NUREG/CR-1794, Vol. IV
LA-8596-PR

Progress Report

Summary of Activities and Accomplishments

Final Report

A Proposal to Develop a Method for the Detection of HE Employing Chemiluminescence Reactions

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663   Los Alamos, New Mexico 87545

8101290825

Previous reports in this series, unclassified, are LA-8593-PR, NUREG/CR-1794, Vol I, LA-8594-PR, NUREG/CR-1794, Vol. II, and LA-8595-PR, NUREG/CR-1794, Vol. III.

This report was not edited by the Technical Information staff.

NUREG/CR-1794, Vol. IV
LA-8596-PR
Progress Report

RS

Summary of Activities and Accomplishments

Final Report

A Proposal to Develop a Method for the Detection of HE Employing Chemiluminescence Reactions

Michael P. Neary

Manuscript submitted: January 1981
Date published: January 1981

Prepared for
Division of Safeguards, Fuel Cycle, and Environmental Research
Office of Nuclear Regulatory Research
US Nuclear Regulatory Commission
Washington, DC 20555

NRC FIN No. [illegible]10

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

FOREWORD

An increase in the level of terrorist activity in the United States during the 1980s is highly probable, and prominent among the probable targets are nuclear facilities. Historically, terrorists have resorted to a wide variety of methods, but the use of high explosives is a likely choice. The effect of destructive use of explosives in nuclear facilities is substantial All nuclear plants are built with redundant safety systems so that randomly occurring faults will not disable the entire safety system. This single-failure criterion is used in the design of safety systems in reactors. High explosives use by saboteurs can easily negate the single-failure design feature and cause significant complexity for the design of security systems to prevent sabotage. It is both timely and technically feasible to consider seriously countermeasures to terrorist activities that are centered on the use of high explosives introduced into nuclear facilities by employees or visitors. Other than paper studies, little comprehensive laboratory attention has been devoted to such countermeasures.

The Nuclear Regulatory Commission (NRC) has recognized the potential for high explosives use by saboteurs, and 10 CFR Part 73.55 addresses this problem. Licensees must require that all individuals, packages and material entering the plant protected areas be searched for explosive devices. Applying this regulation during the past three years has shown that commercially available detection devices have certain inadequacies.

Recently the NRC Safeguards Research Branch funded the Los Alamos Scientific Laboratory (LASL) to perform a detailed feasibility study of the detection of high explosives using an innovative technique in the application of chemiluminescence. The LASL study was aimed at delineating and developing the required technology to develop instrumentation and methodologies that could be used to detect high explosives.

The remainder of this report outlines the outcome of the NRC-funded feasibility study.

CONTENTS

ABSTRACT 1

I. INTRODUCTION 1

II. BOUNDARY CONDITIONS 2

III. SAMPLING METHOD 3

IV. ANALYTICAL METHOD 3

V. CONCLUSIONS AND RECOMMENDATIONS 5

APPENDIX A 8
MICELLAR EFFECTS ON THE CHEMISTRY AND PHOTOCHEMISTRY OF NITRO-SUBSTITUTED HETEROCYCLES

APPENDIX B 25
PAPER PRESENTED IN PALM BEACH, FL, AT THE 21st ANNUAL MEETING OF THE INSTITUTE FOR NUCLEAR MATERIALS MANAGEMENT, JUNE 23 - JUNE 27, 1980

APPENDIX C 34
PAPER PRESENTED IN RESTON, VA, AT THE NEW CONCEPTS SYMPOSIUM AND WORKSHOP ON DETECTION AND IDENTIFICATION OF EXPLOSIVES, OCTOBER 30 - NOVEMBER 1, 1978

APPENDIX D 39
AGENDA FOR JUNE 12, 1980, TECHNICAL REVIEW IN SILVER SPRING, MD; AND DR. K. HERR'S REVIEW OF THE TECHNICAL MERIT OF THE WORK

SUMMARY OF ACTIVITIES AND ACCOMPLISHMENTS
FINAL REPORT

on

"A Proposal to Develop a Method for the
Detection of HE Employing Chemiluminescence Reactions"

by

Michael P. Neary

ABSTRACT

This is the final and fourth quarter report for the study of high explosive (HE) detection by coupling the chemistry of HE with that of luminol reaction, a well-known chemiluminescence (CL) reaction. Our accomplishments include:

1) success in coupling HE and CL chemistry reliably;
2) the capability to use a micellized solvent to concentrate HE; and
3) the basis for design instrumentation that may exhibit better sensitivity and lower levels of detection than that exhibited by the laboratory apparatus used for this study.

On the basis of these results we are prepared to recommend further study.

I. INTRODUCTION

A project was undertaken by the Los Alamos Scientific Laboratory (LASL) for the U.S. Nuclear Regulatory Commission, SAFERS Division, to determine the feasibility of detecting high explosives (HE) in a predetonation setting. The motivation for the study was centered on thwarting terrorist activity aimed at nuclear power reactors where the use of HE is anticipated.

A good method for air sampling and concentrating HE has been found that depends on surfactants. The method of HE analysis relies on coupling the chemistry of HE with that of the luminol chemiluminescence (CL) reaction. The rationale for the choice of these methods is treated below, in terms of various constraints imposed by the end use setting (that is, the boundary conditions).

Appendices A, B, and C contain papers published during the course of this investigation. Appendix D contains information on supporting technical reviews of this work.

II. BOUNDARY CONDITIONS

The phrase "boundary conditions" describes the set of all known constraints placed on the analytical method by the compound(s) to be analyzed for, the physical and chemical state of the analyte, and specific temporal and/or spacial constraints.

In the case of HE detection at a nuclear power plant, very small amounts of HE vapor mixed in a large volume of air must be detected in small-volume air samples in a highly reproducible way. Further, the analysis must be fast, simple, and fairly inexpensive. Thus, a successful method for routine chemical analysis of HE vapor in air sampled at nuclear power plants must meet or exceed the following criteria imposed by the boundary conditions for personnel and space surveillance:

1) high selectivity - minimum naturally occurring interferences (that is, chemical compounds that give a positive response but are not HEs),
2) high sensitivity - because the vapor pressures of high explosives that might be selected by a terrorist are very low (10^{-10} torr), hign sensitivity is required as well as a very low level of detection (10^9 to 10^5 molecules),
3) rapid analysis - the time required per analysis must be less than 30 seconds with no dead time between analyses,
4) low cost per analysis - less than $0.05 per analysis,
5) high efficiency sampling - the air sampling method must be fast, reproducible, and not require large volumes of air (10 liters maximum),
6) no or few false positive responses - the method should be free from interferences,
7) no false negative responses, and
8) the final or field embodiment of the method should not require highly trained personnel.

The extent to which the method developed meets these criteria will be discussed in the last section of this report.

III. SAMPLING METHOD

For this study three chemically different HEs were selected, trinitrotoluene (TNT), nitroguanidine (NQ), and cyclotetramethylene tetranitramine (HMX). The vapor pressures of these HEs range from 10^{-6} to 10^{-9} torr. Because the analyte, HE, is in the vapor state and therefore a component of air at the sampling site, and the luminol CL reaction is carried out in the liquid phase, a sampling method was developed that mediated between the HE gas phase and CL reaction liquid phase.

The mediating means selected was an ionic surfactant dissolved in water. In particular, cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulfate (SDS) were used. When surfactants, like those mentioned, are dissolved in water, the surfactant molecules organize into small (ca 40 Angstroms) sphere-like arrangements called micells. The reason is that the surfactant molecule has a hydrophylic (polar) head and a hydrophobic (aliphatic) tail; thus in a polar solvent such as water the hydrophobic tails form close associations, known as micells. In such a micellized solution if a hydrophobic analyte is added, after a short period of time (ca 100 milliseconds or less), the bulk of the hydrophobic material is found inside the micellar phase. Because the micellar phase is a very small fraction of the solution, a concentrating effect is often observed for the hydrophobic material.

Such concentrating behavior has been observed for TNT in the cationic micells of CTAB in water. Therefore, if TNT vapor in air is bubbled through CTAB micellized water, TNT is effectively removed from the air stream and concentrated in the micells. Thus the use of micellized solvents appears to form a sound basis for sampling air for HE.

More technical detail on micellized solvents is presented in Appendix A.

IV. ANALYTICAL METHOD

The development of the analytical method for detection of HE was based on the following facts.

Analytical methods based on the emission of light are the most sensitive available to the chemist. CL-based emission methods usually exhibit the lowest levels of detection as well as high sensitivity.

One of the best characterized CL reactions relies on luminol (3-aminophthalhydrazid) whose CL is catalyzed by certain first-row transition metals in intermediate oxidation states (Cu^{+2}, Fe^{+2}, Co^{+2}, Cr^{+2}).

HE chemicals are usually either heterocyclic nitramines or aromatic nitro compounds that can be photochemically converted to the corresponding nitrosamine or nitroso compounds.

Nitrosamines and nitroso functionalized compounds are fairly good complexing agents for first-row transition metals in intermediate oxidation states such as the catalysts for the luminol CL reaction.

These facts form the basis for the analytic method, which can be summarized as follows. The luminol CL reaction is carried out in a continuous manner (that is, it is a flowing system) and the light output is measured as a function of time. The concentration of the metal catalyst is adjusted to about three times that anticipated of the HE to be detected. All other components of the luminol CL reaction are in excess concentration. By means of a 4-way sampling valve, a small aliquot, 80 microliters, of photolyzed HE is introduced into the luminol CL reaction that is in progress. The nitroso derivative of the HE complexes the catalyst and, as a result, the intensity of CL emission diminishes in proportion to the concentration of HE in the sample. Appendix B presents the method in greater detail with results. The same appendix along with Appendices A and C provides detailed data regarding the photochemical conversion of HE in micellized solvent as well as unmicellized solvents.

V. CONCLUSIONS AND RECOMMENDATIONS

The outcome of the HE detection work has been favorable and the following milestones have been achieved.

High sensitivity has been demonstrated along with very low levels of detection - currently 10^9 molecules. Ultimately 2×10^5 molecules is the expected lowest level of detection.

High selectivity has been demonstrated, and therefore few false positive responses are to be expected.

The time required per analysis is currently 3 to 5 minutes; however, there are no technical obstacles to achieving 15 to 30 second time per analysis.

Current cost per analysis is approximately $0.05.

Small aliquots of air samples are required - currently 0.3 to 300 liters, but ultimately less than one liter.

No false negatives have been observed for HE concentrations greater than or equal to the lowest level of detection.

It now appears that an instrument based on the technology developed to date could operate unattended.

Based on the milestones achieved to date, it is recommended that the study continue along the following lines.

Further optimization of the instrumentation and sampling system so that the ultimate performance can be observed. Figure 1 shows an improved sample/CL reaction cell.

Further detailed study of micellized solvents as sampling media with the aim of improving HE collection efficiency and carrying out both photolysis and the CL reaction in the micellar phase.

Further study of chemical interferences with particular attention given to chemicals that could "mask" HE, resulting in false negative responses.

