

2

RD TN NO. 135
24 JULY 1967

**DETERMINATION OF THE AMOUNT OF
ENERGY RADIATED IN THE VISIBLE REGION
BY AN ILLUMINATING FLARE FLAME**

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED



PREPARED BY

RECEIVED
JAN 31 1985
D

**RESEARCH AND DEVELOPMENT DEPARTMENT
NAVAL AMMUNITION DEPOT, CRANE, INDIANA**

85 01 23 005

DTIC FILE COPY

AD-A953 986

11/8

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

A953 986

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS None		
2a. SECURITY CLASSIFICATION AUTHORITY --		3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) RDTN-135		5. MONITORING ORGANIZATION REPORT NUMBER(S) --		
6a. NAME OF PERFORMING ORGANIZATION Naval Ammunition Depot	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION --		
6c. ADDRESS (City, State, and ZIP Code) Crane, Indiana 47522		7b. ADDRESS (City, State, and ZIP Code) --		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Naval Air Systems Command	8b. OFFICE SYMBOL (If applicable) AIR-320R	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER --		
8c. ADDRESS (City, State, and ZIP Code) Washington, DC 20361		10. SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO. --	PROJECT NO. --	TASK NO. --
11. TITLE (Include Security Classification) Determination of the amount of energy radiated in the visible region by an illuminating flare flame.				
12. PERSONAL AUTHOR(S) Bernard E. Doua				
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 1966 TO 1967	14. DATE OF REPORT (Year, Month, Day) 67 07 24	15. PAGE COUNT 31	
16. SUPPLEMENTARY NOTATION None				
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Pyrotechnics, illuminating flares, illuminating flames		
FIELD	GROUP			SUB-GROUP
19	1901			
10	1002			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The objective is to determine the absolute spectral energy radiated in the visible region by a Mk 24 illuminating flare. A spectrum of the flame in the visible region is obtained with a scanning spectrometer. The integrated visible energy radiated by a flare has a measured value of 2510 kcal which is about 11 percent of the energy of the flare reaction. Important components of the radiation from a magnesium-sodium nitrate flare are presented along with a description of excitation processes which may be present. The processes include chemical excitation of the sodium atoms, thermal excitation of the sodium atoms, and thermal excitation of other substances. It is concluded that thermal radiation by sodium is more probably the major component of the visible energy than chemiluminescence. A calculated 17 percent of the total radiated energy is found in the visible. This is compared to 10.8 percent of its total that a blackbody at 3000°K can radiate in the				
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL B. E. Doua		22b. TELEPHONE (Include Area Code) 812-854-3420	22c. OFFICE SYMBOL 50C	

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

REPRODUCED AT GOVERNMENT EXPENSE

REPRODUCED AT GOVERNMENT EXPENSE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

Block 19, continued

Visible. These comparisons are made to show that the spectral emissivity of the flare in the visible region is generally greater than elsewhere. The practical importance of selective emitters is discussed in relation to possible improvement of the light output.

Originator furnished keywords include:

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Avail and/or	
Dist	Special

A-1



UNANNOUNCED

See DD14731 (Field 18)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPRODUCED AT GOVERNMENT EXPENSE

REPRODUCED AT GOVERNMENT EXPENSE

SUMMARY

The objective is to determine the absolute spectral energy radiated in the visible region by a MK 24 illuminating flare. A spectrum of the flame in the visible region is obtained with a scanning spectrometer. The integrated visible energy radiated by a flare has a measured value of 2510 kcal which is about 11 percent of the energy of the flare reaction.

Important components of the radiation from a magnesium-sodium nitrate flare are presented along with a description of excitation processes which may be present. The processes include chemical excitation of the sodium atoms, thermal excitation of the sodium atoms, and thermal excitation of other substances. It is concluded that thermal radiation by sodium is more probably the major component of the visible energy than chemiluminescence.

A calculated 17 percent of the total radiated energy is found in the visible. This is compared to 10.8 percent of its total that a blackbody at 3000°K can radiate in the visible. These comparisons are made to show that the spectral emissivity of the flare in the visible region is generally greater than elsewhere. The practical importance of selective emitters is discussed in relation to possible improvement of the light output.

INTRODUCTION AND HISTORICAL

One of the most successful and widely used pyrotechnic illuminating devices is the U. S. Navy Mark 24 Aircraft Parachute Flare. The flame from this flare is typical of flames produced by combustion of magnesium and sodium nitrate. The flare is normally released from aircraft over the area to be illuminated. A parachute automatically suspends the illuminating element at a preselected time. During the descent, the flame radiates with an average luminous intensity of about 1.7 million candles for nearly 180 seconds. Additional data about the flare are listed in Appendix A.

The spectrum of this flame shows a strong, broad continuum distributed about the sodium resonance lines. This continuum is superimposed on a weaker background continuum which extends throughout the visible region. The sodium related continuum extends from about 550 mμ to 700 mμ. The radiant energy represented by the sodium feature represents a significant portion of the total radiant energy in the visible region. The relatively large amount of energy radiated by this flare in the visible region is the reason that the flame resulting from the magnesium-sodium nitrate reaction has been adopted as a common pyrotechnic means for producing light.

In the early 1950's, investigators¹ at Picatinny Arsenal, Dover, New Jersey, learned that pyrotechnic light could be produced more efficiently by burning a magnesium-sodium nitrate mixture than by burning the then standard magnesium-barium nitrate-sodium oxalate-

aluminum composition. Since that time, the major effort was directed toward improvement of the magnesium-sodium nitrate system and its development in various signalling and illuminating devices. Most of these engineering efforts have applied empirical methods to optimize the system for a given purpose.

