various particle sizes of potassium chlorate were prepared by recrystallizing saturated solutions of potassium chlorate at several thermal programs of cooling. They were separated into nine fractions (average particle size of 25, 50, 75, 90, 130, 160, 200, 290, and 350 microns) by means of a sieving machine. Particle sizes were checked with a Topocon Electron Microscope model SR-50.

Preparation of Samples

Pyrotechnic mixtures of 73.1% potassium chlorate and 26.9% lactose were prepared by carefully sieving small quantities of the components through a slightly coarser sieve (i.e., with larger holes) than the particle size of the potassium chlorate being used in that sample.

Calorimetry of Samples

Each sample was weighed into a steel tube [1.5 × 5.8 in. (38 × 147 mm), closed at one end] and consolidated using a ram under hand pressure. The sample was ignited by electrically heating a coil of nichrome wire buried in the composition at the open end of the tube and burned with a self-sustaining reaction similar to that which normally takes place in a pyrotechnic generator. For a composition that was difficult to ignite, a layer (1g) of igniter composition of known exothermicity was used. The experiments were carried out in air.

Determination of Ignition Temperature

DTA/TG thermograms were used to obtain the ignition temperature for samples (all 9 mixtures) of pure potassium chlorate and lactose.[7]

Discussion and Conclusions

Heat of Reaction

Figure 1 shows that a decrease in the particle size results in an increase in the heat of reaction. The total reaction between potassium chlorate and lactose is as follows:

$$8\ KClO_3 + C_{12}H_{22}O_{11}\cdot H_2O \rightarrow 8\ KCl + 12\ CO_2 + 12\ H_2O$$

$$\Delta H = -4515\ J/g$$

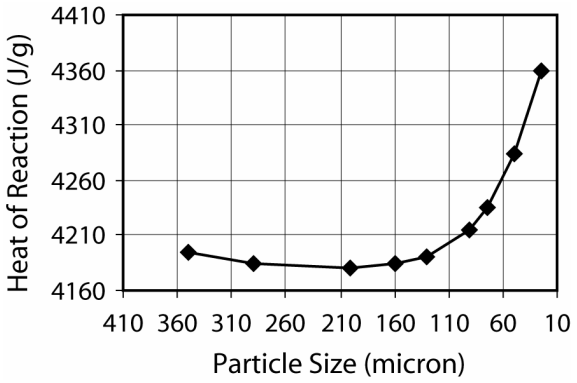


Figure 1. Change in heat evolved relative to particle size. (Note that the range of change is approximately 1%.)

The type of reactants and their percentages are the same for all samples; therefore, the propagation reaction and its products are the same for all determinations. The division of crystals into smaller pieces does not contribute significantly to bond breaking or loosening of the crystal structure, as measured by the exposure of relatively larger numbers of atoms at the particle surfaces. It is easy to show by calculation that the increase in the ratio of surface atoms to the total number of atoms is negligible compared to the increase in the heat of reaction.[7]

The lattice looseness, which results from defects in the crystal lattice, is the principle factor in the pyrochemical reactions.[8] The preparation of potassium chlorate of known particle size from chemicals by the method used in this work is likely to cause the formation of crystals with imperfect structures including dislocations, cracks, and other discontinuities, particularly for the smaller crystals. With smaller crystals, the lattice defects increase and those lattice defects operate as reactive sites. They increase the heat of reaction by reducing the energy required to break up the crystal lattice. This is consistent with the heat of reaction being somewhat greater with the smallest particle sizes than with the largest ones.[8]

Ignition Temperature

Figure 2 shows that a decrease in particle size, results in a lower ignition temperature. The smaller the particle size is, the lower the ignition temperature.

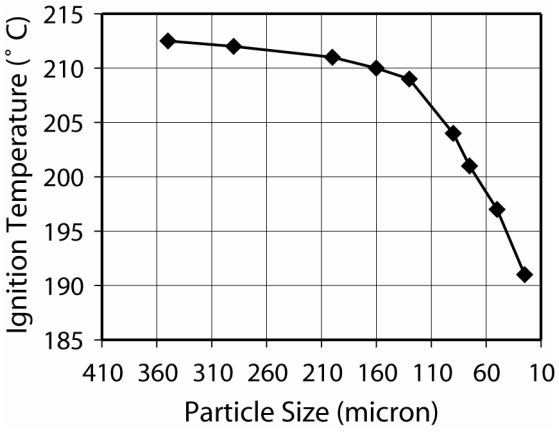


Figure 2 Change of ignition temperature relative to particle size.

The formation of localized regions of high temperature ('hotspots') is known to be an important step in the ignition of energetic materials. When the particles in a pyrotechnic mixture are small and jagged, lesser amounts of thermal energy (or other type energy, such as frictional or impact energy) are needed to produce hotspots. This is because energy is localized at the stress points. Dislocations, cracks, and other discontinuities in the crystal structure of the particles provide sites favorable to the formation of hotspots. These sites may come about from structural dislocations that run between grain boundaries or other discontinuities. These form as the growing crystal acquires more molecules that do not fit properly in to the normal pattern. The faults do not heal with continued overgrowth.[9]

Some crystal faults may be due to the inclusion of impurities. Impurities that occupy sites for which they are too large or too small, compared to the normal occupants, may generate defects that propagate through the crystal like a run in a nylon stocking. Cracks and dislocations in the crystal structure contribute to the chemical reactivity of solids. At crystal decomposition temperature, material is lost first at edges or corners.[10]

In the preparation of potassium chlorate particles of different sizes by recrystallization at various temperatures, it is likely that conditions used to obtain smaller particle sizes caused the crystals to be formed with imperfect structures including: dislocations, cracks, and other discontinuities. As crystals become smaller, these imperfections increased. Therefore, the reactivity increased and ignition temperature decreased with decreasing particle size.

Based on the curves in Figures 1 and 2, 100 to 250 microns appears to be the best potassium chlorate particle size range for this pyrotechnic application.

References

1) Allen J. Tulis, "The Particle Size Factor in Explosives and Pyrotechnics", *Proc. 10th Symp. Explos. Pyrotech.*, 1979, Paper No. 39, 9 pp.

2) B. P. Mullins, "Studies of Spontaneous Ignition of Fuels Injected into Hot Air Streams", *Fuel*, Vol. 32 (1953) pp 211–252, 327–379.

3) H. L. Wood and D. A. Charvonia, "The Ignition of Fuel Droplets Descending Through an Oxidizing Atmosphere", *Jet Propulsion* (1954) pp 162–165.

4) J. A. Browing, T. L. Tyler, W. G. Krall, "Effect of Particle Size on Combustion of Uniform Suspensions", *Ind. and Eng. Chem*., Vol. 49, No. 1 (1967) pp 142–147.

5) S. R. Mott, R. L. Peskin, and D. G. Levine, "Effect of Fuel Molecular Weight of Particle Ignition", *Combustion and Flame*, Vol. 16 (1971) pp 17–27.

6) L. V. de Yong and G. Wilson, *Comparison of Several Techniques for Measuring the Particle Size of Powder Used in Pyrotechnics*, RAAF General Ammunition Dept., Kingswood, NSW 2750 Australia, 1986.

7) F.S. Scans, "Thermal Analysis of Pyrotechnic Compositions Containing Potassium Chlorate and Lactose", *Combustion and Flame*, Vol. 23 (1974) pp 363–371.

8) D. M. Griffiths and J. A. Oliver, "The Reaction of Potassium Chlorate with Lactose: Analysis of Combustion Gases", *Combustion and Flame*, Vol. 24 (1975) pp 21–25.