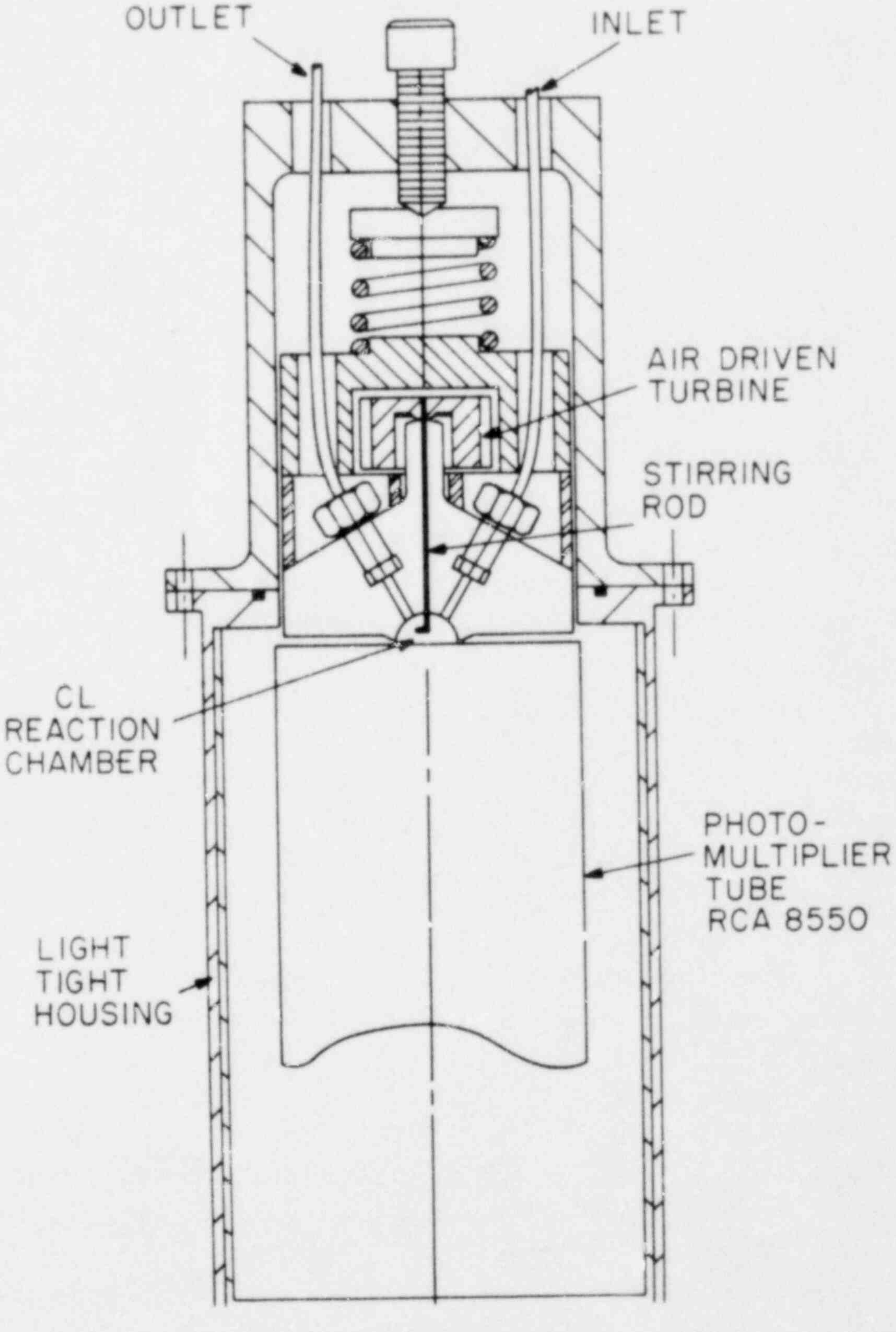


Fig. 1. A cross-sectional diagram of the new CL reaction chamber with parts labeled on the diagram.

APPENDIX A

MICELLAR EFFECTS ON THE CHEMISTRY AND PHOTOCHEMISTRY OF NITRO-SUBSTITUTED HETEROCYCLES*

Richard R. Hautala
Department of Chemistry
University of Georgia
Athens, GA 30602

I. INTRODUCTION

The effects of micelle-forming detergents on the aqueous solution chemistry and photochemistry of HMX, NQ, and TNT have been screened. The principal technique employed has been UV spectroscopy because of the intimate relationship of this technique to photochemistry as well as its useful qualitative diagnostic capabilities. Further work in this area (see below) using more incisive techniques for product identification is sorely needed, but the main function of this particular research was to survey a variety of conditions and identify those most promising for further work.

In cases where it was possible to do so, the photochemistry of each substrate was studied in aqueous solution; in aqueous solution containing a cationic micelle-forming detergent; and in aqueous solution containing an anionic micelle-forming detergent. Again, in each case a study was made under acidic (pH=3); neutral (pH=7) and basic (pH=11) conditions. In addition, the effects of sodium borohydride and of cyanide ion were studied in select cases. In the case of TNT, spectacular "dark" chemistry was observed for micellar solutions. An analysis of these effects compared to reports in the literature is included.

II. OVERALL RESULTS AND CONCLUSIONS

Without exception, each substrate (HMX, TNT, and NQ) studied is highly photoreactive in aqueous solution. The presence of

---

*Performed for the Los Alamos Scientific Laboratory under Contract No. 4-129-5116L-1.

micelle-forming detergents does not alter the photoreactivity (in terms of quantum efficiency for loss of substrate), but does alter the course of the chemistry (possibly through stabilization or destabilization of primary photoproducts). An interesting effect of micelle-forming detergents on the "dark" chemistry of TNT was observed.

Without doubt the most important area for future work involves identification of photoproducts. In particular it will be important to determine whether the qualitative changes in the spectral scans resulting from the addition of micelles is due to new chemical pathways.

III. PHOTOLYSIS OF NITROQUANIDINE (NQ)

NQ has an absorption maximum at 264 nm in water. Photolysis of 5.2×10^{-5}M NQ in water using 254 nm lamp (penray) and monitoring the reaction by UV shows the disappearance of the starting compound and increase in absorption around 330 nm. This new species decreases on increasing the photolysis time (2 min). (Figure 1) A similar effect was observed at pH=3. (Figure 2) Upon changing the pH of the solution to 11 NQ undergoes photochemistry as seen by the decrease in the UV spectrum, but far less of the new species absorbing at 330 nm was observed. (Figure 3) In the presence of a cationic detergent, cetyltrimethyl ammonium bromide, CTAB, (6×10^{-3}M) photolysis of NQ produces the product absorbing 330 nm. (Figure 4) The case containing CTAB at pH=3 and pH=11 are distinctly different, however. (Figure 5 and 7) In sodium dodecyl sulfate (SDS) (0.1 M) no evidence for the "330 nm product" could be detected. (Figures 7, 8, 9) We observed that changing the pH of the solution (3, 7 or 11) in aqueous medium or in detergents does not change the quantum yield of the disappearance of NQ. The presence of CN^- results in no unusual photochemistry. (Figure 10) Addition of $NaBH_4$ to an aqueous solution of NQ induces a dark reaction to the extent of 56% after 24 h. Photolysis of a freshly prepared solution, however, exhibits typical photochemistry. (Figure 11) The quantum yields for disappearnce of NQ were measured using ferrioxalate as actinometry and are given in Table 1. Correction was made for the fraction of the light absorbed by the solution. No appreciable dark reaction could be detected either in unphotolyzed solutions or during "dark" periods following photolysis.

Table 1. Quantum Yield for the Disappearance of NQ

Medium	Φ
Water	0.10, 0.09
Water/HCl	0.10, 0.10
Water/OH^-	0.13, 0.11
CTAB	0.08, 0.11
CTAB/H^+	0.12, 0.10
CTAB/OH^-	0.14, 0.12
SDS	0.09, 0.12
SDS/H^+	0.11, 0.12
SDS/OH^-	0.09, 0.09
H_2O/CN^-	0.11, 0.10
H_2O/BH_4^-	0.12, 0.10

IV. PHOTOLYSIS OF 1,3,5,7-TETRANITRO-1,3,5,7-TETRAAZACYCLOOCTANE (HMX)

HMX is very insoluble in water but can be solubilized in CTAB. It has a wavelength maximum at 225 nm. A 4×10^{-5}M HMX solution in 6×10^{-3}M CTAB was photolyzed at 254 nm and its disappearance was followed by UV. (Figure 12) It is observed that there is an increase in absorption ~270 nm with increasing photolysis time. Further irradiation (3 min) shows the product also undergoes photoreaction. The photolyzed solution also undergoes a thermal reaction to the extent of 32% when left in the dark for 3 h. When the photolysis is done in presence of acid (pH=3) no absorption increase ≃270 nm could be detected although HMX disappears. (Figure 13) There is a thermal reaction in 2 h (loss of

16%). Photolysis in solutions containing 0.1 M SDS results in disappearance of HMX as well as an absorption increase at 270 nm. (Figure 15) No thermal reaction was observed when the photolyzed solution was kept in the dark for 24 h. Irradiation in the presence of CTAB with added base (Figure 14) or in SDS with added acid (Figure 16) or base (Figure 17) show the typical decrease in HMX concentration. In all cases no dark reaction could be observed on unphotolyzed solution. The quantum yields for HMX disappearance are given in Table 2.

Table 2. Quantum Yield for the Disappearance of HMX

Medium	Φ	
CTAB	3.3×10^{-2},	3.9×10^{-2}
CTAB/H^+	3.3×10^{-2},	2.9×10^{-2}
CTAB/OH^-	6.4×10^{-2},	5.6×10^{-2}
SDS	------	-----
SDS/H^+	2.4×10^{-2},	2.6×10^{-2}
SDS/OH^-	4.2×10^{-2},	4.5×10^{-2}

V. PHOTOLYSIS OF TNT

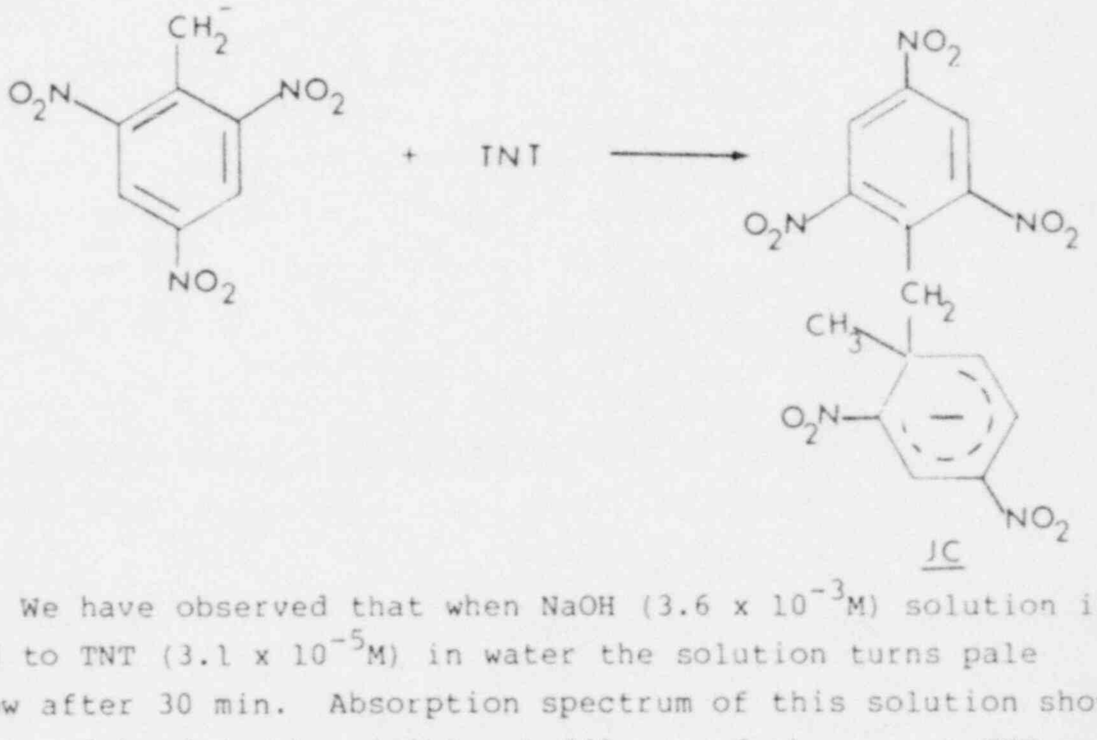
Trinitrotoluene (TNT) has an absorption maximum at 232 nm in water. Upon photolysis of a solution containing 3.1×10^{-5}M TNT in water the absorption decreases and this is accompanied by a moderate increase in absorption between 290-350 nm. The solution turns yellow after two minutes irradiation. (Figure 18) In the presence of CTAB (6×10^{-3}M) TNT gave similar results as in water. TNT in CTAB turns red-orange immediately when NaOH (3.57×10^{-3}M) is added to it (see the next section for a complete discussion). The UV spectrum of this solution has two maxima at 350 and 442 nm and a shoulder ~480 nm. After 24 h in the dark the color of this solution fades, the intensity of 442 and 480 nm bands decreases and that of 350 nm band increases. On the other hand, TNT in basic solution in water turns yellow after 20 min with a broad band in the visible at 440 nm. This solution turns red-orange after 24 h in the dark and intensity of this band increases. No such observation is seen in presence of SDS. (Figure 19) After 4 min of irradiation, the solution turns slightly yellow with the product absorbing between 290-350 nm with no detectable absorption in the visible. In presence of acid or base in SDS, (Figure 20,21) TNT undergoes similar photochemistry. When cyanide is added to solutions containing TNT in water, (Figure 22) water with CTAB (Figure 23) or water with SDS (Figure 24), the behavior is distinctly different. The "original" spectra do not resemble TNT and the extent or photochemistry appears to diminish although in the absence of further studies no firm conclusions should be made. Quantum yields for the disappearance of TNT are given in Table 3.