Ellern² discusses some of the practical aspects of producing flares with these mixtures. He also reviews other historical, thermochemical, and relative performance data related to white light production. Bond and Jacobs³ report measurements of isothermal kinetics and self-heating in binary mixtures of magnesium and sodium nitrate over a range of compositions up to stoichiometric.

Blunt⁴ notes in a recent report that results of studies of these reactions are not often published in the open literature. For this reason, he reproduced a large number of flame spectra. Included are examples of flames containing binary and ternary mixtures of magnesium as a fuel with oxidizing agents such as sodium nitrate, potassium nitrate, barium nitrate, strontium nitrate, and potassium perchlorate. A dominant feature of typical pyrotechnic spectra is the formation of a strong broad continuum about the resonance lines of the alkali metals when these are present. This feature often accounts for a large portion of the total radiated energy. On the other hand, flames containing the alkaline earth metals do not show this broadening about the principal elemental lines. Instead, band structure of the metal oxides or halides is the characteristic feature of the visible spectra.

The data presented by Blunt⁴ also shows that a degradation of luminosity from these flames occurs as the ambient pressure is reduced and that the effect grows sharply in magnitude at pressures of less than 150 torr. In all cases, the line and band structure is superimposed on a weaker background continuum. The observation of the different types of structure in the spectra leads naturally to questions regarding their origin and their relative importance in producing light.

One of the most important and prominent features of the flare spectrum is the broadened region around the sodium resonance lines. The observed pressure dependence leads to the question whether the theory of line broadening is applicable to the study of this region.

Breene⁵ reviews the evolution and derivation of the theories of Interruption Broadening which includes the Lorentz theory and Statistical Broadening which includes the Jablonski theory. Mitchell and Zemansky⁶ note that the effect of collisions upon the emitting characteristics of a classical oscillator-atom was treated by Lorentz⁷ in a manner analagous to that of radiation damping. That is, if an absorbing atom performs Z collisions per second, with the molecules of a foreign gas, the resulting effect is equivalent to Z interruptions per second in an undamped wave train. The equation derived by Lorentz gives a symmetrical curve about the absorption line and therefore is not capable of handling experiments in which line shift and asymmetry are present. One should note that Lorentz reported his work in the pre-quantum mechanical period, and that Lenz⁸, Weisskopf⁹, and others later derived expressions to account for line shift and

asymmetry. These refinements lead to expressions similar to those resulting from the Statistical Theory.

The first attempt at a quantum theory of Lorentz broadening was made by Jablonski.¹⁰ He considered a collision between an absorbing atom and a foreign gas molecule as a temporary formation of a quasi-molecule. Breene goes on to note that the intensity distribution and the line width resulting from the Jablonski theory is dependent on the potential surfaces and the probability of different separation distances between the colliding particles. It is also clear that almost any form of asymmetry of the spectral line can be obtained depending on relative profiles of the potential surfaces. It is this notion that may best explain the sodium broadening observed in our flare involving a collisional process such as represented by reaction (5).



Although Jablonski laid the basis for the Statistical Theory, Breene notes that Margenau¹¹ first developed an applicable mathematical form for it. The equivalence of the Lorentz and Jablonski theories is also discussed by Breene. Although there is some controversy regarding the justifiability of the approximations involved, a mathematical route was developed by Foley¹² for obtaining the Lorentz form from the Jablonski form. Nevertheless, neither of these theories can be applied to our problem without further study.

Statement of the Problem

The objective is to determine the nature of the interaction which causes the continuum about the sodium resonance lines to be so strong and broad.

The broadened region about the sodium lines is pressure dependent. On the other hand, the Lorentz and Fablonski theories of pressure broadening may not be directly applicable to a complicated system such as the flare flame.

It is unclear at this point whether the sodium emission and broadening is primarily a physical or a chemical property of the system. That is, would other systems containing sodium atoms at this temperature have similar sodium emission characteristics or is the emission specifically a characteristic of this chemical reaction? Immediately related to this question is the further question, could the flare reaction produce the observed sodium excitation merely because of the adiabatic temperature rise or does the sodium emission require a non-equilibrium concentration of sodium atoms?

In the past, some efforts were made to determine the amount of energy radiated by the flare in the visible region on a reactive basis. No published work could be found which reports measurement of the spectral energy from the flare on an absolute scale. Therefore, the immediate objective of this study is to determine the absolute spectral energy radiated by the flare in the visible region. This is to be compared with the energy of the reaction and with temperatures consistent with the difference between the two energies.

EXPERIMENTAL

General Procedure

The main objective was to measure the spectral radiant energy of a flare flame in the visible region. To do this, a lens was used to condense the flame image to such a size that it passed through the monochromator slit. A mask in front of the lens limited the illumination by the image to the central portion of the collimating mirror in the monochromator. The visible region was scanned during the flare burning period and the spectrum was recorded. Next, the monochromator was calibrated for intensity and wavelength. Finally, the corrected spectrum was integrated to determine the quantity of energy radiated in the visible.

Monochromator

The flares were viewed with a Perkin-Elmer model 108 Rapid Scan Spectrometer consisting of a monochromator double-pass scanning system with a calcium fluoride prism and an RCA 1P22 photomultiplier-tube detector. The data was displayed on an oscilloscope and recorded on magnetic tape in analog form. The scan rate of the instrument was set at 30 scans/second. The slit was opened to 2mm. An example of spectral scans as they appear on the oscilloscope is shown in Figure 1.

Standard Lamps

A quartz iodine lamp calibrated in μ watts/cm²/10Å at 40 cm distance was used to calibrate the monochromator for energy intensity.