9) J. H. McLain, *Pyrotechnics from the Viewpoint of Solid State Chemistry*, The Franklin Institute Press, 1980, pp 26–37.

10) J. Akhavan, *The Chemistry of Explosives*, The Royal Society of Chemistry, 1998.

Preface to Three Reviews of *Pyrotechnics* by A. Hardt

On occasion, when a book to be reviewed has special significance, we have included more than one reviewer's comments about it. In the present case we are including three reviews by authors with differing backgrounds, and thus viewing the book from differing perspectives. The first short review was written by one of the persons participating in the publication of the book, and for that reason he thought it inappropriate for him to write a detailed technical review. The second short review was written by a pair of authors relatively new to the field of military pyrotechnics. The third review was written as a more complete technical review of the book.

Generally, as a courtesy, book reviews to be published in the *Journal of Pyrotechnics* are sent to the author, with an offer to publish any comments or response they wish to make. In this case, since the primary author is deceased, the reviews were sent to the book's publisher. Although, comments were received from a representative of the book's publisher, permission was not granted for those comments to be published.

Review of:

Pyrotechnics

Alexander P. Hardt

Pyrotechnica Publications
[ISBN 0-929388-06-2] 2001

Bernard E. Douda, PhD

A General Review

In his preface to *Pyrotechnics*, Alexander Hardt indicates that his objective is to present an overview of significant advances. Initially, his effort began as a collaboration with Herbert Ellern in preparing an updated edition of *Military and Civilian Pyrotechnics.* For this reason, the reader will observe similarities between Hardt's book and Ellern's. However, the reader will also note that information in the new book has been updated and significantly expanded. Included are new comprehensive chapters on "Fireworks" and on "Statistical Tests and Analysis Methods."

The book is quite impressive, and very attractive. No other book on pyrotechnics has covered so wide a scope as thoroughly as this one does. Details abound within. The page size is 7 × 10 inches, as compared to other pyrotechnics books where the page size of which is typically 5-1/2 × 8-1/2 inches. Within its thirty pages of introductory material, 430 pages of text, and 24 plates, are 23 chapters including a glossary, 79 tables of data, 42 line illustrations, 45 photographic illustrations, four appendices, a bibliography, and 263 references. The typography, printing, and binding are of exceptionally high quality.

Hardt's draft was begun in 1985, and his personal contributions ended with his untimely death in 1989, still incomplete. The manuscript languished with another publisher for some time before being "rescued" by Pyrotechnica Publications. It is to be expected that a few of the subjects covered do not reflect information and developments subsequent to that period. This is consistent with the publisher's and the editorial team's desire to produce the book without degrading the goals and vision that Hardt had for his book. Nevertheless, a number of topics were added and a great number of areas were updated in an effort to fulfill his desire for quality, correctness and completeness.

The chapter on "Statistical Tests and Analysis Methods" is a major contribution toward satisfying Hardt's goal for completeness. Barry T. Neyer, Ph.D., a noted expert in the field, wrote this chapter. He provides a summary of the evolution of tests and analysis starting with the Probit test in 1935, the later Bruceton test, through the current Neyer D-Optimal test. This information will guide the reader when making a choice of which method to apply and the relative advantages of each.

Barry Bush, recipient of the Pyrotechnics Guild International's 1992 Grand Master award, contributed the chapter on "Fireworks." In a comprehensive review of Hardt's book, Kurt Medlin, author of numerous fireworks articles, past PGI competitor and award winner, display operator, and Trustee of the Fireworks Foundation, recognized the great value of the fireworks chapter and emphasizes its completeness, accuracy, thoroughness and up-to-date contents. His complete review, and the Table of Contents of the book, were published in the November 2001 *PGI Bulletin* (No.126) and on the web at http://www.ipsusa.org/review.pdf.

Just as Medlin points out that many aspects of military pyrotechnics are applicable to fireworks, so there is much information in the fireworks chapter directly applicable to military pyrotechnics. Of particular value are the descriptions of material incompatibilities and associated safety and handling, the precautions needed in dealing with moisture in compositions and high humidity in the processing areas, and the impact of low humidity on electrostatic sensitivity.

The chapter on "Matches" has changed considerably from the Ellern version. Stig Johansson, Ph.D., a leading expert on matches, and author of numerous articles on this subject, provided assistance in ensuring that the information was current and correct. The discussions of the safe mixing of potassium chlorate and phosphorus provide insights into the processing of extremely sensitive materials.

The developer of military pyrotechnics will find many useful tables of relevant material attributes and updated information about colored and obscurant smokes, colored and illuminating flames, generation of light and sound. Delays, primers, igniters, ignition concepts, sample thermodynamic calculations, and characteristics of the principal materials used in pyrotechnics are included as well as discussions of toxicity, hazards, and safety. I am in total agreement with many of my colleagues who have already expressed their desire to have a copy of this book at work and at home for ready reference.

Review of:

Pyrotechnics

Alexander P. Hardt

Pyrotechnica Publications
[ISBN 0-929388-06-2] 2001

Sara K. Poehlein, PhD and
Caroline K. Wilharm, PhD

Dr. Poehlein is an analytical chemist & Dr. Wilharm is a chemical engineer. Both have nearly three years of experience with military pyrotechnics.

A Brief Review

This book exceeded the author's intent to be an introductory volume on pyrotechnics. It is a reasonably extensive overview of the field. The thoroughness with which each subject is covered varies, with some subjects briefly touched upon, and others covered in more detail than necessary for this type of text. In many cases, the lack of detail stems from the fact that most of the book was written more than 10 years ago. For instance, Chapter 3. Disposal of Hazardous Materials is obsolete, as the field of demilitarization has grown extensively over the past decade. Also, the reference for the toxicity guidelines for pyrotechnic ingredients presented in Chapter 2 is from 1963.

This book is easy to read and follow, written in a language that is clear and flows well. The author's subtle humor interspersed throughout the book (see the Glossary) enhances its readability and enjoy-ability. The list of references is quite extensive, giving the reader many opportunities to learn more about a topic.

The inclusion of safety and handling as the second chapter of the book appropriately emphasizes this important subject. There are also references to safety throughout the other chapters, further stressing its importance. However, it would have been advantageous to present some of the other topics in a different sequence. For instance, Chapter 16. Materials Used in Pyrotechnics, should have been placed toward the beginning of the book, rather than the end.

The colorful pictures in the book are of excellent quality, but the reader tends to lose his train of thought when flipping back and forth between the pictures and the text, particularly for Chapter 15. Fireworks. This chapter was added to Hardt's original work to supplement his material, and it covers materials, safety, applications, formulas, assembly instructions, packaging, and history for numerous display fireworks. This chapter is far too long when compared to the other chapters, and much of the material covered here, though informative, would have been better discussed in shorter, specific chapters.

The lists of formulas for pyrotechnic items provided throughout the book are an excellent reference, as is the glossary. The chapters on matches and on materials are also well done. The chapters on mechanisms and rates and on thermochemical calculations have some minor errors, so the reader should be cautious if these methods are to be used.

Having read this book in its entirety, we have a better perspective about the breadth of the field of pyrotechnics. Good information about any area of interest is available, whether your interest is in creating displays, theatrical effects, or military applications.