Table 3. Quantum Yield for the Disappearance of TNT

Medium	Φ
Water	2.1×10^{-2}
CTAB	9.5×10^{-3}
SDS	5.25×10^{-3}, 5.25×10^{-3}
SDS/H^+	1.05×10^{-2}, 6.3×10^{-3}
SDS/OH^-	1.08×10^{-2}, 1.10×10^{-2}

VI. DISCUSSION OF NONPHOTOCHEMICAL OBSERVATIONS REGARDING TNT AND MICELLAR SYSTEMS

The reaction of strong bases with TNT has been the subject of many investigations. It has been reported that TNT reacts with potassium methoxide to form a monohydrated complex.[1] The reaction of base to TNT has been attributed to 2,4,6-trinitrobenzyl anion[2] - the anion absorbing in the visible at 370 and 510 nm. The formation of this carbanion is well documented by Buncel[3] by the exchange of methyl protons in a basic medium containing NaOH-D_2O. Recently the micellar effect on the kinetics of TNT with amines has been studied.[4] It is observed that the rate of formation of the anion in presence of amine is much greater above the CMC of the detergent. A charge transfer interaction is suggested by Ainscough and Caldin for the interaction between TNT and ethoxide ion in ethanol at very high concentration of the base.[5] An extensive kinetic investigation of TNT with base in different solvents with wide range of concentrations of TNT and base has been reported.[6] It is observed that there are three different relaxation processes depending upon the concentration of reactants and it is concluded that when the base concentration is in excess over TNT, TNT anion is the principal product and when TNT is in excess the anion formed reacts with a second molecule of TNT to form Janovsky complex (JC) and Meisenheimer complex could be a possibility at a very high base concentration.



JC

We have observed that when NaOH (3.6 x 10^{-3}M) solution is added to TNT (3.1 x 10^{-5}M) in water the solution turns pale yellow after 30 min. Absorption spectrum of this solution shows a very broad band in the visible at 445 nm and the parent TNT peak at 232 nm. (Figure 25) This solution turns reddish-yellow after 24 h in dark and intensity of visible band increases and parent band decreases. (Figure 26) The spectrum is quite different from TNT anion in 50% dioxane-50% water.[6] It may be that a fast reaction occurs with the formation of carbanion and a slow reaction with TNT to form another species. It is possible that the spectrum of the anion is overshadowed by this broad visible spectrum. There are numerous examples of nitrotoluenes undergoing free radical reactions in basic media.[7] The possibility of formation of 2,4,6-trinitrobenzyl radical could not be ruled out.

In comparison, a spectrum of basic solution of TNT in the presence of CTAB (6×10^{-3}M) is remarkably different and shows that the addition of a micelle forming detergent has a significant effect on the kinetics of TNT chemistry. When NaOH is added to a solution of CTAB in the TNT, the solution turns immediately to reddish-yellow and the spectrum has two maxima at 350 and 442 nm and a shoulder ~480 nm (Figure 27). The color of the solution fades after 24 h and intensity of peak at 350 nm grows at the expense of other two (Figure 28). The parent TNT band at 232 nm decreases overall. No such observation could be detected in SDS. One can expect on electrostatic consideration that cationic micelles enhance the rate of reaction of nucleophilic anions with uncharged substrates and anionic micelles to retard it.[8]

At present we are unable to explain all of the observations seen for micellar solutions of TNT. Spectral evidence for the presence of TNT anion may be buried under the very broad spectrum of another species. Systematic studies at various concentrations of CTAB will be necessary in order to learn more about the processes involved in this system. The possible formation of benzyl radical as a slow process and reaction of this radical with oxygen present in the system should be considered. A suitable substrate which could react with the anion to form an identifiable product could be worked out.

REFERENCES

1. A. Hantzch and H. Kissel, Ber., 3137 (1899).
2. E. F. Caldin and G. Long, Proc. Roy. Soc. Ser. A. 226, 263 (1955).
3. E. Buncel, K. E. Russell, and J. Wood, Chem. Comm., 252 (1968).

4. Y. Okamoto and J. Y. Wang, J. Org. Chem., 42, 1261 (1977).
5. J. B. Ainscough and E. F. Caldin, J. Chem. Soc. 2546 (1956).
6. C. F. Bernasconi, J. Org. Chem., 36, 1671 (1971).
7. G. A. Russell and E. G. Janzen, J. Am. Chem. Soc., 84, 4154 (1962); G. A. Russel, et al., J. Am. Chem. Soc., 89, 300 (1967).
8. E. J. Fendler and J. H. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press, New York, 1975.

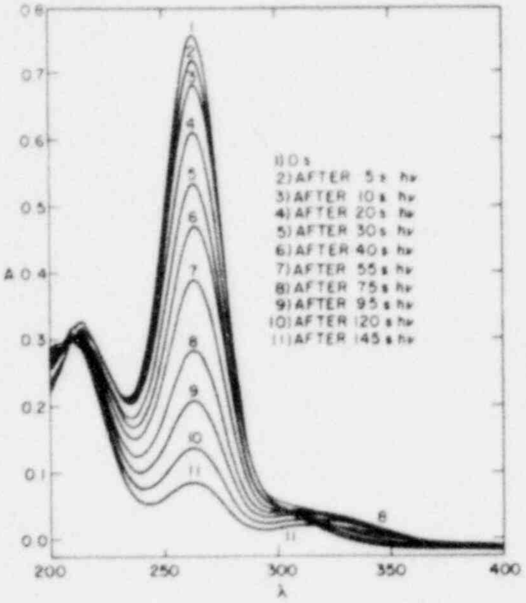


Fig. 1. UV record of the aqueous solution photolysis of NQ. Solution composition: 5.170 x 10^{-5}M NQ, pH = 7.

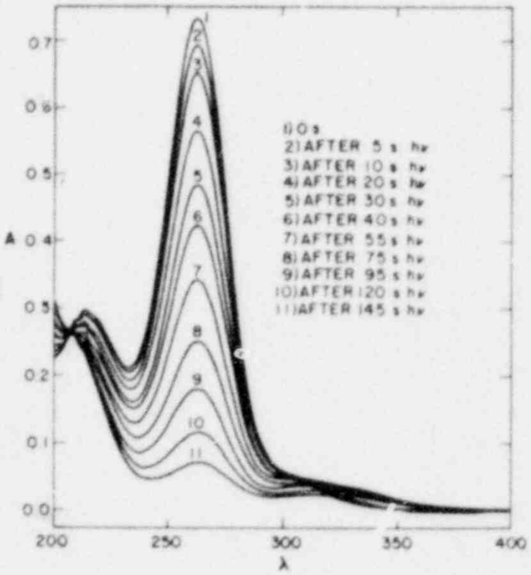


Fig. 2. UV record of the aqueous solution photolysis of NQ. Solution composition: 5.170 x 10^{-5}M NQ, 1.6 x 10^{-3}M HCL pH = 2.8.

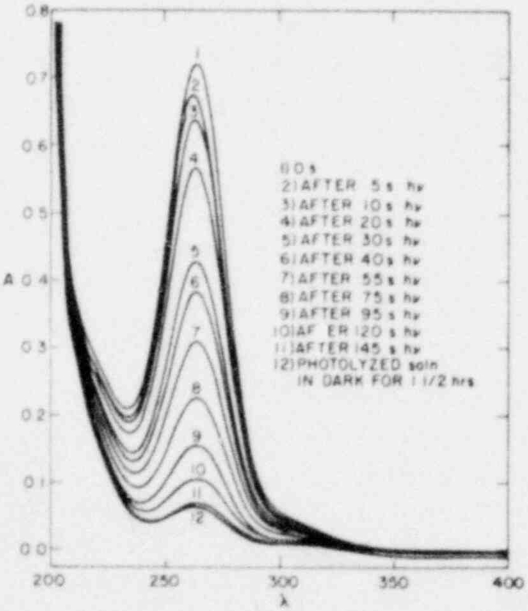


Fig. 3. UV record of the aqueous solution photolysis of NQ. Solution composition: 5.170 x 10^{-5}M NQ, 1.61 x 10^{-3}M NaOH pH = 11.1.

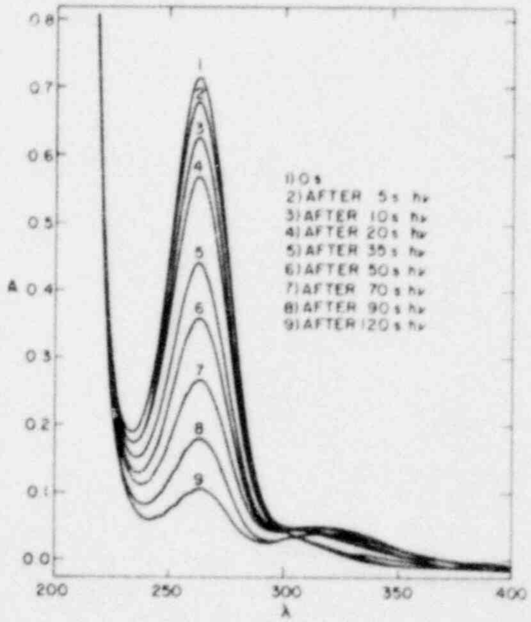


Fig. 4. UV record of the aqueous solution photolysis of NQ. Solution composition: 5.170 x 10^{-5}M NQ, 5.992 x 10^{-3}M CTAB pH = 7.

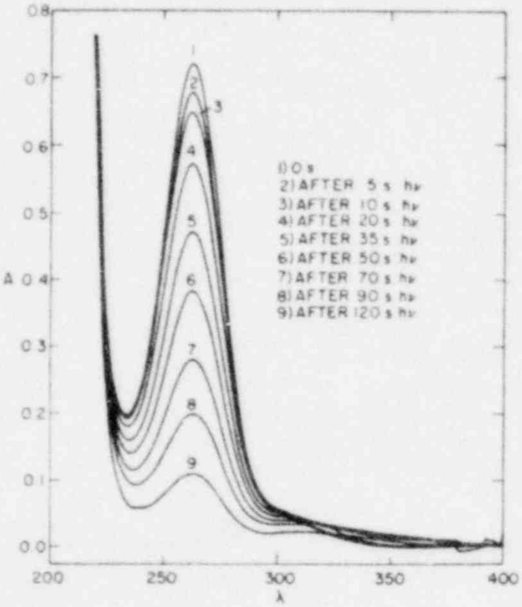


Fig. 5. UV record of the aqueous solution photolysis of NQ. Solution composition: 5.170 x 10^{-5}M NQ, 5.992 x 10^{-3}M CTAB and 1.6 x 10^{-3}M HCL pH = 2.8.

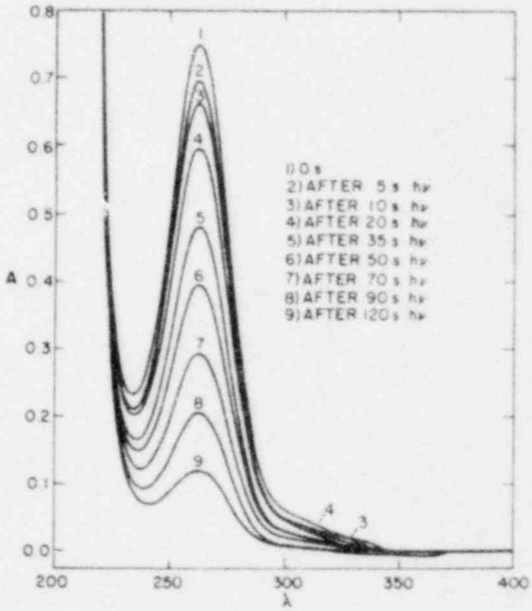


Fig. 6. UV record of the aqueous solution photolysis of NQ. Solution composition: 5.170 x 10^{-5}M NQ, 5.992 x 10^{-3}M CTAB, and 1.548 x 10^{-3}M NaOH: pH = 11.1.