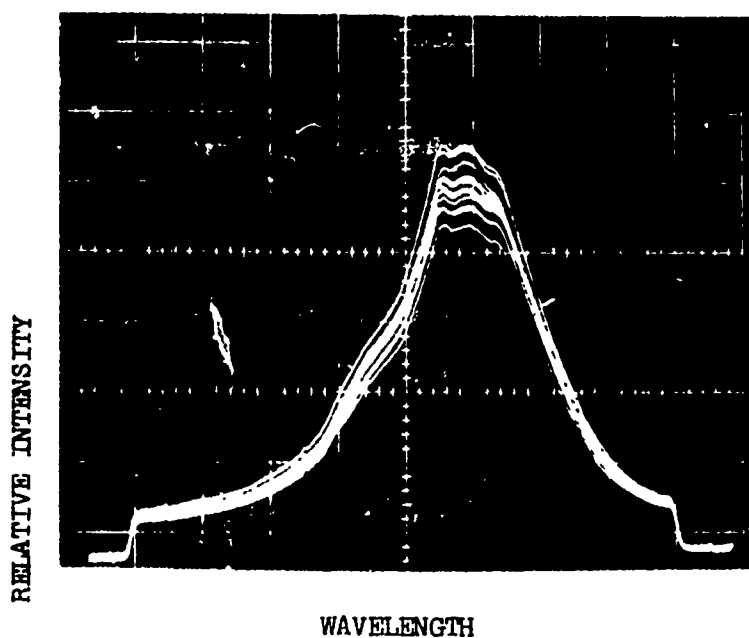


Figure 1: Photograph of a MK 24 Flare spectrum as it appears in uncorrected form on the oscilloscope. The spectrum is obtained with a Model 108 Perkin-Elmer Rapid Scan Spectrometer using an RCA 1P22 photomultiplier, a calcium fluoride prism, and a 2mm slit opening.

Mercury-cadmium, rubidium, sodium, and neon spectral lamps were used to calibrate the monochromator for wavelength.

Optics

A double convex lens with a 42mm focal length was used to condense the image of the flame so that it would all pass through the 2mm slit on the monochromator. In this way, all of the energy could be collected from the entire flame emitting surface which was radiating in the direction of the monochromator. As will be described later, this enables one to compute the amount of energy radiated in all directions. A 4mm mask was placed in front of the lens to limit the energy entering the monochromator to only the center region (about 6 cm²) of the collimating mirror. The flare was placed about 146 feet (4445 cm) from the lens. A magnification of 0.001 was achieved with this arrangement. Further details and computations involving the optics are given in Appendix B.

Flare Spectrum Selection

During this study, several flares were burned. Each flare was viewed continuously with the monochromator for the entire flare burning period of about 190 seconds. During this time, spectral scans were being recorded at the rate of 30 scans/second. The data could not be digitized. This eliminated any possibility of convenient analysis of all the information. Instead, a single scan was manually selected which was considered to be the average of the

flare performance. The chosen scan is one taken 30 seconds after flare ignition and at a time when smoke interference seemed to be minimal.

Figure 1 shows a photograph of unprocessed flare spectra similar to the one selected for evaluation. Next, the chosen scan was replotted as shown in Figure 2. The wavelength axis is identified by use of calibration data from the spectral lamps. Voltage on the oscilloscope is used as a measure of the spectral energy intensity Y_λ , along the ordinate.

Standard Lamp Spectrum

Figure 3 shows the standard lamp spectrum which was used as the radiant energy standard. The intensity, X_λ , along the ordinate is corrected for geometry at each wavelength by

$$X_\lambda = (D_{std}/D_f)^2(I_{std}) \quad (1)$$

where D_{std} is the distance from the standard lamp to the lens, D_f is the distance from the flame to the lens, and I_{std} is the intensity in volts on the oscilloscope before it is corrected for geometry.

Spectral Radiant Energy of the Flare

Figure 4 shows the flare spectrum in its final form. The spectral energy radiated is designated on the ordinate in energy units of kcal/m². The spectral radiant energy, $R_{f\lambda}$, is obtained by

$$R_{f\lambda} = (Y_\lambda Z_\lambda)/X_\lambda \quad (2)$$

where Y_λ is the voltage on the flare spectrum as shown in Figure 2, X_λ is the voltage defined by equation (1), and Z_λ is defined by

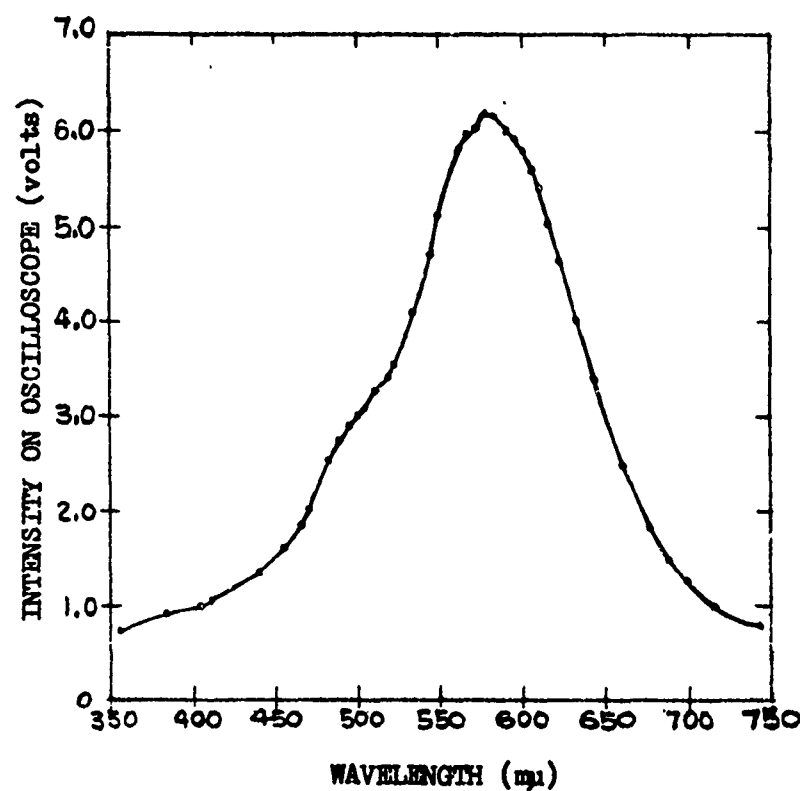


Figure 2: Uncorrected MK 24 Flare Spectrum obtained with a Model 108 Perkin-Elmer Rapid Scan Spectrometer using an RCA 1P22 photomultiplier, a calcium fluoride prism, and a 2mm slit.