Review of:

Pyrotechnics

Alexander P. Hardt

Pyrotechnica Publications
[ISBN 0-929388-06-2] 2001

Barry Sturman

6 Corowa Court, Mount Waverley, Victoria 3149, Australia

The introductory pages of *Pyrotechnics*[1] reveal that Dr. A. P. Hardt died in 1989. We are told that during a long career as a scientist with Lockheed Missiles and Space Co., Inc. Dr. Hardt published extensively in the field of pyrotechnics and became "a good friend" of both Dr. H. Ellern and Dr. T. Shimizu. At the time of his death Dr. Hardt was working on the manuscript of a book intended to be a "revised and updated adaptation" of Dr. Ellern's *Military and Civilian Pyrotechnics*".[2] According to the Publisher's Preface, Dr. Hardt finished the first draft of his manuscript a few weeks before his sudden death. The manuscript "rested for rather a long time with a large publisher" and eventually was retrieved by Dr. Hardt's widow, who requested that the present publisher, Robert G. Cardwell, should "see the manuscript to publication". *Pyrotechnics* is the result of that effort.

This is a beautifully produced book. Its size is similar to that of Brock's classic *Pyrotechnics*[3] and Plimpton's *Fireworks*.[4] Like those books, it has decorative endpapers adorned with historical images that remind the reader that the subject has a long tradition. The front and back boards are tastefully enhanced with borders impressed into the material. The spine is decorated in gold, with the title in gold on a red background, most elegant against the cream cloth of the binding. There is gold decoration above and below the title, and the edges of the pages are red. The book opens easily and stays open on the table with no tendency for the pages to stand up or turn by themselves. The paper has a pleasingly non-glossy finish and the type is clear. A colleague who has won prizes for bookbinding confirmed that the design and construction of this book is of an unusually high standard, rarely found in mass-produced books. A note at the back of the book indicates that the book "has been designed, printed on acid-free paper, and durably bound by the Smyth-sewn process, by Bayport Printing House, Inc, Bayport, Minnesota, United States of America."

The same note discusses the type used for the text. "Grace and legibility, without distracting ornament" are stated to be characteristic of the work of the designer of the typeface. The type is certainly legible, and is indeed free of distracting ornament. One minor aspect of the type setting, however, seemed odd. The word "aerial" is frequently written as "ærial", and "aerosol" as "ærosol", and even "aeroplane' as "æroplane". This looks rather quaint, but it is distracting, and is also, as far as this reader can ascertain, inconsistent with conventional usage.[5–7]

The Table of Contents indicates that the topics covered are appropriate:

- Chapter 1 Definitions, Scope and Literature
- Chapter 2 Safety and Handling of Hazardous Materials
- Chapter 3 Disposal of Hazardous Materials
- Chapter 4 Statistical Test and Analysis Methods
- Chapter 5 Mechanisms and Rates of Pyrotechnic Reactions
- Chapter 6 Color Creation
- Chapter 7 Thermochemical Calculations
- Chapter 8 Some Words on Instrumentation
- Chapter 9 Ignition
- Chapter 10 Primary Ignition
- Chapter 11 Matches
- Chapter 12 Primers and Ignition Mixtures
- Chapter 13 Miscellaneous Ignition Devices
- Chapter 14 Miscellaneous Pyrotechnic Devices
- Chapter 15 Fireworks
- Chapter 16 Materials Used in Pyrotechnics
- Chapter 17 Generation of Light
- Chapter 18 Delay Trains

- Chapter 19 Incendiaries and Tracer Munitions
- Chapter 20 Generation of Smoke
- Chapter 21 Generation of Sound
- Chapter 22 Gas Generators and Heating Devices
- Chapter 23 Glossary
- Appendix I Selected Further Resources for Pyrotechnics
- Appendix II Normal Distribution, Mean and Standard Deviation
- Appendix III Sieve Sizes
- Appendix IV KDNBF and DXN-1 (DXW-1)
- Bibliography
- Index

A Note about the Type and Printing

The content is of extremely variable quality. The best part by far is the chapter on fireworks contributed by B. L. Bush. It is comprehensive, well written and clearly reflects the author's knowledge and enthusiasm for his subject. This chapter alone would certainly justify the purchase of the book. It takes up over one third of the book, and is lavishly and appropriately illustrated with line drawings and colour and monochrome photographs. It seems highly likely that Mr. Bush could have written much more, to judge from his recent excellent contribution to the *Pyrotechnics Guild International Bulletin*.[8] It is greatly to be hoped that he will do just that. A book as well presented as this one, but filled with an even more complete treatment of fireworks by Mr. Bush, would be a delight for any firework enthusiast.

The chapter on statistical test and analysis methods, contributed by Dr. B. T. Neyer, is also of an appropriate standard for a book of this type. One of the services that the writer of a technical book performs for the reader is to act as an interpreter of material from the primary literature. The original papers usually make no concessions to the needs of non-specialists and can be very intimidating for the general reader. The author of a technical book can help make this material more accessible by stating the important facts and providing clarifying explanations. Dr. Neyer's chapter on statistical test and analysis methods is a good example. It is well referenced and provides explanations that would assist the reader in working with those references. It would perhaps have been useful to provide a worked example showing the calculations for each of the methods discussed.

These two chapters contributed by guest authors are consistent with the expectations raised by the impressive presentation of the book. It is unfortunate that much of the rest of the book falls short of the standards set by these two chapters. Dr. Hardt wrote "Pyrotechnic literature is commonly characterized by fragmentation and a lack of a comprehensive outlook." That would be a very fair comment on this book.

The glossary is very good; it is curious, however, that it contains no definition of 'pyrotechnic' or 'pyrotechnics'. The first sentence of the first chapter states that "Pyrotechnics is distinguished from the closely related technology of explosives and propellants, though their functions frequently overlap.' It would have been useful to see a clarification of what is to be considered "pyrotechnics" and what is not. The content of the book would suggest that Dr. Hardt's definition would be very broad indeed, including such things as spontaneously flammable liquids and gases, pyrophoric metals, white phosphorus, and various primary explosives. Outlines for the synthesis of two of the latter are presented as Appendix IV. This Appendix is of only marginal relevance and might well have been omitted, especially as the original references are cited.

Appendix I provides lists of "Selected Further Resources for Pyrotechnics". It is strange that the list of publications has no reference to *American Fireworks News*.[9] One can only wonder what selection criteria led to the exclusion of this valuable source of information.

Over 13 pages of Appendix I are given to a list of companies providing "Services and Supplies". If these companies sponsored the book, well and good; if not, it is hard to see the value of listing them. Companies, or at least their contact details, tend to be very ephemeral. A list that is up-to-date today is likely to be of much less use in a year or two.

A bibliography of 263 titles is a useful feature of this book. The remaining contents can be divided into two categories: chapters of descrip-

tive material about various devices and applications and chapters on scientific matters related to pyrotechnics.

The best that can be said for the science-related chapters is that they provide some useful references. Mostly, they do very little to assist the reader to make sense of those references. They present a few equations; some of them, unfortunately, are gravely misquoted. This can only cause confusion. There is no point in publishing equations just for the sake of displaying them. Equations are of value only if they allow something useful to be calculated or if they aid the understanding. Many of the equations published in this book are useless, either because they are wrong or because an adequate explanation is lacking.