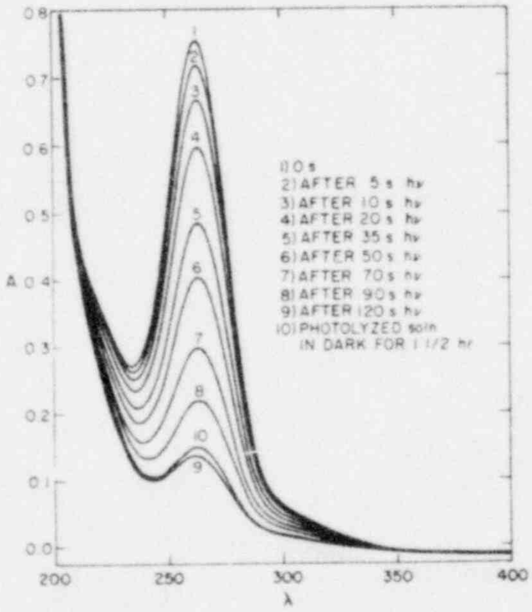


Fig. 7. UV record of the aqueous solution photolysis of NQ. Solution composition: 5.170 x 10^{-5}M NQ, 1.0 x 10^{-1}M SDS pH = 7.

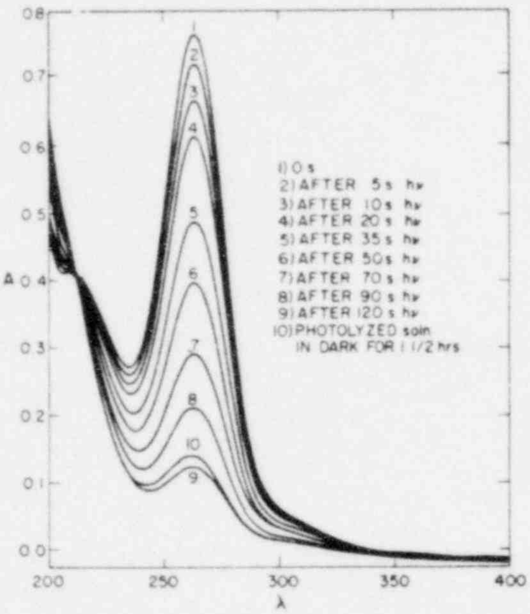


Fig. 8. UV record of the aqueous solution photolysis of NQ. Solution composition: 5.170 x 10^{-5}M NQ, 1.0 x 10^{-1}M SDS and 1.6 x 10^{-3}M HCL pH = 2.8.

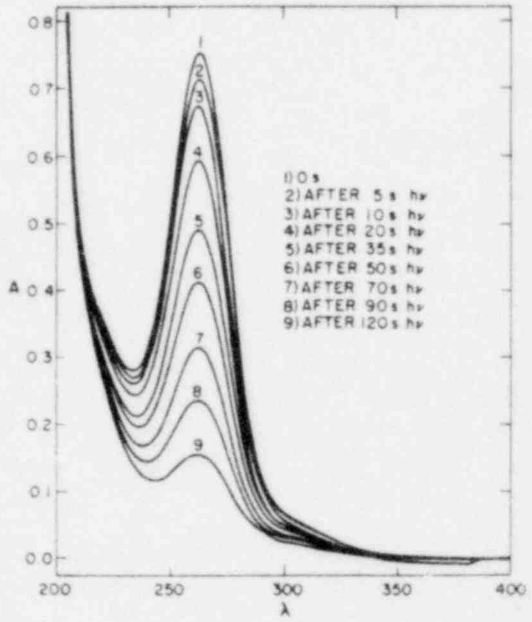


Fig. 9. UV record of the aqueous solution photolysis of NQ. Solution composition: 5.170 x 10^{-5}M NQ, 1.0 x 10^{-1}M SDS and 1.7 x 10^{-3}M pH = 11.2.

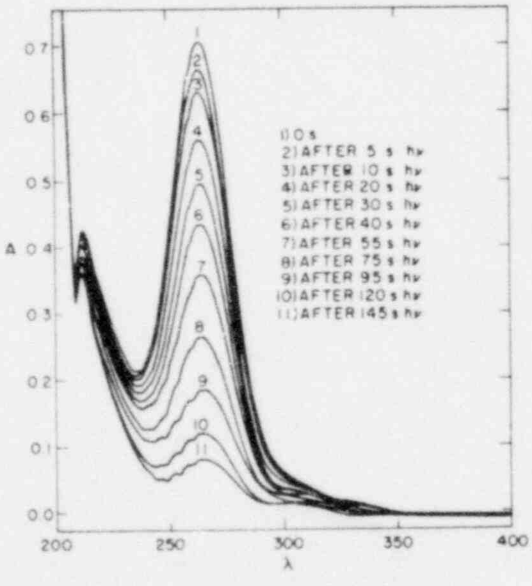


Fig. 10. UV record of the aqueous solution photolysis of NQ. Solution composition: 5.170 x 10^{-5}M NQ, 2.2 x 10^{-1}M NaCN.

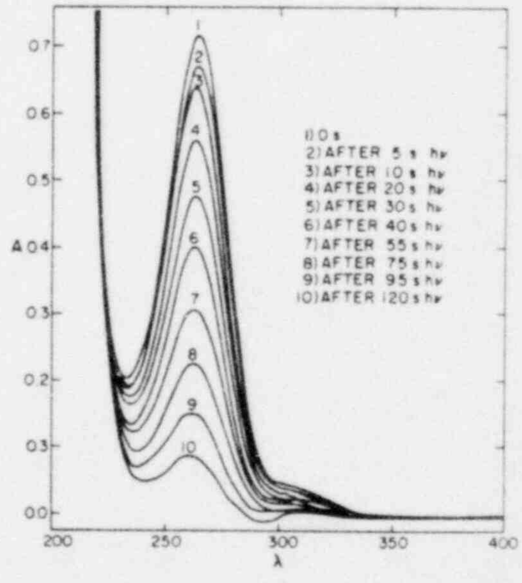


Fig. 11. UV record of the aqueous solution photolysis of NQ. Solution composition: 5.170 x 10^{-5}M NQ, 218 x 10^{-1}M $NaBH_4$.

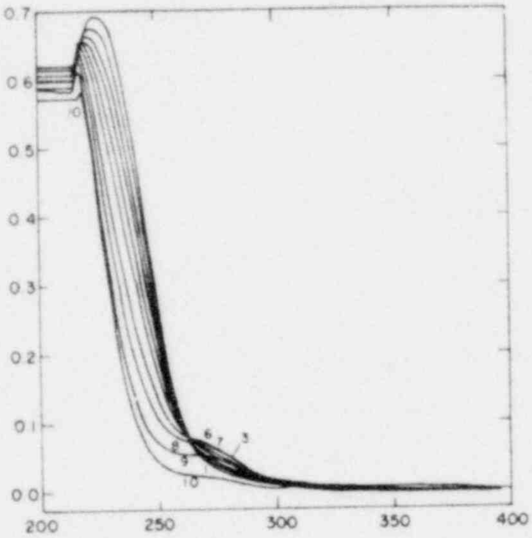


Fig. 12. UV record of the aqueous solution photolysis of HMX. Solution composition: 4.0 x 10^{-5}M HMX, 6.0 x 10^{-3}M CTAB, pH = 7.

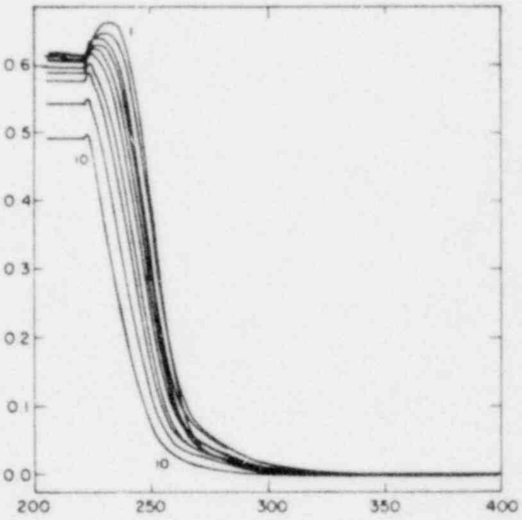


Fig. 13. UV record of the aqueous solution photolysis of HMX. Solution composition: 4.0 x 10^{-5}M HMX, 6.0 x 10^{-3}M CTAB, and 3.6 x 10^{-3}M HCL pH = 2.44.

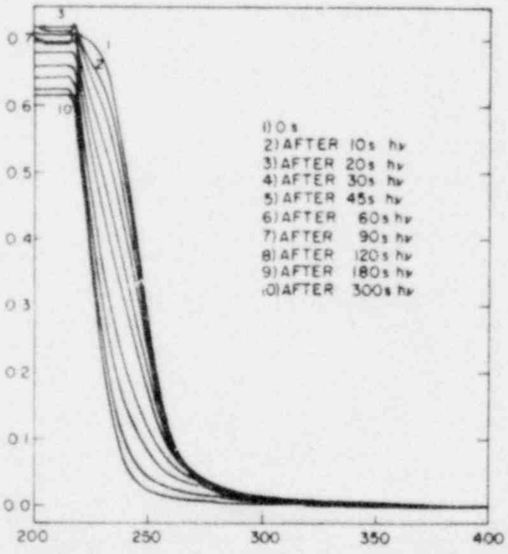


Fig. 14. UV record of the aqueous solution photolysis of HMX. Solution composition: 4.0 x 10^{-5}M HMX, 6.0 x 10^{-3}M CTAB, and 2.9 x 10^{-3}M NaOH pH = 11.5.

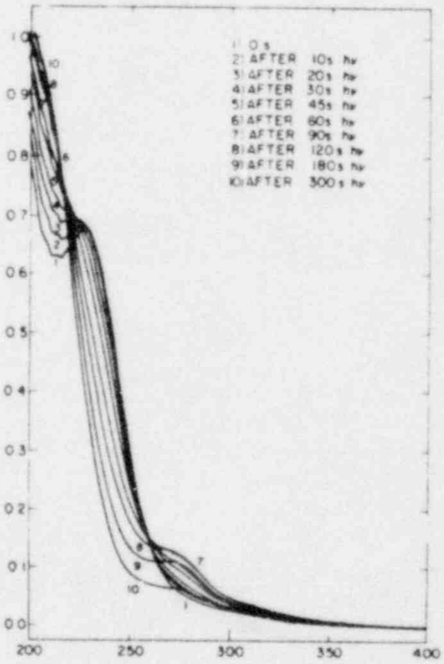


Fig. 15. UV record of the aqueous solution photolysis of HMX. Solution composition: 4.0 x 10^{-5}M HMX, 1.0 x 10^{-1}M SDS pH = 7.

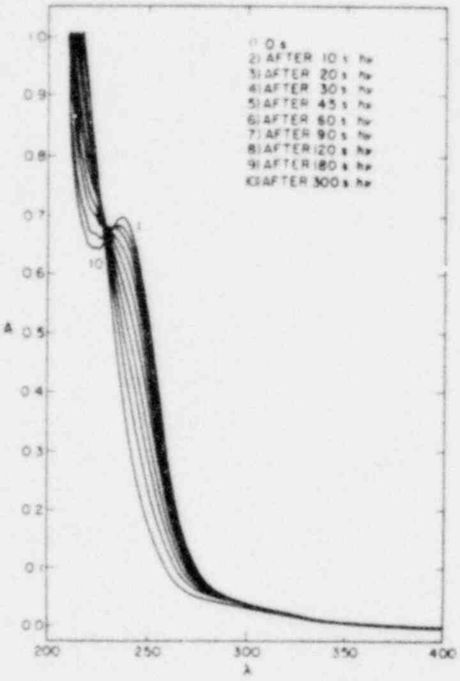


Fig. 16. UV record of the aqueous solution photolysis of HMX. Solution composition: 4.0 x 10^{-5}M HMX, 1.0 x 10^{-1}M SDS, and 3.6 x 10^{-3}M HCL pH = 2.44.