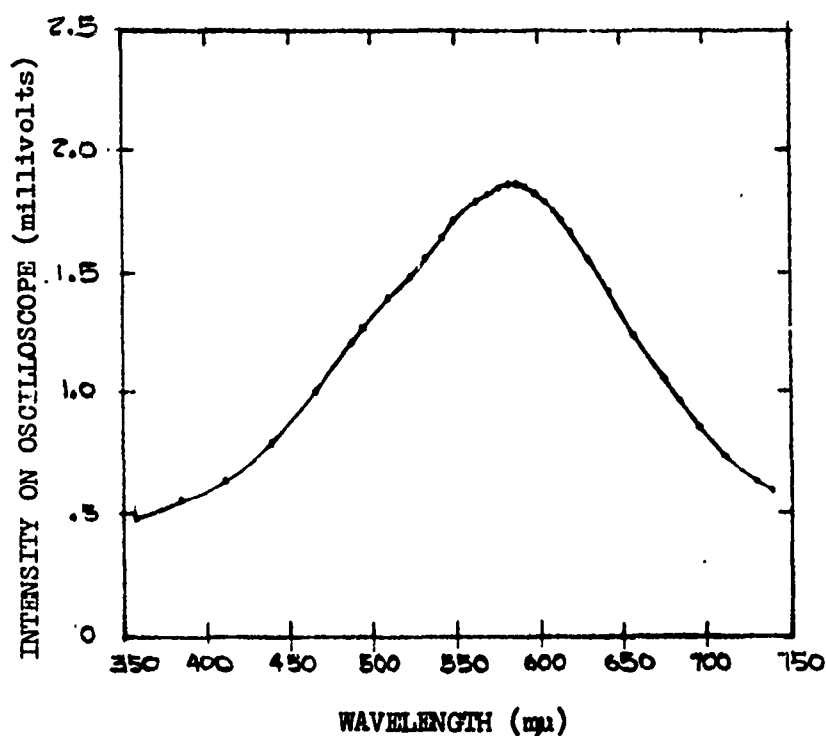


Figure 3: Uncorrected standard quartz-iodine lamp spectrum obtained with a Model 108 Perkin-Elmer Rapid Scan Spectrometer using an RCA 1P22 photomultiplier, a calcium fluoride prism, and a 2mm slit. The ordinate is adjusted to the voltage which would be recorded when the lamp is the same distance from the spectrometer as the flare.

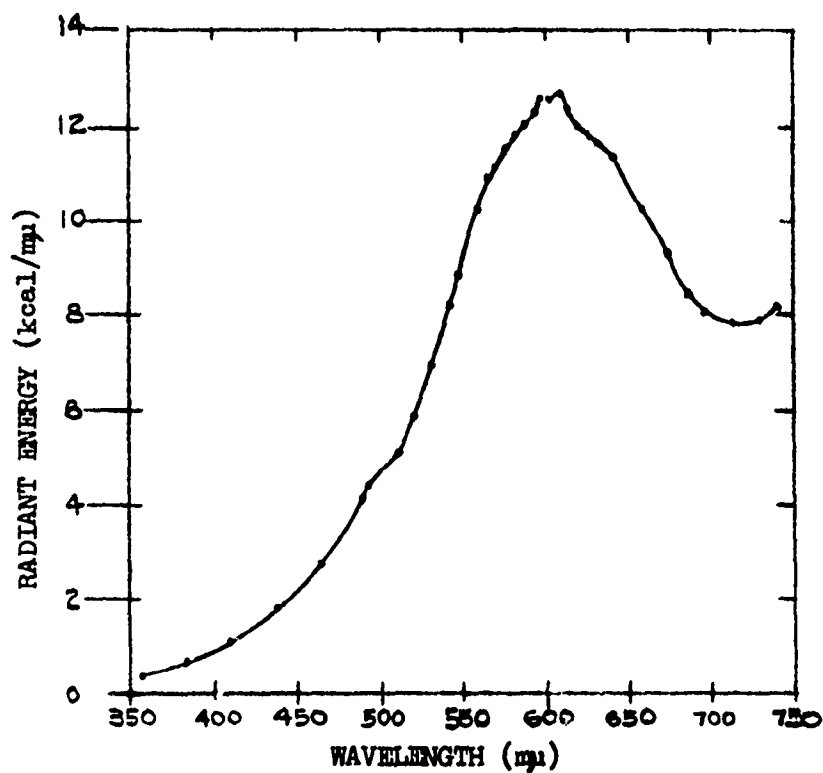


Figure 4: Spectral radiant energy of a MK 24 Flare over a period of 190 seconds. The energy represents emission in all directions (spherical) and from the entire emitting surface of the flame.

$$R_{\lambda} = 4\pi (D_{std})^2 (P_{std\lambda})(M)(BT) \quad (3)$$

where 4π converts $P_{std\lambda}$ to a spherical basis, D_{std} is the distance (40 cm) at which the standard lamp was calibrated, $P_{std\lambda}$ is the spectral power calibration for the standard lamp in μ watts/cm²/10^Å at 40 cm, M is 2.39×10^{-10} kcal·10^Å/μ watt·μ which converts the units to kcal/μ, and BT is the flare burning time (190 seconds). It is important to note that R_{λ} is the spectral radiant energy from the entire emitting surface of the flame and that it was not necessary to define the area of the emitting surface. The cm² from the square of D_{std} cancels the cm² in the $P_{std\lambda}$ term. We therefore can describe the emitting surface as the entire flare flame instead of some measured surface area. Also, we approximated the radiation from the flare flame as being spherical knowing that this leads to an error of unknown magnitude because the flame is probably not radiating equally in all directions.