The errors in the published equations are not, it would seem, mere typographical errors. Regrettably, comparison with the corresponding equations in the original papers suggests that the author apparently did not adequately understand the material. This conclusion was in every way contrary to this reader's expectations and was reached reluctantly. It is, of course, completely inconsistent with Dr. Hardt's reputation and with the standard of his co-authored papers in technical journals. Yet, the material is here for all to see. In the section "Kinetics of Reaction" in Chapter 8, the rate of reaction is given by equation 8.1:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A\left(1-x\right)^n$$

where the exponent

$$n = \frac{-E_a}{RT}$$

There is no need to define the meaning of the various symbols; the point is that the corresponding equation in the original reference[10] is different:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = r_0\left(1-x\right)^n e^{\frac{-E_a}{RT}}$$

where the exponent n is the order of the reaction. The symbol e (for the number 2.71828…)[11] does not appear in the version published in this book. If there had not been the explicit statement that the exponent

$$n = \frac{-E_a}{RT},$$

one might attribute the error to the typesetter and the proof reader.

Similar examples of incorrectly transcribed equations are to be found in Chapter 9. Equation 9.1 is

$$\frac{\partial T}{\partial t} = \alpha\frac{\partial^2 T}{\partial x^2} + \left(\frac{Q}{C\rho}\right)A_0^{\frac{-E_a}{RT}}$$

The corresponding equation in the original[10] is

$$\frac{\partial T}{\partial t} = \alpha\frac{\partial^2 T}{\partial x^2} + \left(\frac{Q}{C\rho}\right)K_0\,\exp\left(\frac{-E}{RT}\right)$$

The expression

$$\exp\left(\frac{-E}{RT}\right)$$

is just another way of writing

$$e^{\frac{-E}{RT}}$$

Can one avoid the conclusion that whoever wrote this material did not understand the difference between $\boldsymbol{ne^x}$ and $\boldsymbol{n^x}$?

Equation 9.4 is evidently Merzhanov and Averson's equation 25,[12] transformed in accordance with the incorrect assumption that $\boldsymbol{ne^x = n^x}$. The same error is evident in equation 9.5, which is adapted from Merzhanov and Averson's definition of a dimensionless variable giving the scale of the width of a chemical reaction zone.[12] The error is also to be found in equation 5.1 on page 33.

An author writing about the scientific subjects treated in this book ought to know about $\boldsymbol{e^x}$. A look at two of Dr. Hardt's co-authored publications[13,14] showed that he certainly did know about it. Furthermore, the 1974 paper by Phung and Hardt[14] on ignition characteristics of gasless reactions is vastly better than any scientific chapter in this book. What went wrong between that work and this?

The chapter on thermochemical calculations is disappointing. It would have been useful to include a general introduction to the subject. For example, I. Barin's *Thermochemical Data of*

Pure Substances[15] provides a concise overview in a 19-page chapter, followed by 9 pages explaining how to calculate the thermodynamic functions and 13 pages giving many worked examples of practical applications. It might be objected that 41 pages on thermodynamics would be excessive in a book about pyrotechnics. However R. H. Parker's *An Introduction to Chemical Metallurgy*[16] is of similar length to Hardt's book, and Parker devotes his first chapter (37 pages) to an introduction to chemical thermodynamics and a second (47 pages) to entropy and free energy. Thermodynamics is certainly as relevant to pyrotechnics as it is to metallurgy, yet this book gives the subject only five pages, including a whole page of conversion factors between various units, many of which are of historical interest only. This page would have been more appropriately placed as an Appendix.

The brief treatment of thermodynamics is confusing. Symbols and equations are used with almost no comment or explanation. The author correctly indicates that changes in the Gibbs free energy have to be calculated from the enthalpy and entropy changes at the temperature of interest, but then proceeds to use values for 298 K in his example for a high-temperature reaction. The example of the application of the Gibbs free energy is made more confusing by an error in the table of numerical values (page 48) that gives the units of entropy as kilocalories/mole instead of calories/mole. The correct units are used (but not mentioned) in the calculation, so a credible temperature is calculated. A reader unfamiliar with the subject would be left wondering where the factor of 0.001 came from. Such a reader would probably leave this chapter thinking that thermodynamics is just too difficult and obscure. Better leave such things to the clever fellows who can handle all those impressive equations.

The chapter on colour creation combines brevity and inaccuracy to create confusion. The subject is obviously important; furthermore, its scientific and practical aspects have been discussed in some detail, and there are interesting differences of opinion that could have been reviewed.[17–23] Yet, here it is given merely five pages, including one page for a table of wavelengths and another showing a monochrome sketch of the C.I.E. chromaticity diagram. The value of the table of wavelengths is questionable, as no comment is given on the possibilities and limitations of using the various species as colour emitters in pyrotechnics. The sketch of the C.I.E. chromaticity diagram is nowhere near as informative as that presented by Dr. Shimizu.[20] A coloured plate of the chromaticity diagram appears as Plate 1. Something has gone badly wrong with this plate. The region that ought to appear orange and yellow is a sickly green, the green region is brown, and blue is rendered as violet. The standard of this plate is, regrettably, consistent with the three-page treatment of pyrotechnic color creation. It seems incredible that an author who has cited Dr. Shimizu's writings on the subject[20,21] could produce such vague and misleading work. The author cites *Pyrotechnica* as a source of information on the subject, but does not refer to any specific articles. He does his readers a disservice. Anyone seeking an introduction to pyrotechnic color creation would do well to read the two-part article in *Pyrotechnica* on the physics and chemistry of colored flame.[22,23] Had the author studied and understood these articles, he would have been able to provide a far clearer explanation of the nature of molecular emission spectra. He wrote: "Many ionized species exist in the gaseous phase as bi- and tri-atomic molecules which give off molecular band spectra that arise from the ability of the molecule to absorb vibrational and rotational energy. Because molecules have fixed masses, sizes and interatomic spacing their rotational and vibrational energies are also quantized and so can take up and emit energies in discrete wavelengths. To the extent that these band spectra are in the visible range, they are of interest to pyrotechnics." One has to wonder about the use of the word "ionized". As indicated in Table 6.2, the species of interest as molecular band emitters in pyrotechnics are simple neutral molecules, not "ionized species". The importance of molecular vibration and rotation in the generation of molecular bands in the visible is, as clearly explained in reference 22, a consequence of the effect of these quantized molecular motions on the electronic energy states. The rotational and vibrational motions produce a great many more electronic energy states than there would otherwise be. Consequently the electronic spectrum of a molecule is a set of "bands" of closely spaced "lines" rather than the set of well-separated lines seen

in the electronic spectrum of an atom. A reader seeking a more detailed discussion will find it in any textbook on molecular spectroscopy.[24]

It is hard to believe that the person who wrote this inadequate exposition on colour generation was also responsible for the related chapter on light generation. This chapter is quite good. It would have been useful to include a sketch of the black body spectrum at various temperatures, to complement the table of subjective colours (Table 17.1, p 277), and to have provided some explanation of the difference between radiometric and photometric units. Nonetheless, this chapter seems free from obvious errors and provides some interesting technical details. Even here, however, one gets the feeling that the information might not always be reliable. Referring to the use of organic solvents to dilute the binder when combining metal powder and binder in the manufacture of magnesium flares, the author writes: "The older literature mentions trichloroethane but the current practice of blaming half the world's ills on chlorinated hydrocarbons has probably made this practice a thing of the past". Yet, as noted earlier in the book, "Reactive metals reduce chlorinated hydrocarbons… chlorinated hydrocarbons may be excellent degreasing agents, but they must never be used in place of hydrocarbon solvents." One does not have to blame "half the world's ills on chlorinated hydrocarbons" to feel that it is probably wise not to mix trichloroethane with powdered magnesium.