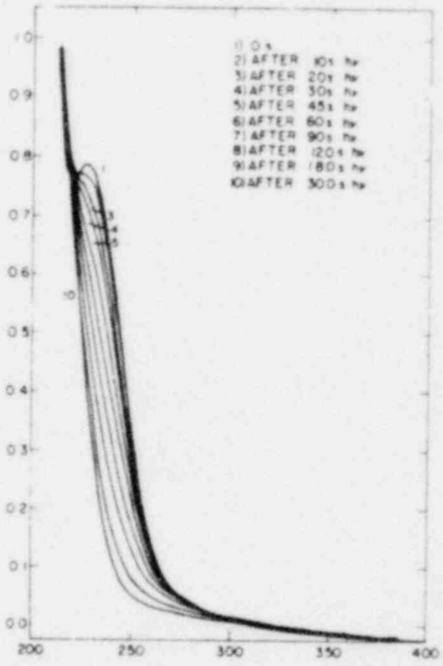


Fig. 17. UV record of the aqueous solution photolysis of HMX. Solution composition: 4.0 x 10^{-5}M HMX, 1.0 x 10^{-1}M SDS, and 3.7 x 10^{-3}M NaOH pH = 11.6.

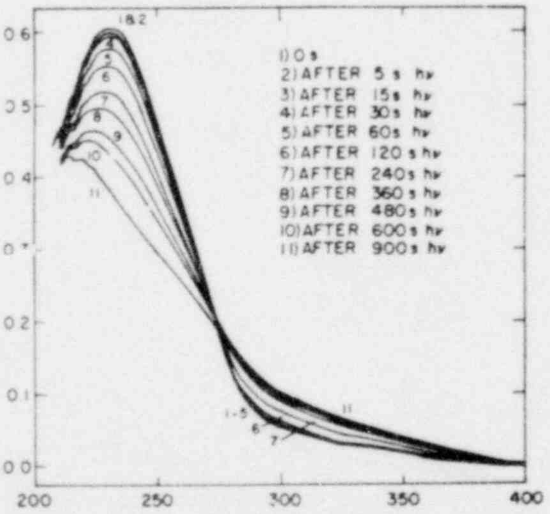


Fig. 18. UV record of the aqueous solution photolysis of TNT. Solution composition: 3.102 x 10^{-5}M TNT pH = 7.

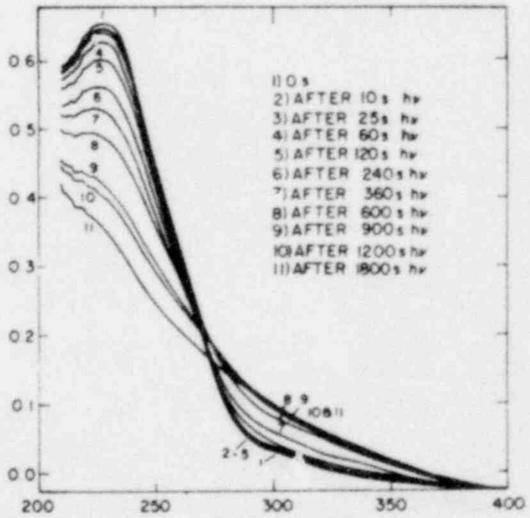


Fig. 19. UV record of the aqueous solution photolysis of TNT. Solution composition: 3.102 x 10^{-5}M TNT, 1.026 x 10^{-1}M SDS pH = 7.

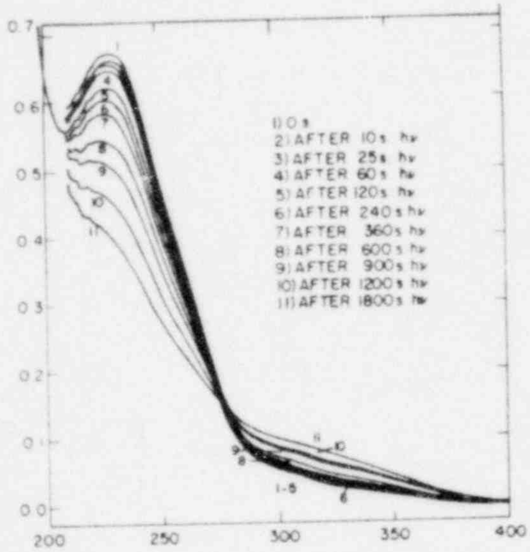


Fig. 20. UV record of the aqueous solution photolysis of TNT. Solution composition: 3.102 x 10^{-5}M TNT, 1.026 x 10^{-1}M SDS, and 2.4 x 10^{-3}M HCL pH =262.

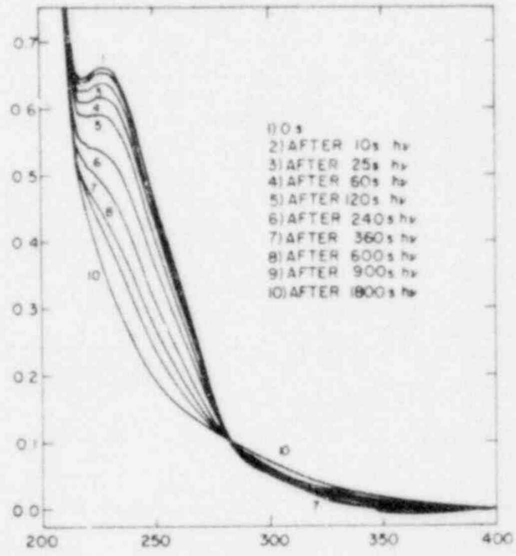


Fig. 21. UV record of the aqueous solution photolysis of TNT. Solution composition: 3.102 x 10^{-5}M TNT, 1.12 x 10^{-1}M SDS, and 3.262 x 10^{-3}M NaOh pH = 11.5.

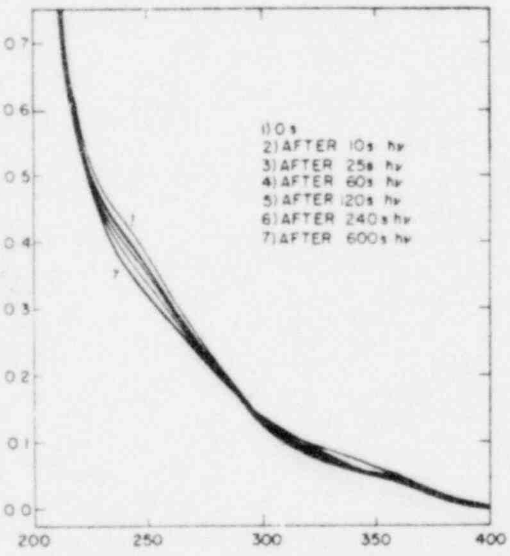


Fig. 22. UV record of the aqueous solution photolysis of TNT. Solution composition: 3.102 x 10^{-5}M TNT, 2.141 x 10^{-1}M NaCN.

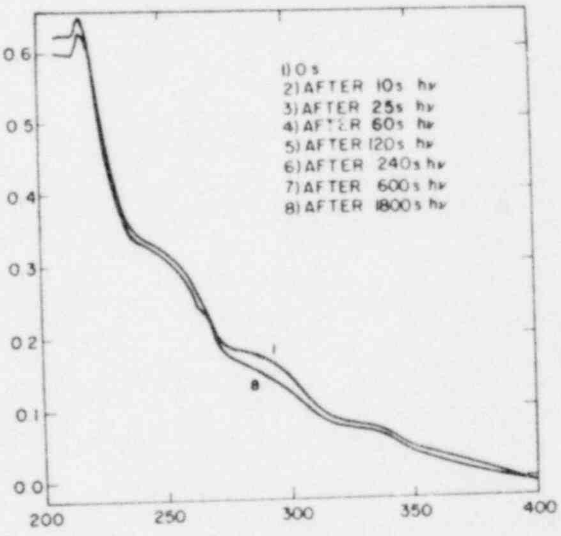


Fig. 23. UV record of the aqueous solution photolysis of TNT. Solution composition: 3.102 x 10^{-5}M TNT, 6.0 x 10^{-3}M CTAB, and 2.076 x 10^{-1}M NaCN.

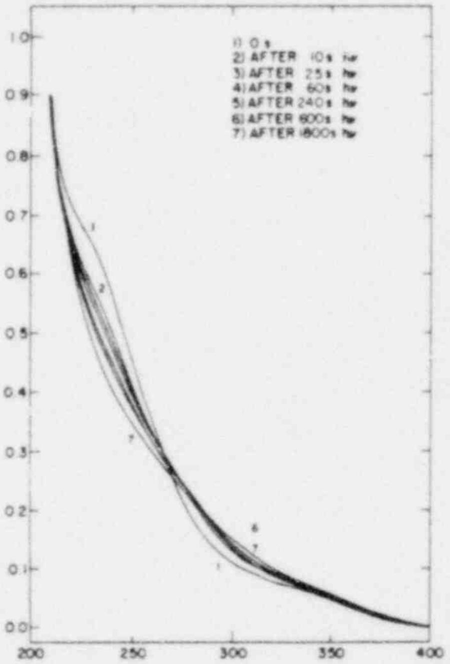


Fig. 24. UV record of the aqueous solution photolysis of TNT. Solution composition: 3.102×10^{-5}M TNT, 1.037×10^{-1}M SDS, and 2.037×10^{-1}M NaCN.

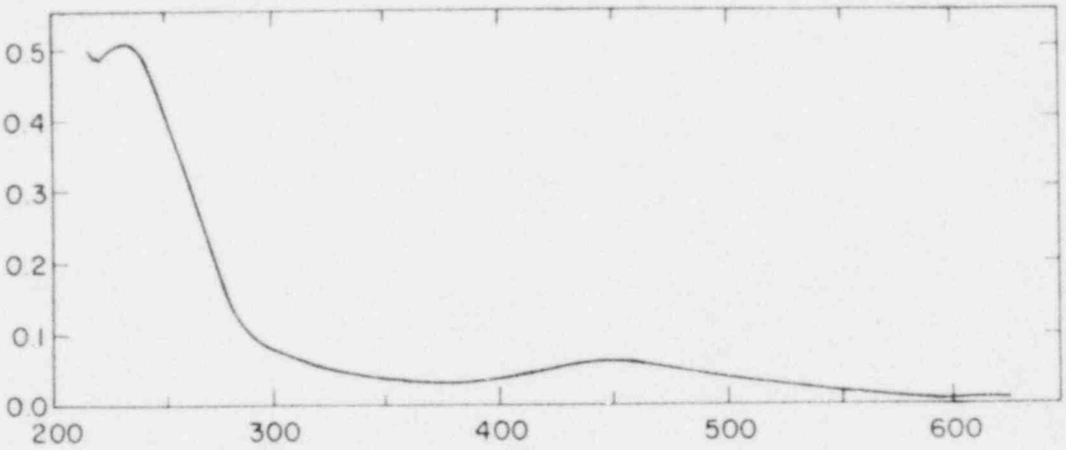


Fig. 25. UV-Vis spectrum of 3.102 x 10^{-5}M TNT is aqueous 3.57 x 10^{-3}M NaOH.

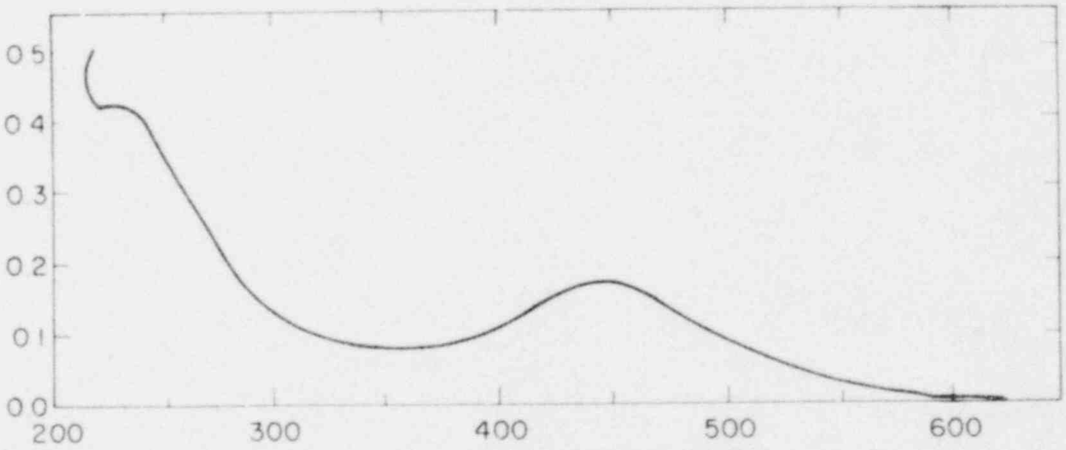


Fig. 26. UV-Vis spectrum of 3.102 x 10^{-5}M TNT is aqueous 3.57 x 10^{-3}M NaOH after 24 h in the dark.