Total Radiant Energy in Visible

The area under the radiant energy curve in Figure 4 was determined manually with a planimeter. The area between 380 μ and 742 μ is 2510 kcal which represents the total amount of energy, ψ , radiated by the flame in the visible region. The determination of this quantity was the main objective of this investigation.

DISCUSSION

The integrated visible energy (Φ) radiated by a flare has a measured value of 2510 kcal. This value includes radiation from all sources of visible emission.

Inspection of the spectrum in Figure 4 shows a large amount of energy around the sodium resonance lines. From the overall shape of the spectrum it is clear that the flame is not exclusively a Planckian radiator. The visible energy may be resulting partly from thermal emission and partly from non-equilibrium processes and thus may be composed of radiation of a variety of types originating from a number of different processes.

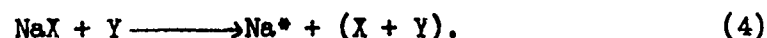
The spectrum in Figure 4 lacks resolution because it was taken through a 2mm slit opening and at a fast scan rate. Nevertheless, since it is the integrated value and not the fine structure which is important, the error introduced by the lack of resolution is shown to be tolerable. Flare spectra were also taken with a 1.5 meter B&L grating spectrograph with a ten micron slit opening. In these high resolution spectra which are not reproduced herein, we observe the sodium line reversal at 588.89 μ and 589.59 μ , the MgO band structure near 500 μ , and the 516, 517, and 518 μ magnesium lines.* The resolution of these features are comparable to resolution of the features in Figure 4, showing that instrumental resolution is not a serious factor.

*Blunt, reference 16, reproduced several of these spectra.

Radiative Components of the Flame

The flare flame is a quasi-gas system which cannot be expected to exhibit only the normal properties of systems in total equilibrium. Conversely, the system may exhibit some non-equilibrium characteristics. It is therefore necessary to distinguish some of the processes which may be responsible for the radiation.

First, sodium can be excited by



The sodium is, in this case, an excited product of the exothermic reaction. The radiation released by sodium excited in this way is defined for our purposes as specific emission or chemiluminescence. The extent of excitation in a process such as this does not depend directly on the temperature of the system in a well defined way. Each sodium atom is unlikely to undergo reaction (4) more than once during the life of the flare.

Sodium can also be excited by thermal collisions,



This reaction involves excitation by energy exchange through a collisional process. Its probability is temperature dependent and thus may be considered thermal excitation of sodium. Such a reaction can occur more than once for each sodium atom.

A more general case of a thermal process is



In this case, Z may be any particle which collides with particle M. Analogous to equation (5), the general thermal excitation is

temperature dependent and can occur more than once during the life of a given emitter within the flame. This is to be taken as a generalized mechanism for exciting components of radiation in the flame as a result of its thermal energy. This radiation may be continuous and is known as blackbody radiation when the spectral emissivity is 1, or graybody radiation when the emissivity is less than 1.

Temperature

It is clear that the radiated energy may be composed of parts from several sources. To speak of a flame temperature can be misleading unless the temperature is defined or is used in a restricted manner.

Although the concept of temperature in this flame may not be definitive, temperatures having restricted definitions can be used to describe various features of the system in order to establish some of the boundary conditions.

Maximum Flame Temperature

The maximum flame temperature (T_{av}) is defined by the energy balance equation

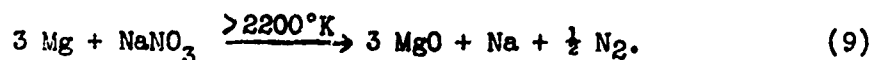
$$T_{av} = (Q - \dot{Q} - K)/C \quad (7)$$

where $\dot{Q}$ is the total heat lost by radiation from the flare, K is the total heat lost from the flare by convection, C is the weighted sum of the heat capacity of the combustion products, and Q is the total enthalpy of the flare reaction less the latent heats of the combustion products.

$$Q = (\Delta H_c)(W) - (\Delta H_f + \Delta H_v) \quad (8)$$

where ΔH_c is the heat of combustion, W is the weight of the flare composition (6810g), ΔH_f and ΔH_v are the weighted sum of the heats of fusion and vaporization of the combustion products. From thermodynamic tables prepared by Stull¹³ and a team of investigators, the weighted sum of $\Delta H_f + \Delta H_v$ is estimated as 1030 kcal/flare at temperatures below 3098°K and 3420 kcal/flare above 3098°K. The heat capacity (C) is approximately 2.17 kcal/°K/flare.

The numerical value for the heat of combustion (ΔH_c) probably lies between two extremes. One is 2.01 kcal/g which corresponds to the maximum energy released by stoichiometric reaction of the flare ingredients alone and the other is 3.21 kcal/g which corresponds to maximum energy released by air augmentation of combustion of the fuel-rich flare formula. The latter value includes additional energy supplied by burning the excess magnesium and sodium with the surrounding air and with oxidants included in the binder. The stoichiometric equation for reaction of the flare ingredients is



The actual flare formula is given in Appendix A.