Enough shortcomings have been mentioned to indicate that this is not a book to be completely relied upon. It would have benefited from a highly critical editor, willing to take the time to check everything against the references. Understandably, that would have been a mammoth task. Some of the chapters, however, do not just need editing – they deserve to be rewritten and some irrelevant material ought to be removed. Were it not for the two excellent chapters by the guest authors, this book would best be left on the shelf. As it is, it is still worth purchasing and will certainly make a very handsome addition to the pyrotechnic library.

References

1) A. P. Hardt, *Pyrotechnics*, Pyrotechnica Publications, Post Falls, ID, 2001.

2) H. Ellern, *Military and Civilian Pyrotechnics*, Chemical Publishing Co., New York, 1968.

3) A. St. H. Brock, *Pyrotechnics the History and Art of Firework Making*, Daniel O'Connor, London, 1922.

4) G. Plimpton, *Fireworks A History and Celebration*, Doubleday, New York, 1984.

5) *The Shorter Oxford English Dictionary*, 2nd ed., Oxford University Press, Oxford, 1936.

6) T. Davidson and J. L. Geddie, *Chambers's Twentieth Century Dictionary*, W. & R. Chambers Ltd., London, 1943.

7) H. W. Fowler and E. Gowers, *A Dictionary of Modern English Usage*, Oxford University Press, Oxford, 1968.

8) B. L. Bush, "Chertier's Copper(s)", *Pyrotechnics Guild International Bulletin*, No. 129 (May/June 2002) pp 37–44.

9) J. Drewes, ed., *American Fireworks News*, HC 67- Box 30, Dingmans Ferry, PA 18328, USA.

10) R. T. Yang and M. Steinberg, "Differential Thermal Analysis and Reaction Kinetics for *n*th Order Reaction", *Analytical Chemistry*, Vol. 49 (1977) pp 998–1001.

11) E. Maor, *e: The Story of a Number*, Princeton University Press, Princeton, NJ, 1994.

12) A. G. Merzhanov and A. E. Averson, "The Present State of the Thermal Ignition Theory: An Invited Review", *Combustion and Flame*, Vol. 16 (1971) pp 89–124.

13) A. P. Hardt and P. V. Phung, "Propagation of Gasless Reactions in Solids – 1. Analytical Study of Exothermic Intermetallic Reaction Rates", *Combustion and Flame*, Vol. 21 (1973) pp 77–89.

14) P. V. Phung and A. P. Hardt, "Ignition Characteristics of Gasless Reactions", *Combustion and Flame*, Vol. 22 (1974) pp 323–335.

15) I. Barin, *Thermochemical Data of Pure Substances*, Parts 1 and 2, 2nd ed., VCH Verlag GmbH, Weinheim, Germany, 1993.

16) R. H. Parker, *An Introduction to Chemical Metallurgy*, Pergamon Press, Oxford, 1967.

17) R. F. Barrow and E. F. Caldin, "Some Spectroscopic Observations on Pyrotechnic Flames", *Proceedings of the Physical Society (London)*, 62 B (1949) pp 32–39.

18) A. A. Shidlovskiy, *"Principles of Pyrotechnics"*, Mashinostoyeniye Press, Moscow, 1964.

19) B. E. Douda, *Theory of Colored Flame Production*, RDTN No. 71, U.S. Naval Ammunition Depot, Crane, IN, AD-A951815, 1964.

20) T. Shimizu, *Fireworks from a Physical Standpoint*, Part II, Pyrotechnica Publications, Austin, TX, 1983.

21) T. Shimizu, *Fireworks: The Art, Science and Technique,* Maruzen Co. Ltd, Tokyo, 1981.

22) K. L. Kosanke, "The Physics, Chemistry and Perception of Colored Flames", Part I, *Pyrotechnica VII* (1981) pp 5–20.

23) K. L. Kosanke, "The Physics, Chemistry and Perception of Colored Flames", Part II, *Pyrotechnica IX* (1984) pp 42–54.

24) G. Herzberg, *The Spectra and Structures of Simple Free Radicals: An Introduction to Molecular Spectroscopy*, reprint of 1971 ed., Dover Publications, Inc., New York, 1988.

Review of: Black Powder Manufacturing, Testing, and Optimizing

Ian von Maltitz

American Firework News
[ISBN 0-929931-21-1] 2003

John Bergman

5438 E. Rotamer Rd., Milton, WI 53563 USA

As Mr. von Maltitz states in the preface, this work is not merely a second edition of his earlier book, *Black Powder Manufacture, Methods and Techniques*, as reviewed in *Journal of Pyrotechnics* No. 7 (Summer 1998). Despite similarities in its content and organization, the new book has been overhauled from cover to cover and has been greatly expanded. This rewriting reflects recent changes in approaches to small-scale powder making and testing methods, as well as a substantial body of new practical knowledge.

Like the original work, this book does not delve deeply into theory. It is mainly a practical guide for the amateur pyrotechnist and a compilation of facts for the pyro historian. In these objectives, however, it succeeds quite brilliantly as what must surely be the most concise and complete reference available on the subject of Black Powder. While an exhaustive discussion of the specific improvements to the book is not possible in a short review, the most significant are summarized below.

Chapter one, "Safety First", has been substantially expanded and includes several new and useful cautions. The author's counsel on keeping batches small, sticking to the safer methods, and giving forethought to the possible consequences of an accident is good advice for anyone who works with pyrotechnic materials. While this reviewer would still suggest a more pointed emphasis on not making powder in a residence, the list of safety tips is very pertinent and the

author's approach is quite responsible.

A much more comprehensive treatment of raw materials is very evident in the new book. Various types and grades of commercial potassium nitrate, and several types of sulfur, are discussed. The amateur will find the comparative usefulness and economy of these various types and grades to be quite informative.

The real treasure-trove of new materials information, however, concerns charcoal, to which two new and separate chapters have been dedicated. The first of these describes the basics of charcoal, and also includes a very comprehensive list of charcoals made from various woods and other materials. The relative merits of many of these charcoals in powder making are discussed. The second chapter on charcoal is devoted to charcoal-making methods, and will be of interest to those who wish to make various charcoals for themselves. The importance of charcoal to the qualities of finished Black Powder is frequently overlooked, and the author's thorough treatment of this subject is very useful.

Also new to the book are two chapters on milling. The first of these describes a number of types of mills, and their applicability to both commercial and amateur powder making. The other chapter deals specifically with ball milling. Several types of ball mills and milling media are discussed, as are wet and dry milling methods. Safety precautions specific to milling are included.

Finally, several chapters are devoted to the testing of Black Powder. A large variety of test methods, both historical and modern, are presented and compared, and those adaptable to amateur experimentation are discussed in detail.

The book incorporates many new charts, graphs, tables, and illustrations, as well as a number of useful and interesting appendices. The appendices include a description of the author's visit to Goex's Moosic, Pennsylvania Black Powder plant, specifications for commercial Black Powder, and useful data on lift charges for various types of aerial shells.

Even more than Mr. Von Maltitz's original book, *Black Powder Manufacturing, Testing, and Optimizing* is a notably readable and practical work that will be of use to both amateur pyrotechnists and historians.

Guide for Authors

Style Guide

The *Journal of Pyrotechnics* has adopted the *ACS Style Guide* [ISBN 0-8412-3462-0]. It is not necessary that authors have a copy; however, a copy can be ordered through a local bookstore.