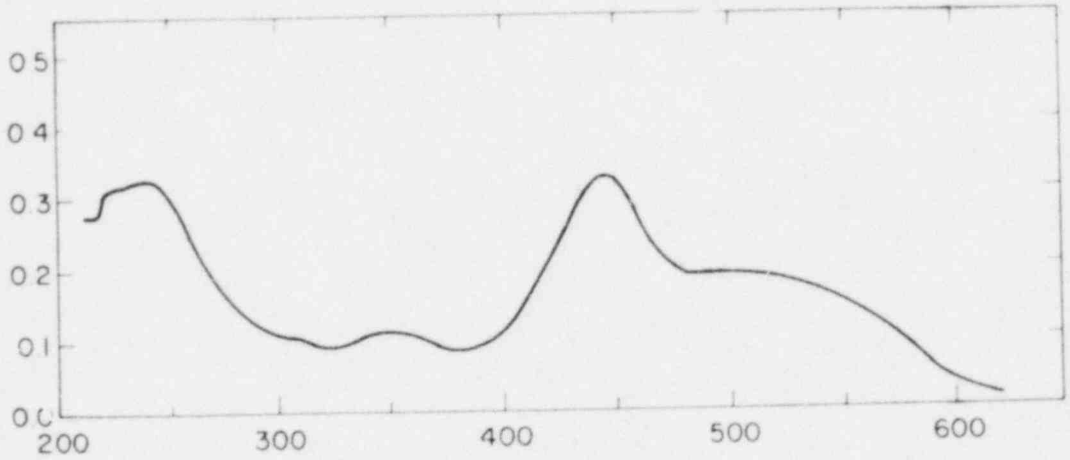


Fig. 27. UV-Vis spectrum of an aqueous solution of TNT. Solution composition: 3.102×10^{-5}M TNT, 6×10^{-3}M CTAB, and 3.57×10^{-3}M NaOH.

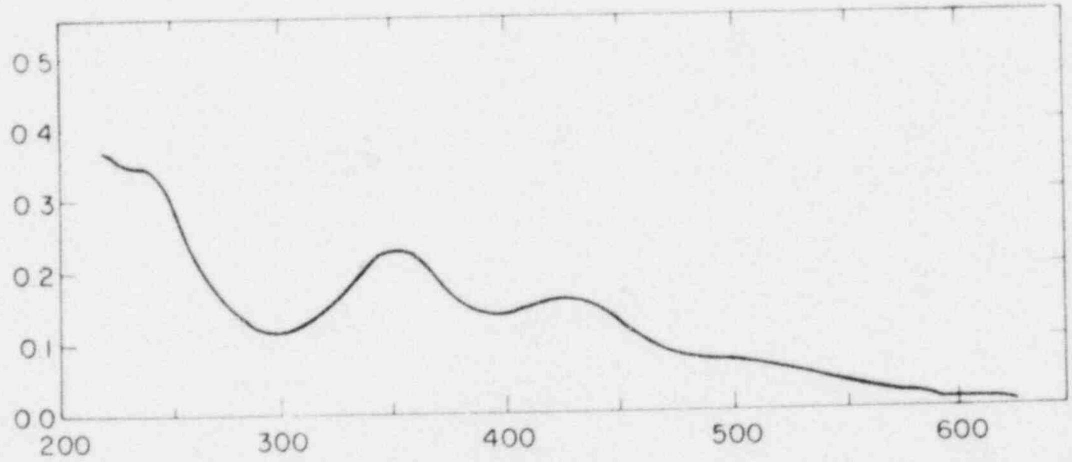


Fig. 28. UV-Vis spectrum of an aqueous solution of TNT after 24 h in the dark. Solution composition: 3.102×10^{-5}M TNT, 6×10^{-3}M CTAB, and 3.57×10^{-3}M NaOH.

were formed. Table 1 lists the composition of each working solution.

TABLE 1

HE	Solvent	Concentration (M)
TNT	acetonitrile	4.802×10^{-5}
HMX	"	4.054×10^{-5}
NQ	"	5.360×10^{-5}

One to three milliliter aliquots of each of these solutions were photolyzed for time intervals ranging from 0.5 to 30 minutes. Dark reactions were checked for after photolysis. The solutions shown in Table 1 were used as "stock" solutions for both photolysis and routine chemical analysis and as such represent the maximum concentration of HE used in this part of the study.

The effects of micell-forming detergents on the aqueous solution chemistry and photochemistry of TNT, HMX, and NQ have been screened. The principal technique employed was UV spectroscopy. In cases where it was possible, the photochemistry of each HE was studied in aqueous solution, in aqueous solution containing cationic micell-forming detergent, and in aqueous solution containing anionic micell-forming detergent. The cationic micell-forming detergent was cetyltrimethylammonium bromide and the anionic micell-forming detergent was sodium dodecyl sulfate. A study of each solution was conducted under acidic (pH=3), neutral (pH=7), and basic (pH=11) conditions. In addition, the effects of sodium borohydride and cyanide ion were studied in selected cases. In the case of TNT, spectacular "dark" chemistry was observed for micellar solutions.

APPARATUS

1) Photolysis Apparatus

Two types of photolysis apparatus were used in this study and routinely checked for agreement.

The first type was of the "merry-go-round" type commonly employed in photochemical studies. The light source used was an unfiltered, 450 watt, medium pressure, mercury vapor lamp. The photon output of the lamp was routinely measured using a potassium ferrioxalate actinometer. All actinometric measurements have been corrected for absorption.

The second type was a static photolysis cell holder to which a small unfiltered 10 watt, medium pressure, mercury vapor lamp was fixed.

Typically photolysis of HE solutions was carried out on 2 to 4 milliliters of stock solution contained in a 1 cm x 1 cm x 4.5 cm quartz, rectangular cell. Photolysis times ranged from 5 seconds to 30 minutes; however, it was found that, in terms of the detection scheme, 5 minutes was the maximum required. Quantum yield measurements based on the disappearance of HE never exceeded 0.2 for any of the HE studied regardless of the solvent or micell-forming detergent used. Even though the quantum yield was lower than had been hoped, on the average, adequate photolysis had occurred in 2 to 5 minutes to be easily detected by the luminol reaction.

2) <u>CL Monitoring Apparatus</u>

Figure 3 shows schematically the apparatus used to monitor the variations in CL light intensity caused by sample introduction.

A solution of 1 x 10^{-4} M luminol in 0.1 M borate buffer, pH 10.5, was mixed with a 1 x 10^{-3} M hydrogen peroxide solution and the mixture flowed through a 180 microliter reaction cell located in front of a photomultiplier tube (RCA 1P21) housed in a light-tight box. Another input to the reaction cell was provided by the output of the sampling valve, which received as an input an aqueous solution of 1 x 10^{-9} M chromium III. Thus in the absence of a sample (HE photoproducts), the luminol-peroxide solution combines with the chromium solution to give a constant intensity light output.

were formed. Table 1 lists the composition of each working solution.

TABLE 1

HE	Solvent	Concentration (M)
TNT	acetonitrile	4.802×10^{-5}
HMX	"	4.054×10^{-5}
NQ	"	5.360×10^{-5}

One to three milliliter aliquots of each of these solutions were photolyzed for time intervals ranging from 0.5 to 30 minutes. Dark reactions were checked for after photolysis. The solutions shown in Table 1 were used as "stock" solutions for both photolysis and routine chemical analysis and as such represent the maximum concentration of HE used in this part of the study.

The effects of micell-forming detergents on the aqueous solution chemistry and photochemistry of TNT, HMX, and NQ have been screened. The principal technique employed was UV spectroscopy. In cases where it was possible, the photochemistry of each HE was studied in aqueous solution, in aqueous solution containing cationic micell-forming detergent, and in aqueous solution containing anionic micell-forming detergent. The cationic micell-forming detergent was cetyltrimethylammonium bromide and the anionic micell-forming detergent was sodium dodecyl sulfate. A study of each solution was conducted under acidic (pH=3), neutral (pH=7), and basic (pH=11) conditions. In addition, the effects of sodium borohydride and cyanide ion were studied in selected cases. In the case of TNT, spectacular "dark" chemistry was observed for micellar solutions.

APPARATUS

1) Photolysis Apparatus

Two types of photolysis apparatus were used in this study and routinely checked for agreement.

The first type was of the "merry-go-round" type commonly employed in photochemical studies. The light source used was an unfiltered, 450 watt, medium pressure, mercury vapor lamp. The photon output of the lamp was routinely measured using a potassium ferrioxalate actinometer. All actinometric measurements have been corrected for absorption.

The second type was a static photolysis cell holder to which a small unfiltered 10 watt, medium pressure, mercury vapor lamp was fixed.

Typically photolysis of HE solutions was carried out on 2 to 4 milliliters of stock solution contained in a 1 cm x 1 cm x 4.5 cm quartz, rectangular cell. Photolysis times ranged from 5 seconds to 30 minutes; however, it was found that, in terms of the detection scheme, 5 minutes was the maximum required. Quantum yield measurements based on the disappearance of HE never exceeded 0.2 for any of the HE studied regardless of the solvent or micell-forming detergent used. Even though the quantum yield was lower than had been hoped, on the average, adequate photolysis had occurred in 2 to 5 minutes to be easily detected by the luminol reaction.

2) <u>CL Monitoring Apparatus</u>

Figure 3 shows schematically the apparatus used to monitor the variations in CL light intensity caused by sample introduction.

A solution of 1 x 10^{-4} M luminol in 0.1 M borate buffer, pH 10.5, was mixed with a 1 x 10^{-3} M hydrogen peroxide solution and the mixture flowed through a 180 microliter reaction cell located in front of a photomultiplier tube (RCA 1P21) housed in a light-tight box. Another input to the reaction cell was provided by the output of the sampling valve, which received as an input an aqueous solution of 1 x 10^{-9} M chromium III. Thus in the absence of a sample (HE photoproducts), the luminol-peroxide solution combines with the chromium solution to give a constant intensity light output.

An electrical analogue of the time-dependent variations in CL light intensity was produced by the photomultiplier tube and a permanent record of the variations was formed by a stripchart recorder.

The size of the sample aliquot was controlled by the volume of the sample loop, which was one leg of the sampling valve as shown in Figure 3. The volume of the sample loop used in this study was 80 microliters and was filled by suction provided by a syringe. When the sample valve was actuated, the flow into the valve was routed through the sample loop causing the sample to mix with the metal ion solution before entering the reaction chamber.

RESULTS AND DISCUSSION

1) TNT

Figure 4 shows the results of introducing 1) solvent (acetonitrile) alone, 2) unphotolyzed TNT in solvent, and 3) photolyzed TNT (5 and 30 minute photolysis times) into the CL reaction. The up-scale excursions for solvent alone and unphotolyzed TNT are probably due to the elution of adsorbed Cr^{+3} ions from the surface of the tubing through which the solution flows. The down-scale excursion for the photolyzed TNT gives an indication of photolysis products of TNT diminishing the light intensity of the steady-state luminol CL reaction. The mechanism for the observed effect on the intensity of the luminol reaction is believed to be complexation of the Cr^{+3} ions by the photolysis products of the high explosives, TNT in this case. The total amount of TNT in the sample introduced into the CL apparatus was 3.84×10^{-9} moles.

2) HMX

Figure 5 shows the results of introducing 1) solvent (acetonitrile) alone, 2) unphotolyzed HMX in solvent, and 3) photolyzed HMX in solvent (5 minute photolysis) into the CL reaction. The rationale for explaining the observed behavior for HMX is the same as that for TNT. The total amount of HMX in the sample introduced into the CL apparatus was 3.24×10^{-9} moles.