Neglecting losses by radiation and convection, the maximum flame temperature is computed to be 3533°K which is the boiling point of magnesium oxide. The temperature is limited by the heat of vaporization of the MgO. If 32 percent of the available energy is lost by radiation and convection, the maximum theoretical temperature is

limited by the heat of fusion of magnesium oxide at its 3098°K melting point. Both of these temperatures were computed using 3.21 kcal/g as the heat of combustion (ΔH_c) for the flare reaction.

Distribution of the Radiation

A pyrotechnic illuminating flame is a grossly ill-defined mixture of reacting gases and smoke. Progress at the present state of knowledge requires information about gross features of the system. Superficial grounds for suspecting that emission by sodium is an important component of the radiation from a sodium nitrate-magnesium flare have been presented as a reason and basis for distinguishing among excitation processes. These processes include chemical excitation of the sodium atoms (equation 4), thermal excitation of sodium atoms (equation 5), the thermal excitation of other substances (equation 6). The reactions in the flame are by no means limited to these processes. Other less dominant energy transfer and chemiluminescent processes may also be present. Ten such atomic and molecular collision processes involving high energy species are presented by Shuler.¹⁴

Radiation by sodium atoms is expected to lie mostly in the vicinity of the yellow lines at 5890Å. While the width of the feature of the flame spectrum associated with the sodium emission is yet to be explained, its association with sodium is important mainly if there is some reason to believe that emission of this magnitude would not occur if sodium were absent.

We have already shown that the flare does not have a Planckian distribution. Let us next consider the source of emission associated with sodium (i.e., equations (4) and (5)). There are 30.8 moles of sodium in the flare. Also, we compute that sodium radiation is equivalent to 48.6 kcal/mole by

$$E_0 = Lhc/\lambda \quad (10)$$

where E_0 is an einstein in energy/mole, L is Avagadro's number, h is Planck's constant, c is the velocity of light, and λ is the wavelength of the strongest sodium resonance line. The product of the number of moles sodium and the number of einsteins gives about 1500 kcal. Thus, if each sodium atom were to radiate once by equation (4), a maximum of 1500 kcal would result. This requires 100 percent radiative efficiency which, in itself, is unlikely. Furthermore, even if the process were 100 percent efficient, it could only account for about 60 percent of the radiation observed in the visible. Thus it is clear that all of the visible radiation cannot be originating from the chemical excitation of sodium. Therefore, the chemiluminescent process described by equation (4) is not considered to be a significant contributor of sodium emission. This leaves thermal excitation of sodium atoms (equation 5) as the remaining process by which the gross radiation in the vicinity of the yellow lines at $5890\text{\AA}$ may be explained. Such a process is reasonable because we observe this energy mainly as a broadened region which is a normal characteristic of a collisional process. In addition, the broadened region is temperature and pressure dependent. Such behavior further supports the choice of thermal excitation of sodium as the predominant process.

We previously called attention to the magnesium oxide bands near 500 mμ. These are but one example of non-sodium related radiation which is due to thermal excitation by the process shown in equation (6).

Finally, we will provide evidence to show that the emissivity in the visible region is generally greater than emissivity elsewhere. We start with equation (7),

$$T_{av} = (Q - \bar{\Phi} - K)/C, \quad (7)$$

and neglect K. At a temperature (T_{av}) of 3000°K, $\bar{\Phi}$ is computed to be 14,360 kcal which represents the total energy radiated by the flare. Thus, $\Phi/\bar{\Phi}$ is about 0.17 which is the fraction of the total radiated energy found in the visible. By comparison, $\Phi_{bb}/\bar{\Phi}_{bb}$ for a blackbody at 3000°K is 0.108. Other values of $\Phi_{bb}/\bar{\Phi}_{bb}$ as a function of temperature are plotted in Figure 5. The considerably larger fraction of flare energy in the visible in comparison to the fraction expected from a blackbody results from greater emissivity of the flare in the visible region than elsewhere. Limited additional information is provided by Sarnow¹⁵ who notes that the magnesium-sodium nitrate reaction peaks near 1.0 micron in the infrared, then falls very sharply at the longer wavelengths, and rises again between 4 and 5 microns. This information also suggests large regions of low spectral emissivity outside of the visible.

These experiments did not provide any data which can be used to locate the limit of efficiency of light production by this flare. If the present flare system is not already at maximum efficiency,