Subject Areas

Fireworks, Pyrotechnic Special Effects, Propellants, Rocketry and Civilian Pyrotechnics

Manner of Submission

Submissions should be made directly to the publisher at the address at bottom of page. Upon receipt of an article, the author will be sent an acknowledgment and a tentative publication date. For specific requests regarding editors, etc. please include a note with that information. Preferably the text and graphics will be submitted electronically or on a 3-1/2" diskette or CD in IBM format with a print copy as backup. The Journal is currently using Microsoft Word 2002, which allows for the import of several text formats. Graphics can also be accepted in several formats. Please also inform us if any materials need to be returned to the author.

General Writing Style

- The first time a symbol is used, it is preferred to write it out in full to define it [e.g., heat of reaction (ΔH_r) or potassium nitrate (KNO_3)].
- Avoid slang, jargon, and contractions.
- Use the active voice whenever possible.
- The use of third person is preferred; however, first person is acceptable where it helps keep the meaning clear.

Format

In addition to the authors' names, please include an affiliation for each author and an address for at least the first author.

A short abstract is needed. (An abstract is a brief summary of the article, not a listing of areas to be addressed.)

Include 3 to 7 keywords to be used in a reference database: However, multi-word names and phrases constitute only one keyword (e.g., potassium nitrate and heat of reaction are each one word).

Use of SI units is preferred. If English units are used, please provide conversions to SI units.

Figures, Photos, and Tables are numbered consecutively. For submission, place them at the end of the text or as separate files. During page composition, they will be inserted into the text as appropriate. For graphs, please also submit "raw" X–Y data.

References cited in the text are referred to by number (i.e., "Smith[1] states"; or "the research[2,3] shows ..."). In the reference section, they will be ordered by usage and not alphabetically. It is preferred that a full citation, including author, title, book or journal, publisher for books, and volume and pages for journals, etc. be provided. Examples:

1) A. E. Smith, *Pyrotechnic Book of Chemistry*, XYZ Publishers (1993) [p nn–nn (optional)].
2) A. E. Smith, R. R. Jones, "An Important Pyrotechnic Article," *Pyrotechnic Periodical*, Vol. 22, No. 3 (1994) [p n–n, (optional)].

Editing

The *Journal of Pyrotechnics* is refereed. However, the editing style is friendly, and the author makes the final decision regarding what editing suggestions are accepted.

More Information

Contact Bonnie Kosanke, Publisher, the Journal of Pyrotechnics, Inc., 1775 Blair Road, Whitewater, CO 81527, USA.
or
email bonnie@jpyro.com

Events Calendar

Pyrotechnics and Fireworks

Special Topics in Pyrotechnics

June 13–18 2004 Chestertown, MD, USA
Contact: John Conkling
PO Box 213
Chestertown, MD 21620, USA
Phone: +1-410-778-6825
FAX: +1-410-778-5013
email: JConkling2@washcoll.edu
web: www.John.Conkling@washcoll.edu

1st Workshop on Pyrotechnic Combustion Mechanisms

July 10, 2004, Fort Collins, CO, USA

Contact: Dr. Steve Son
Los Alamos National Lab
PO Box 1663
Los Alamos, NM 87545, USA
email: son@lanl.gov
web: http://www.intlpyro.org/pyro-combustion-mechanisms.htm

31st Int'l Pyrotechnics Seminar

July 11–16 2004, Fort Collins, CO, USA

Contact: Linda Reese, Appl. Res. Assoc., Inc.
5941 S. Middlefield Rd., Suite 110
Littleton, CO 80127, USA
Phone: +1-303-795-8106
FAX: +1-303-795-0125
email: lreese@ara.com

Chemistry of Pyrotechnics & Explosives

July 25– 30 2004 Chestertown, MD, USA
Contact: John Conkling
PO Box 213
Chestertown, MD 21620, USA
Phone: +1-410-778-6825
FAX: +1-410-778-5013
email: JConkling2@washcoll.edu
web: www.John.Conkling@.washcoll.edu

Pyrotechnics Guild Int'l Convention

Aug. 7–13 2004, Fargo, ND, USA
Contact:, Frank Kuberry, Sec. Treas.
304 W Main St
Titusville, PA 16354, USA
Phone: +1-814-827-0485
e-mail: kuberry@earthlink.net
web: www.pgi.org

Energetic Materials

Computational Mech. Assoc. Courses–2004

Contact: Computational Mechanics Associates
PO Box 11314,
Baltimore, MD 21239-0314, USA
Phone: +1-410-532-3260
FAX: +1-410-532-3261
email: 74047.530@compuserve.com
web: www.compmechanics.com

PARARI 2003 – An International Explosive Ordnance Symposium

October 29–31, 2003, Canberra, Australia

Contact: Ordinance Safety Group
Dept. of Defence, CP4-3-160
Canberra, ACT, 2600
Australia
Phone: +61-2-6266-3058
FAX: +61-2-6266-4781
email: dmo-jlc-osg-parari@cbr.defence.gov.au
web: www.defence.gov.au/dmo/jlc/osg/osg.cfm

3rd Int'l. Disposal Conference

November 10–11, 2003, Karlskoga, Sweden

Contact: Prof. Dan Loyd
LiTH, SE-581 83
Lingoeping, Sweden
Phone: +46-13-281-112
FAX: +46-13-281-101
Email: danlo@ikp.liu.se

30th ISEE Conf. on Explosions and Blasting Technique

Feb 1–4 2004 New Orleans, LA, USA

Contact: Lynn Mangol
Phone: 440-349-4400

13th Int'l Symp. on Chemical Problems Connected with the Stability of Explosives

May 2004 (tentative) Sweden

Contact: Stig Johansson
Johan Skyttes väg 18, SE 55448
Jönköping, Sweden
Phone/FAX: +46-3616-3734
email: srj@telia.com

35th Int'l Annual Conf. ICT – Energetic Materials – Structure and Properties

June 29–July 2 2004, Karlsruhe, Germany

Contact: Manuella Wolff
Fraunhofer-Inst. für Chem. Technologie (ICT)
P. O. Box 1240
D-76318 Pfinztal (Berghausen), Germany
Phone: +49-(0)721-4640-121
FAX: +49-(0)721-4640-120
email: mw@ict.fhg.de
web: www.ict.fhg.de

Franklin Applied Physics Lectures

July 26–30, 2004, Oaks, PA, USA

Contact: James G. Stuart, Ph.D., Pres.
Franklin Applied Physics, Inc.
98 Highland Ave., PO Box 313
Oaks, PA 19456, USA
Phone: +1-610-666-6645
FAX: +1-610-666-0173
email: JStuartPhD@aol.com

Propulsion

AIAA/ASME/SAE/ASEE Joint Propulsion Conference

July 11–14 2004, Fort Lauderdale, FL, USA

Contact:
Phone: +1-703-264-7500 / 800-639-2422
web: www.aiaa.org

High Power Rocketry

LDRS 2004

Contact: see web site
www.tripoli.org/calendar.htm

Model Rocketry

NARAM 2004

Contact: — see web site for details:
web: www.naram.org
For other launch information visit the NAR
Web site: www.nar.org

Future Events Information

If have information concerning future—explosives, pyrotechnics, or rocketry—meetings, training courses or other events that you would like to have published in the *Journal of Pyrotechnics*, please provide the following information:

Name of Event

Date and Place (City, State, Country) of Event

Contact information — including, if possible, name of contact person, postal address, telephone and fax numbers, email address and web site information.