3) <u>NQ</u>

Figure 6 shows the results of introducing 1) solvent (acetonitrile) alone, 2) unphotolyzed NQ in solvent, and 3) photolyzed NQ in solvent (5 minute photolysis) into the CL reaction. The rationale for explaining the observed behavior of NQ includes that for TNT. However in addition, NQ in the solvent routinely showed reactivity with the reactants of the CL reaction before and after photolysis. The post-photolysis data showed the typical down-scale response, and the pre-photolysis data showed up-scale response. Thus unphotolyzed NQ in acetonitrile increases the CL light intensity. The mechanism for this response is unclear.

The results of photolysis of HE in micellized solvent can be summarized as follows. Without exception, each substrate (TNT, HMX, and NQ) studied is highly photoreactive in aqueous solution. The presence of micell-forming detergents does not alter the photoreactivity (in terms of quantum yield for loss of substrate), but does alter the course of the chemistry (possibly through stabilization <u>or</u> destabilization of primary photoproducts).

ACKNOWLEDGEMENT

The financial support for this work by the US Nuclear Regulatory Commission, SAFERS Division, is gratefully acknowledged.

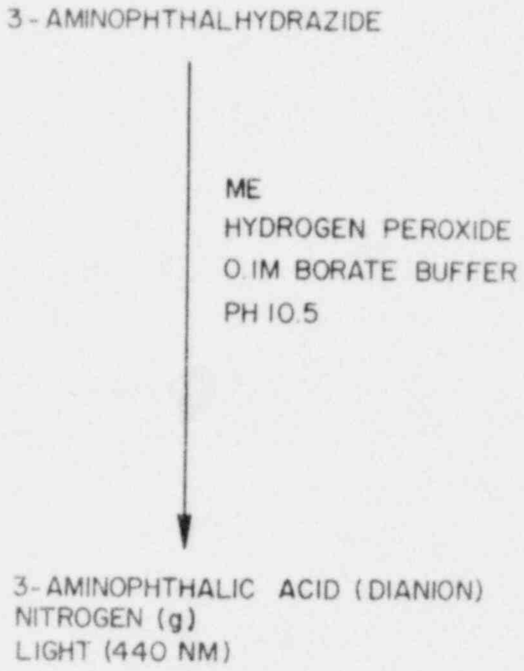


Fig. 1. The luminol chemiluminescence reaction.

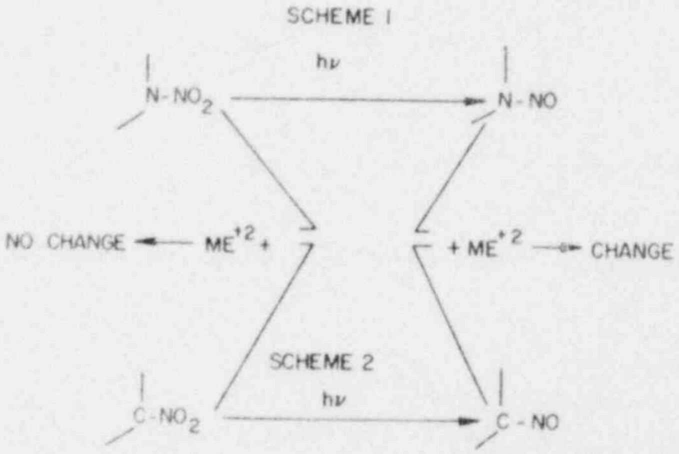


Fig. 2. Coupling pathways for nitramines, nitrosamines, nitro aromatic and nitroso aromatic compounds such as certain high explosives.

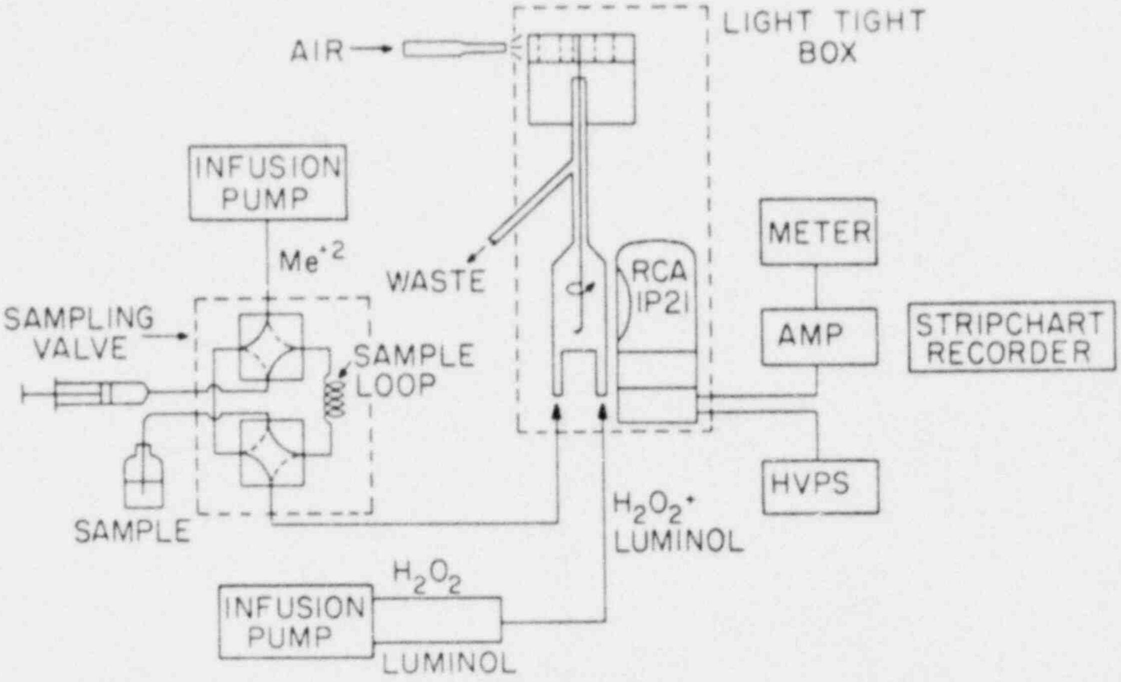


Fig. 3. Apparatus used for measuring the changes in chemiluminescence intensity is shown. The pumps, associated valve arrangement, mixing chamber (working volume 180 microliter) and block diagrammed electronics are shown. The mixing chamber is shown oversized for illustrative convenience.

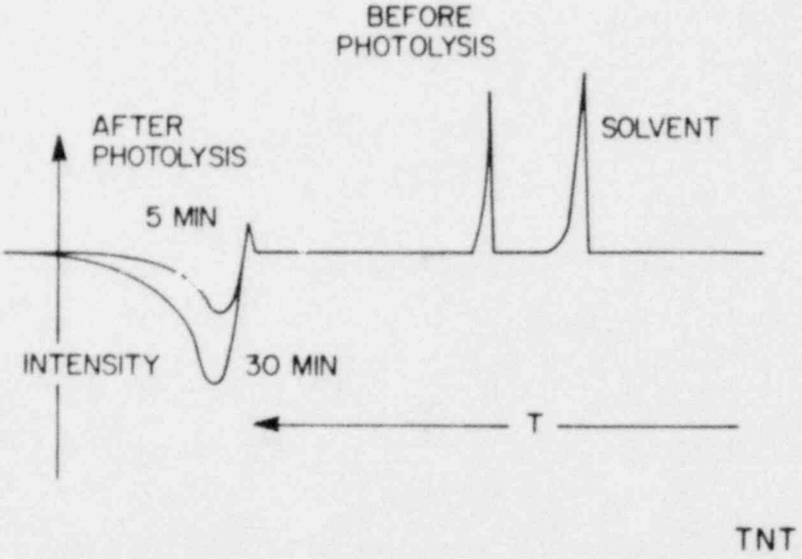


Fig. 4. Typical response for 80 microliter solvent alone, solvent-TNT (unphotolyzed), and solvent-TNT photolyzed for 5 and 30 minutes.

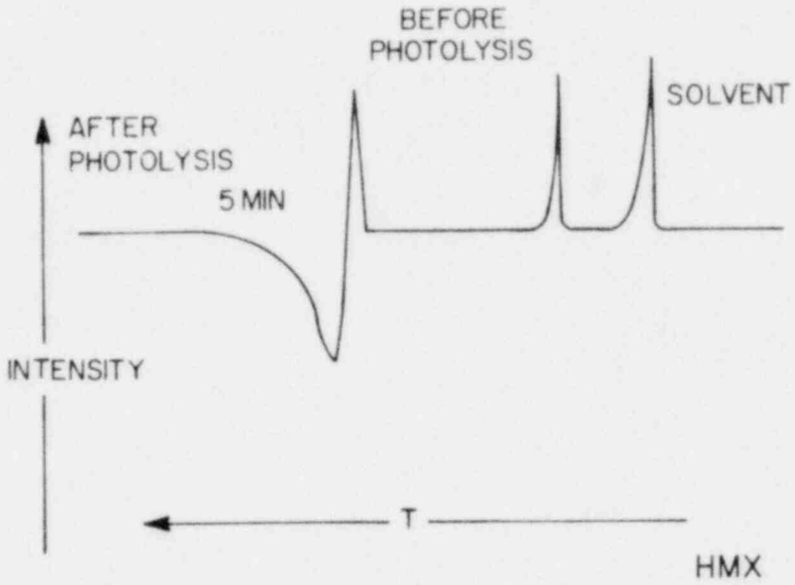


Fig. 5. Typical response for 80 microliter solvent alone, solvent-HMX (unphotolyzed), and solvent-HMX photolyzed for 5 minutes.

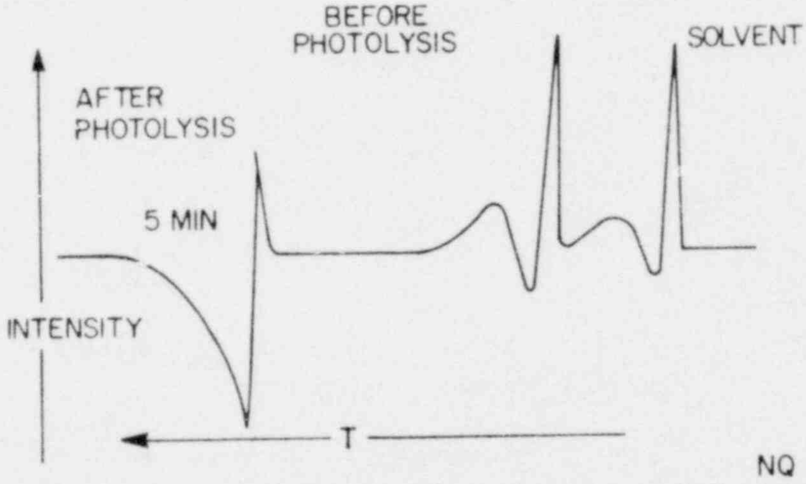


Fig. 6. Typical response for 80 microliter solvent alone, solvent-NQ (unphotolyzed), and solvent-NQ photolyzed for 5 minutes.

APPENDIX C

PAPER PRESENTED IN RESTON, VIRGINIA, AT THE "NEW CONCEPTS SYMPOSIUM AND WORKSHOP ON DETECTION AND IDENTIFICATION OF EXPLOSIVES," OCTOBER 30 TO NOVEMBER 1, 1978.

CHEMILUMINESCENCE APPROACH TO EXPLOSIVE TRACE ANALYSIS

by

M. P. Neary

ABSTRACT

Chemiluminescence (CL) analyses that depend on both naturally derived and synthetic chemiluminesing compounds have received serious attention from analytical chemists only in the last ten years. The features of CL that account for the interest received from analytical chemists are: (1) extremely high sensitivity (10^{-15} moles) and excellent linear response (as much as seven orders of magnitude), (2) good to excellent selectivity, (3) short analysis time (less than 1 min), (4) low cost per analysis ($\leq$ 5 cents/analysis), and (5) inexpensive instrumentation ($5-10k).

Some of the types of compounds to which CL analysis can be applied include: certain organic and inorganic oxidants and reductants, certain transition metal ions, water at trace levels, and enzymes. With this chemical variety, the possibility of coupling the chemistry of high explosives (HE) to a CL reaction is assured.