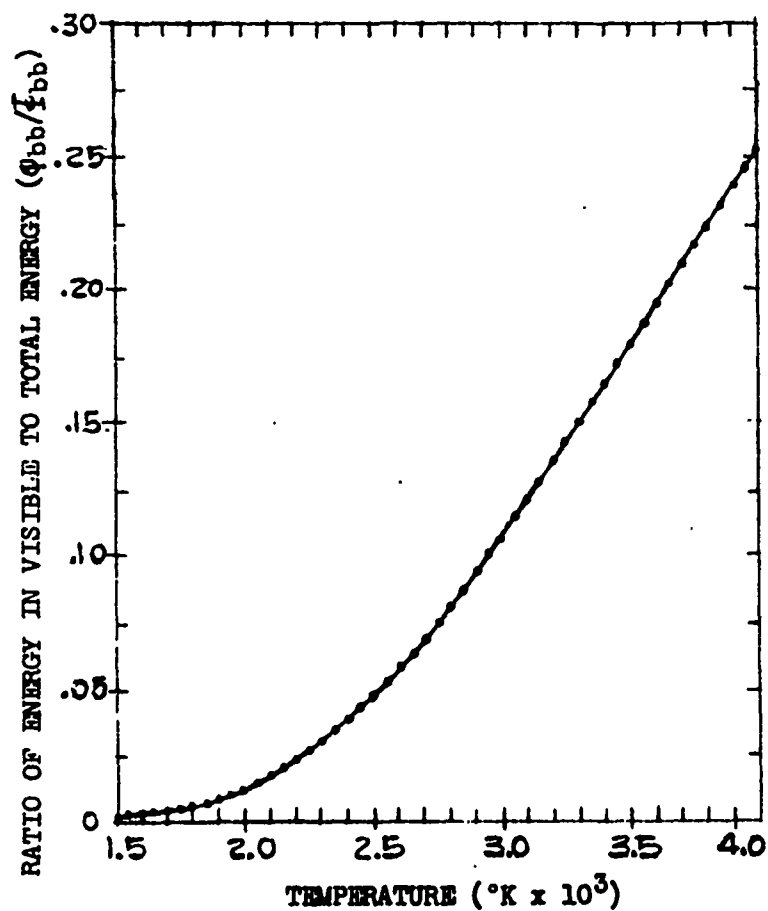


Figure 5: Ratio of blackbody energy in the visible region to the total blackbody energy as a function of temperature. The energy in the visible is determined by Planck's equation between 400 and 750 mμ. The total energy is determined by the Stefan-Boltzmann equation.

the flare can be improved in only two ways. First, more sodium and other emitters can be excited in the visible by increase of the energetics of the reaction. Secondly, the amount of radiation loss in regions outside of the visible can be reduced by selecting emitters which radiate only in the visible. An increase in the amount of energy available to excite the visible emitters will result in an increase in the visible radiation. From these alternatives, one can see that it is of equal importance to give consideration to the loss of energy by radiation outside of the visible as it is to concentrate on increasing the integral energy in the visible.

Conclusions

The amount of energy radiated by the flare in the visible region was measured as 2510 kcal which is about 11 percent of the energy of the flare reaction.

The exact nature of the interaction which causes the continuum in the vicinity of the sodium D lines was not determined. On the other hand, we showed that the visible energy does not have a Planckian distribution and provided evidence that the excitation of sodium is more likely to be the result of a thermal than a chemiluminescent process.

A maximum of 60 percent of the visible radiation can originate by a chemiluminescent (non-thermal) mechanism by which each emitter may only be excited once. If sodium is the principal emitter, each sodium atom must be excited more than once. Multiple excitation is not allowed if the process is solely non-thermal. On the other hand,

excitation of sodium by a thermal process which allows reported excitation is favored because we observe a broadened region near the sodium yellow lines and because of the reported temperature and pressure dependence of this region. All of these characteristics are normal for a thermal process as described by equation (5).

Another important feature of this flare is that about 17 percent of the total radiated energy is found in the visible. To obtain this energy distribution, emitters in the visible must generally have greater emissivity than the emitters in other regions. This emphasizes the practical aspects of formulating an illuminating flare. Not only is it important to select emitters with a high emissivity for visible radiation but also, every effort must be made to exclude emitters capable of radiating outside of the visible. Increase of the reaction energetics and emitter selection are the only ways one can increase the amount of light produced by this system.

ACKNOWLEDGEMENTS

The study was supported by the Research and Technology Ordnance Administrator, Naval Air Systems Command, U. S. Department of the Navy. Professor Edward J. Bair, Indiana University, helped me in many important ways. He suggested an approach to the problem, provided guidance in the work, and contributed many ideas and many hours during the last year. For all of this, I am particularly indebted. The assistance by J. A. Swinson and D. L. DeMoss in obtaining spectra is gratefully acknowledged. The support by the Commanding Officer and other senior management personnel at the U. S. Naval Ammunition Depot, Crane, is also valued highly.

REFERENCES

1. D. Hart, H. J. Eppig, and W. J. Powers, "Self-Hardening Pyrotechnic Composition," U. S. Patent 2,700,603, Class 52-24, 25 Jan 1955.
2. H. Ellern, "Modern Pyrotechnics; Fundamentals of Applied Physical Pyrochemistry," Chemical Publishing Company, New York, N. Y., 1961.
3. B. D. Bond and P. W. M. Jacobs, "Chemical Reaction and Ignition in Mixtures of Magnesium and Sodium Nitrate," Combustion and Flame, 10, 349-354 (1966).
4. R. M. Blunt, "Processes Occurring in Pyrotechnic Flames," AD No. 637512, Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314 (April 1966)
5. R. G. Breene, Jr., The Shift and Shape of Spectral Lines, Pergamon Press, New York, N. Y., 1961.
6. A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms, Second Impression, Cambridge University Press, New York, N. Y., 1961.
7. H. A. Lorentz, The Absorption and Emission Lines of Gaseous Bodies, Proc. Roy. Acad. Amsterdam 8, 591-611 (1906)*
8. W. Lenz, Z Physik 25,299 (1924)*
9. V. F. Weisskopf, Z Physik 75,287 (1932)*
10. A. Jablonski, Über die Stossverbreiterung der Spektrallinien und den, Energieaustausch bei Zusammernstößen, Z Physik 70,723-732 (1931)*
11. H. Margenau, Phys. Rev. 40, 387 (1932)*
12. H. M. Foley, Phys. Rev. 69, 616 (1946)*

*These references are cited by Breene in reference 5.