This information will also be published on the Journal of Pyrotechnics Web Site:
http://www.jpyro.com

Journal Sponsors

***Journal of Pyrotechnics* wishes to thank the following Sponsors for their support.**

Individual Sponsors:

Ed Brown
P.O. Box 177
Rockvale, CO 81244, USA
Phone: 719-784-4226
email: edwinde@cs.com

Gerald Laib
17611 Longview Lane
Olney, MD 20832, USA
Phone: 301-744-4358
FAX: 301-744-4784

Sgt. John Giacalone
5500 E. Tudor Rd.
Anchorage, AK 99507, USA
Phone: 907-269-5689
FAX: 907-338-6614
email: jrgiacalone@hotmail.com

Corporate Sponsors:

Aerotech & Industrial Solid Propulsion Inc.
Gary Rosenfield
2113 W 850 N St
Cedar City, UT 84720, USA
Phone: 435-867-9998
FAX: 435-865-7120
email: garyr@powernet.net
web: aerotech-rocketry.com

Allied Specialty Insurance
David H. Smith
10451 Gulf Blvd.
Treasure Island, FL 33706, USA
Phone: 800-237-3355
FAX: 727-367-1407
email: info@alliedspecialty.com
web: www.alliedspecialty.com

American Fireworks News
Jack Drewes
HC 67 Box 30
Dingmans Ferry, PA 18328, USA
Phone: 570-828-8417
FAX: 570-828-8695
email: afn@fireworksnews.com
web: www.fireworksnews.com

American Pyrotechnics Association
Julie Heckman
4808 Moorland Lane - Ste 109
Bethesda, MD 20814, USA
Phone: 301-907-8181
email: jheckman@americanpyro.com
web: www.americanpyro.com

Astro Pyrotechnics
Leo Autote
2298 W. Stonehurst
Rialto, CA 92377, USA
Phone: 909-822-6389
FAX: 909-854-4749
web: www.astropyro.com

Australian Soc. of Accredited Pyros.
Chris Larkin
PO Box 606
Mt. Ommaney, QLD 4074, Australia
Phone: +617-371-20804
FAX: +617-327-90614
email: nitrotech@smartchat.net.au

Brooke Mawhorr, PC
Douglas K Mawhorr
112 East Gilbert StPO Box 1071
Muncie, IN 47305, USA
Phone: 765-741-1375
FAX: 765-288-7763
email: dlmmawhorr@aol.com

Canadian Explosives Research Laboratory
Dr. Phil Lightfoot, Manager
CANMET - 555 Booth St.
Ottawa, ON K1A 0G1, Canada
Phone: 613-947-7534
FAX: 613-995-1230
email: plightfo@nrcan.gc.ca
web: www.nrcan.gc.ca/mms/cerl

Combined Specialties Int'l. Inc.
John and Alice Allen
8362 Tamarack Village, Ste. 119
Woodbury, MN 55125, USA
Phone: 651-855-0091
FAX: 651-855-0088
email: jallen@combinedspecialties.com

Daveyfire, Inc.
Alan Broca
2121 N California Blvd. Ste. 290
Walnut Creek, CA 94596, USA
Phone: 925-926-6414
FAX: 925-926-6439
email: info@daveyfire.com

Delcor Industries Inc.
Sam Bases
19 Standish Ave.
Yonkers, NY 10710, USA
Phone: 914-779-6425
FAX: 914-779-6463
email: delcor@hotmail.com
web: www.delcorind.com

European Pyrotechnic Arts Newsletter
Rob Driessen
Grenadiersweg 55
Riemst, B 3770, Belgium
Phone: +32-12-210-630
FAX: +32-12-210-630
email: epan@pandora.be
web: http://users.pandora.be/epan

Fawkes Fireworks
Tony Cardell and David Watts
89 Lingfield Road
Edenbridge, Kent TN8 5DY, UK
Phone: 44-1732-862-862
FAX: 44-1342-317-818
email: Tony@fawkes.co.uk

Fire One
Dan Barker
863 Benner Pike
State College, PA 16801, USA
Phone: 814-238-5334
FAX: 814-231-0799
email: info@fireone.com
web: www.fireone.com

Firefox Enterprises Inc.
Gary Purrington
11612 N. Nelson
Pocatello, ID 83202, USA
Phone: 208-237-1976
FAX: 208-237-1976
email: custserv@firefox-fx.com
web: www.firefox-fx.com

Firework Professionals
Anthony Lealand
PO Box 19-912
Christchurch, 8030, New Zealand
Phone: 64-3-982-3473
FAX: 64-3-982-3474
email: firework@firework.co.nz
web: www.firework.co.nz

Fireworks
PO Box 40
Bexhill, TN40 1GX, England
Phone: 44-1424-733-050
FAX: 44-1424-733-050
email: editor@fireworks-mag.org
web: www.fireworks-mag.org

Fireworks and Stage FX America
Kevin Brueckner
P.O. Box 488
Lakeside, CA 92040-0488, USA
Phone: 619-596-2800
FAX: 619-596-2900
email: go4pyro@aol.com
web: www.fireworksamerica.com

Fireworks Business
Jack Drewes
HC 67 Box 30
Dingmans Ferry, PA 18328, USA
Phone: 717-828-8417
FAX: 717-828-8695
email: afn@fireworksnews.com
web: www.fireworksnews.com

Fullam's Fireworks, Inc.
Rick Fullam
P.O. Box 1808 CVSR
Moab, UT 84532, USA
Phone: 435-259-2666
email: Rfullam_3@yahoo.com

Goex, Inc.
Mick Fahringer
PO Box 659
Doyline, LA 71023-0659, USA
Phone: 318-382-9300
FAX: 318-382-9303
email: email@goexpowder.com
web: www.goexpowder.com

High Power Rocketry
Bruce Kelly
PO BOX 970009
Orem, UT 84097-0009, USA
Phone: 801-225-3250
FAX: 801-225-9307
email: 71161.2351@compuserve.com
web: www.tripoli.org

IPON srl
Pagano Benito
Via Trofa
Ottaviano, Napoli 80044, Italy
Phone: +39-81-827-0934
FAX: +39-81-827-0026
email: info@ipon.it
web: www.ipon.it

Island Fireworks Co. Inc.
Charles Gardas
N735 825th St.
Hager City, WI 54014, USA
Phone: 715-792-2283
FAX: 715-792-2640
email: islndfwk@pressenter.com
web: www.pyro-pages.com/island

Lantis Fireworks & Lasers
Ken Lantis
PO Box 491
Draper, UT 84020, USA
Phone: 801-768-2255
FAX: 801-768-2433
email: info@fireworks-lasers.com
web: www.fireworks-lasers.com

LaRosa Fireworks
Lorenzo LaRosa
Via Mortillaro No. 57
Bagheria, Palermo 90011, Italy
Phone: +39(0)91-969-031
FAX: +39(0)91-967-580
email: info@larosa-firewoks.it
web: www.larosa-fireworks.it

MagicFire, Inc.
Paul McKinley
PO Box 896
Natick, MA 01760-0896, USA
Phone: 508-647-9645
FAX: 508-647-9646
email: pyrotech@magicfire.com
web: www.magicfire.com

Marutamaya Ogatsu Fireworks Co., Ltd.
1-35-35 Oshitate Fuchu
Tokyo, 183-0012, Japan
Phone: 81-42-363-6251
FAX: 81-42-363-6252
email: hanabi@mof.co.jp
web: www.mof.co.jp

Mighty Mite Marketing
Charlie Weeth
122 S. 17th St.
LaCrosse, WI 54601-4208, USA
Phone: 608-784-3212
FAX: 608-782-2822
email: chzweeth@pyro-pages.com
web: www.pyro-pages.com

MP Associates Inc.
P.O. Box 546
Ione, CA 94640, USA
Phone: 209-274-4715
FAX: 209-274-4843

Precocious Pyrotechnics, Inc.
Garry Hanson
4420 278th Ave. N.W.
Belgrade, MN 56312, USA
Phone: 320-346-2201
FAX: 320-346-2403
email: ppinc@tds.net
web: www.pyro-pro.com

Pyro Shows, Inc.
Lansden Hill
P.O. Box 1406
LaFollette, TN 37766, USA
Phone: 800-662-1331
FAX: 423-562-9171
email: info@pyroshowsusa.com
web: www.pyroshowsusa.com

Pyrodigital Consultants
Ken Nixon
1074 Wranglers Trail
Pebble Beach, CA 93953, USA
Phone: 831-375-9489
FAX: 831-375-5225
email: pyrodig@aol.com
web: www.infinityvisions.com/pyrodigital

PyroLabs, Inc.
Ken Kosanke
1775 Blair Road
Whitewater, CO 81527, USA
Phone: 970-245-0692
FAX: 970-245-0692
email: ken@jpyro.com

Pyrotechnics Guild Int'l., Inc.
Frank Kuberry, Sec.-Treas.
304 W Main St
Titusville, PA 16354, USA
Phone: 1-814-827-0485
email: kuberry@earthlink.net
web: www.pgi.org

RES Specialty Pyrotechnics
Steve Coman
21595 286th St.
Belle Plaine, MN 56011, USA
Phone: 952-873-3113
FAX: 952-873-2859
email: respyro@earthlink.net
web: www.respyro.com

Rozzi Famous Fireworks
Arthur Rozzi
PO Box 5
Loveland, OH 45140, USA
Phone: 513-683-0620
FAX: 513-683-2043
email: art@rozzifireworks.com
web: rozzifireworks.com

Service Chemical, Inc.
Ben Cutler
2651 Penn Avenue
Hatfield, PA 19440, USA
Phone: 215-362-0411
FAX: 215-362-2578
email: ben@servicechemical.com
web: www.servicechemical.com

Skylighter, Inc.
Harry Gilliam
PO Box 480
Round Hill, VA 20142, USA
Phone: 540-338-3877
FAX: 540-338-0968
email: orders@skylighter.com
web: www.skylighter.com

Starburst Pyrotechnics & Fireworks Displays Ltd
Bonnie Pon
2nd Fl-Sui Hing Hong Bldg
17 Commissioner St
Johannesburg, Gauteng 2000,
South Africa
Phone: 27-11-838-7704
FAX: 27-11-836-6839
email: info@starburstpyro.co.za
web: www.starburstpyro.co.za

Western Pyrotechnics, Inc.
Rudy Schaffner
2796 Casey Road
Holtville, CA 92250, USA
Phone: 760-356-5426
FAX: 760-356-2051
email: rudys@holtville.net

Sam & Trudy Zarkoff
Sam & Trudy Zarkoff
1241 S. Hayworth Ave.
Los Angeles, CA 90035, USA
email: Trudybeadspirit@aol.com

Sponsorships

No advertising as such is printed in the *Journal of Pyrotechnics*. However, a limited number of sponsors have been sought so that the selling price of the Journal can be reduced from the listed cover price. The cost of helping sponsor an issue of the *Journal of Pyrotechnics* is $70 per issue for business and organizations [$35 for individuals]. In addition to a listing in the Sponsor section of the Journal, full sponsors receive two free copies of the sponsored Journal [one copy for individual sponsors] and a brief listing on a flyer inserted under the transparent cover of the Journal.

Additionally, if you so desire, we will provide a link from the Journal of Pyrotechnics Web Site to sponsors' web site, e-mail address or simply a company name, address and phone information listing. If you would like to be a sponsor contact the publisher.

Below are listed the articles that have appeared in the past 6 issues. All of the back issues are still available. If you would like to purchase back issues, you can look at the titles and abstracts at the Journal of Pyrotechnics web site: http://www.jpyro.com. You can also contact the publisher at:

Journal of Pyrotechnics, Inc., 1775 Blair Rd., Whitewater, CO 81527, USA. Phone/FAX: +1-970-245-0692

Issue 17:

Color Purity Measurements of Traditional Pyrotechnic Star Formulas

A Study of the Combustion Behaviour of Pyrotechnic Whistle Devices (Acoustic and Chemical Factors)

Reasons for Fuse Failure and Drift Distance of Spherical Fireworks Shells

Some Properties of Explosion Generated Toroids

Feasibility Study on the Use of Nanoscale Thermites for Lead-Free Electric Matches

Issue 16:

Evaluation of the Hazards Posed by High Energy Bangers Part 2. Damage to Hand Simulants

Thermodynamic Modeling of High-Temperature Systems

Test Burn of a Temporary Fireworks Stand

Thermodynamics of Black Powder and Aerodynamics of Propelled Aerial Shells

Accidents and their Role in Aiding the Management of Health and Safety in Pyrotechnics Manufacture

Effect of Ultrasound on Single-Base Propellants for Pyrotechnic Purposes

The Effects of External Fire on Fireworks Stored in Steel ISO Transport Containers

Application of Hydroxyl (OH) Radical Ultraviolet Absorption Spectroscopy to Rocket Plumes

Issue 15:

Evaluation of the Hazards Posed by High Energy Bangers Part 1. Noise, Overpressure and TNT Equivalence

Special Materials in Pyrotechnics Part 2 Application of Cæsium and Rubidium Compounds in Pyrotechnics

An Introduction to Chemical Thermodynamics Part 3. Free Energy and Equilibrium

Studies of Electric Match Sensitiveness

Multi-Wavelength Laser Opacity Study of a Hybrid Rocket Plume

Issue 14:

Hazards Associated with the Storage of Fireworks

Thermal Techniques Used in the Hazard Evaluation of Pyrotechnics

Our Present Knowledge of the Chemistry of Black Powder

A Brief Introduction to Noise and Data Filtering

Applying Explosives Testing Techniques To Obtain Insight into the Explosion (Or Is It Detonation?) Phenomenon of Piles of Fireworks

Ground Test Rocket Thrust Measurement System

Hypotheses Regarding "Star-Shell Detonations"

Issue 13:

Evaluation of Lithium Compounds as Color Agents for Pyrotechnic Flames

Pyrotechnic Delays and Thermal Sources

Fireworks Shell Drift due to Shell-to-Bore Clearance

Pressure, Plume Flicker, and Acoustic Data Correlation in Labscale Hybrid Rockets

Pyrotechnic Reaction Residue Particle Identification by SEM / EDS

Commercial Developments in Red Phosphorus Performance and Stability for Pyrotechnics

Summary Report on Tests on Display Fireworks Conducted by the Bureau of Mines for the U.S. Department of transportation Relative to Hazard Classification of Display Fireworks

Issue 12:

Speculation on the Effects of Gunshot or Explosive Residues on Historic Silk Flags

Pyrotechnic Particle Morphology—Low Melting Point Oxidizers

A Survey of Analytical Tools for Explosion Investigations

An Introduction to Chemical Thermodynamics Part 2—Entropy, Molecular Disorder, and the Second and Third Laws

Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures Part 4. Firework Compositions and Investigation of the Sulfur/Chlorate Initiation Reaction

Practical Applications of Capillary Extrusion Rheometry to Problems in the Processing of Energetic Materials

Fixed and Scanning Infrared Radiometers for Combustion Studies