13. D. R. Stull, et. al., JANAF Thermochemical Tables. Prepared by Dow Chemical Company, Midland, Michigan, under Advanced Research Projects Agency Program and U. S. Air Force Contract, PB 168370. Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314 (1960-1966)
14. K. E. Shuler, "On the Kinetics of Elementary Gas Phase Reactions at High Temperatures" in "Fifth Symposium (International) on Combustion," p. 56-74, Reinhold Publishing Corporation, New York, N. Y., 1955.
15. J. W. Sarnow, "Infrared Emitters" in "Aerospace Ordnance Handbook" by F. B. Pollard and J. H. Arnold, Jr., Prentice-Hall, Englewood Cliffs, N. J. 223-253, 1966.
16. R. M. Blunt, "Evaluation of Processes Occurring in Pyrotechnic Flames," RDTR No. 91, U. S. Naval Ammunition Depot, Crane, Indiana, available from Defense Documentation Center, Cameron Center, Alexandria, Virginia 22314 (15 March 1967).

APPENDIX A

MK 24 Flare Candle Data*

1. Flare tube inside diameter	4.25 in
2. Composition length	16.5 in
3. Area of burning	14.18 in ²
4. Composition volume	234 in ³ ; 3833 cm ³
5. Composition mass	15.0 lbs; 6810 g
6. Composition density	1.78 g/cm ³
7. Consolidation pressure	8464 psi; (dead load) 60 ton
8. Burning time	180 sec
9. Burning rate	0.0916 in/sec; 10.9 sec/in
10. Consumption rate	37.9 g/sec; 2.64×10^{-2} sec/g
11. Luminous intensity	1.7×10^6 candles (cd)
12. Luminous energy density	4.5×10^4 (cd sec)/g 8 x 10 ⁴ (cd sec)/cm ³
13. Flame length	5 ft (max)
14. Flame width	3 ft (max)
15. Composition formula (by weight)	
Magnesium	57.0%
Sodium Nitrate	38.5%
Polyester binder	4.5%
16. Heat of combustion (stoichiometric).	2.02 kcal/g
17. Heat of combustion (excess fuel)	3.21 kcal/g 13.45 kwatt sec/g
18. Power of flare	508 kwatt 5.08×10^{12} erg/sec

*Values given are typical and in some instances estimated.

APPENDIX B

OPTICS

Lens Focal Length Computation

The optical layout is given in Figure 1 on the next page. The maximum size of flame we will measure is estimated as eight feet (244 cm) long and five feet (152 cm) wide. The maximum slit opening on the monochromator is about 2mm by 12mm. The lens magnification (m) is determined by

$$m = q/p = i/o \quad (1)$$

where q is image distance, p is object distance, i is image height, and o is object height. If we assume a magnification of 0.001, we get

$$0.001 = i/244 \quad i = 2.44\text{mm} \quad (2)$$

$$\text{and} \quad 0.001 = i/152 \quad i = 1.52\text{mm}. \quad (3)$$

Since $2.44\text{mm} < 12\text{mm}$ and $1.52\text{mm} < 2\text{mm}$, both dimensions of the flare will pass through the slit if $m = 0.001$.

In equation (1), if p is 4445 cm and m is 0.001, then q is 4.445 cm. Next, the focal length of the lens required for this purpose is computed by the lensmakers' formula.

$$\frac{1}{p} + \frac{1}{q} = \frac{1}{f_l} \quad (4)$$

where p and q are defined for equation (1) and f_l is the lens focal length. Substituting into equation (4), we get

$$\left(\frac{1}{4445} + \frac{1}{4.445} = \frac{1}{f_l} \right) \approx \left(\frac{1}{4.445} \approx \frac{1}{f_l} \right) \quad (5)$$

The focal length needed is about 4.5 cm. The first term in equation (5) is negligible.

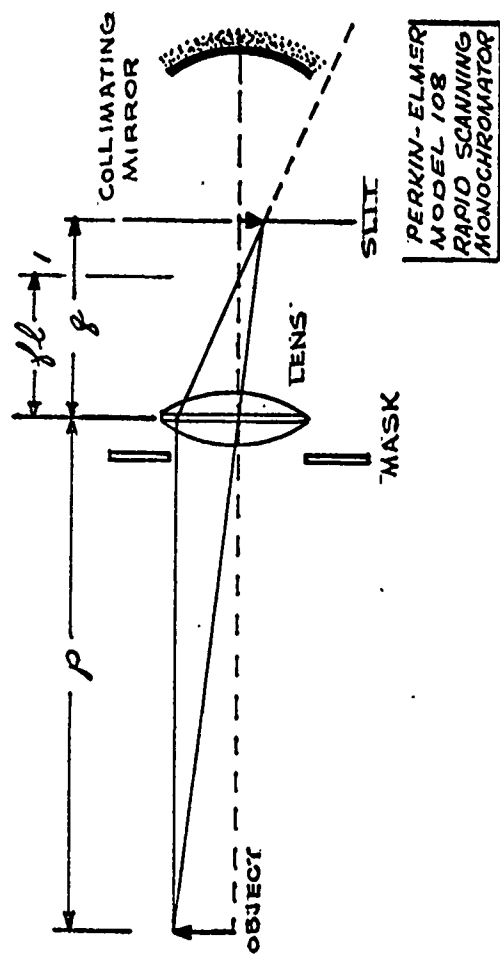


Figure 1: Schematic of the optical layout used to measure the absolute spectral radiant energy of a MK 24 Flare.

Lens Mask Aperture Computation

Figure 2 on the next page is the optical schematic which illustrates the use of the mask to restrict the size of the collimating mirror surface which is illuminated by the image. Let us estimate that a 25mm height (h_2) area on the mirror is that surface which is viewed by the detector. Also, it is known that the distance (s) from the slit to the mirror inside the monochromator is 273mm and that the focal length (f_1) from equation (5) is about 45mm. The size of the mask aperture (h_1) is computed by

$$h_1 = (h_2)(f_1)/l_2 = (25)(45)/273 = 4.12\text{mm} \quad (6)$$

where $l_2 \approx s = 273\text{mm}$. A mask of 4mm diameter was actually used.