Two CL reactions will be discussed that are good candidates for CL-HE analysis. The following topics will be presented: (1) CL in general, (2) luminol CL, (3) CL-HE coupling reactions, and (4) TATB-CL.

1. CL in General - CL may be defined as the emission of light whose upper wavelength limit defines the minimum excess energy produced by the CL reaction. It is generally true that the emitter is a product of the CL reaction.

In order that detectable CL occurs, certain physical conditions must exist.

a. There must be sufficient energy released by the reaction so that the formation of the product in an electronic excited state is favored.

b. There must exist a kinetically feasible pathway leading to the electronic excited state of the product.

c. Reasonably high quantum efficiency must exist for the excited product.

The quantum efficiency for a CL reaction is defined as follows:

$$\varphi_{CL} = \varphi_R \cdot \varphi_F = \frac{\text{No. of photons emitted}}{\text{No. of molecules reacted}}$$

$$\text{where } \varphi_R = \frac{\text{No. of molecules reaching the excited state}}{\text{No. of molecules reacted}}$$

$$\text{and} \qquad \frac{\text{No. of molecules emitting}}{\text{No. of molecules reaching the excited state}}$$

It can be shown that the integrated intensity (I) is related to the concentration of the analyte (C) by the following relationship:

$$I = \varphi_{CL}\,\varphi_M \,\{C(t_0) - C(t_1)\} + \overline{N}(t_1 - t_0) \qquad (1)$$

where:

φ_M = instrument or detection efficiency

t_0 = time at which the analyte is introduced and measurement started

t_1 = time at which the measurement is terminated

$\overline{N}$ = mean noise on the closed interval $[t_0, t_1]$

Furthermore, the minimum level of detection may be calculated. Assuming a practical signal to noise ratio of 3, then the minimum detectable signal, I_{min}, may be written,

$$I_{min} = 3\sqrt{\overline{N}(t_1 - t_0)} \qquad (2)$$

and by equation (1) related, the analyte concentration by,

$$C_{min} = \frac{3\sqrt{\overline{N}(t_1 - t_0)}}{\varphi_{CL}\,\varphi} \qquad (3)$$

By using equation (3) with typical values for the parameters, a minimum level of detection may be calculated to be ≃2 x 10^5 molecules of analyte.

2. <u>Luminol CL Reaction</u> - Luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) is a synthetic compound, whose CL is known to proceed in the presence of base, oxidant, and trace amounts of certain first-row transition metals, with an emission maximum at 440 nm and φ_{CL} of about 0.04. The product emitter is thought to be the dianion of the amino dicarboxcylic acid.

Analysis of trace amounts of first-row transition metals using luminol CL has been carried out successfully to concentrations as low as 5 x 10^{-12} moles and linear response over 4-5 orders of magnitude. Analysis of trace amounts of oxidant (H_2O_2) has been carried out successfully to concentrations as low as 10^{-9} M. Also, by using I_2 as an oxidant, As^{+3} and SO_2 have been analyzed using the luminol reaction at 10^{-9} M and 10 ppb, respectively.

3. <u>Coupling Reactions</u> - In an effort to couple HE chemistry to a CL reaction, it is necessary to form a reactive derivative of the HE. Regarding the luminol reaction, it is clear that if the concentration of either the oxidant or the catalyst (metal ion) can be chemically or physically influenced by the HE derivative, then the light output per unit oxidant or catalyst will vary with the concentration of the HE derivative. Two types of coupling reactions are considered in view of the CL luminol reaction.

The first type of coupling reactions are those reactions that give rise to HE derivatives that can form stable complexes with first-row transition metals. The second type of coupling reactions give rise to HE derivatives with more reaction functional groups that can alter the oxidation state of the metal ions or react with the oxidant.

Coupling reactions, of those under consideration of either type, result in the partial or complete reduction of the nitro group(s) either by chemical means, uv irradiation, or both.

4. TATB*-CL Analysis - The very low solubility of TATB (60 ppm in DMSO) adds difficulty to the quantitative analysis of TATB and its impurities. In order to improve the precision of the analysis, an effort was made to couple TATB derivatives with the luminol reaction. By using DMSO as the solvent, a 40-ppm TATB stock solution was formed. A "blank" solution, composed of 10^{-6} M Co^{+2} in 50/50 DMSO-H_2O, was also formed. When an aliquot of the blank solution was irradiated with uv light and added to a solution of luminol and basic peroxide, the measured CL intensity was the same as that measured when no uv irradiation was used. However, when the stock TATB solution was mixed with the blank and irradiated with uv light, a reduction in the CL intensity of 35% and 100% was observed after 15 and 45 min irradiation, respectively. Thus, in the case of TATB, HE derivatives can be coupled to the luminol reaction.

---

*1,3,5-Triamino-2,4,6-trinitrobenzene

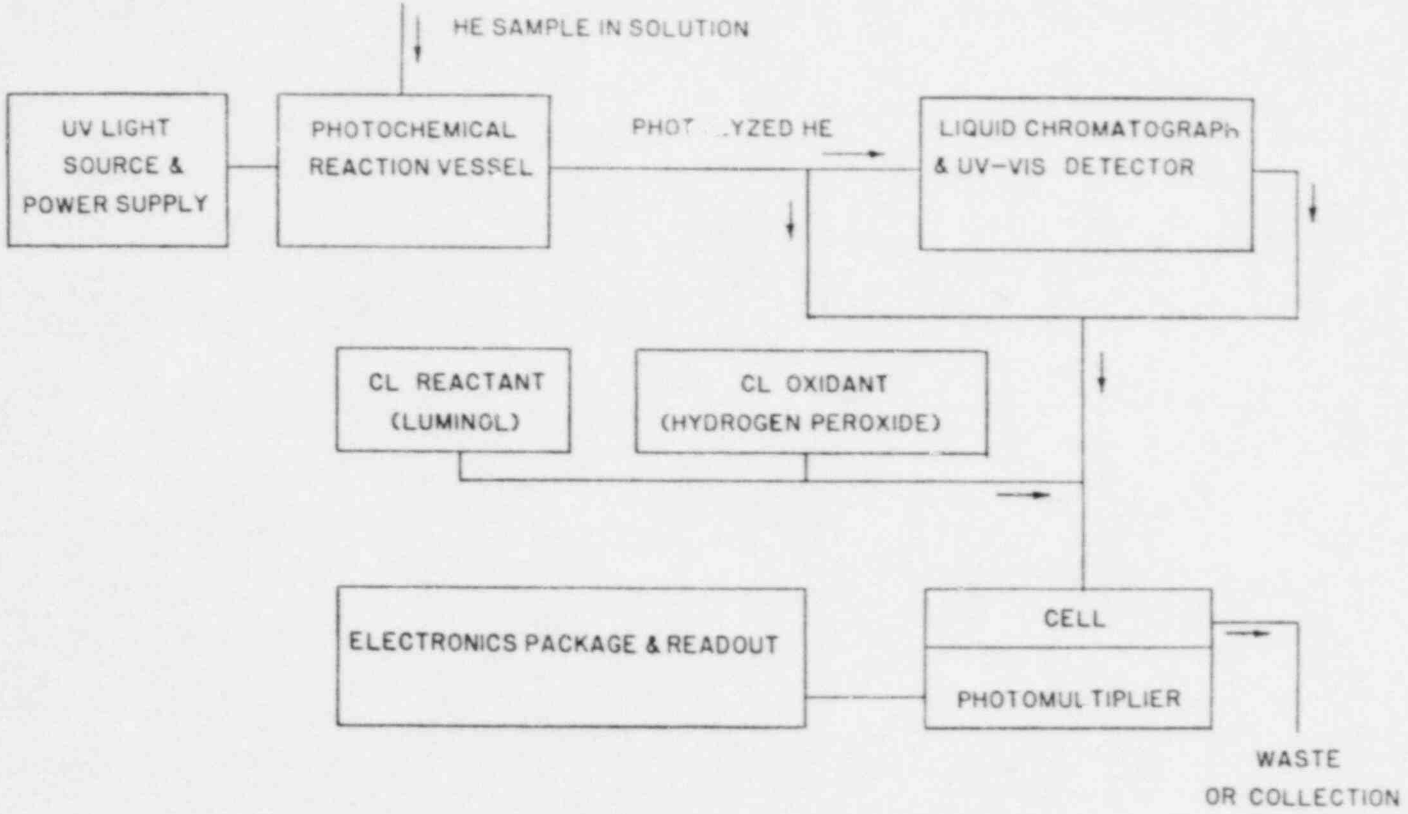


FIGURE I

FLOW DIAGRAM FOR HE DETECTION BY CHEMILUMINESCENCE (CL)

APPENDIX D

AGENDA FOR JUNE 12, 1980, TECHNICAL REVIEW IN SILVER SPRING, MARYLAND; AND DR. K. HERR'S REVIEW OF THE TECHNICAL MERIT OF THE WORK.

Following the technical presentation of HE detection work at NRC in Silver Spring, Maryland, on June 10, 1980, a short discussion ensued between Dr. M. P. Neary, the speaker, LASL; Dr. K. Herr, the technical referee, Aerospace Corporation; Mr. J. Durst, NRC, SAFERS Division; Mr. H. Blumenthal, NMSS, NRC; and Mr. J. Rielly and Mr. R. Getty, both of OSS, DOE. Mr. E. Richard, SAFERS Division, NRC, served as moderator.

Mr. Blumenthal raised a question regarding the future of the technology as it relates to implementation or end use. Dr. Neary and Mr. Durst responded that personnel screening was the central objective of the technology's application to be implemented by a small, well engineered version of the apparatus developed at LASL. They further commented that development of a "field prototype" was a near-term aim for FY 1981 or 1982. Dr. Herr added that a collateral application should be considered that was centered on space surveillance. Dr. Herr went on to point out that instead of having many portable HE detectors, a better approach might be to have a single large, sophisticated device that was fed by tubes located surreptitiously in vulnerable locations. This comment met with substantial approval from all present. Messers Rielly and Getty approached Dr. Neary at the meeting's end to state the OSS, DOE, position, namely, that DOE through OSS would be interested in participating with funds in further research and development.

In this Appendix, Dr. Herr's comments on the technology provide a detailed description of the single HE detector with many sample sources.

AGENDA

- I. Introduction
    - A. Background
        - 1. Need for HE detection in a predetonation setting
        - 2. Other methods
            - a. Pyrolysis → NO_x → chemiluminescence
            - b. GC with electron capture
            - c. Quadrupole mass spectrometry
    - B. Summary of HE detection by chemiluminescence (CL)
        - 1. LASL approach
        - 2. LASL approach vs other methods
- II. HE Detection by CL
    - A. Nature of CL reactions
        - 1. CL in general
        - 2. Luminol chemistry
        - 3. Analytically significant features
    - B. Nature of the HE sample
        - 1. Physical properties of the sample
        - 2. Chemical properties of the sample
        - 3. Sampling
            - a. Preconcentration
                - i. Vapor-liquid exchange
                - ii. Micellized solvent extraction
    - C. Chemistry related to coupling HE and CL reactions
        - 1. Photolysis of HE
        - 2. Bimolecular photoinduced HE reactions
- III. Results of the Work Performed to Date
    - A. Sampling HE vapor
        - 1. Using micellized solvents
        - 2. Using unmicellized solvents

B. HE's influence on the luminol reaction
    1. Without photolysis
    2. With photolysis
    3. Lower levels of detection
        a. HMX
        b. TNT
        c. NQ
    4. Interferences

IV. Summary and Recommendations
    A. HE detection by CL
        1. Limitations
        2. Advantages
    B. Proposed follow-on work
        1. Identification of HE photolysis
        2. Further optimize the apparatus in an effort to lower the current detection levels
        3. Further characterize the HE sampling scheme

PREDETONATION DETECTION OF HE VAPORS BY CHEMILUMINESCENT METHODS

A review of research presented to the NRC
by the Los Alamos Scientific Laboratory

by

K. C. Herr

August 1980

EXECUTIVE SUMMARY

- LASL is developing a chemiluminscent detection scheme for HE vapor which in the near term may realistically detect as few as 10^9 molecules of material (ultimately 2×10^5 molecules).

- Laboratory detection of 10^{12} molecules in a 10^{-3} ppb solution has been demonstrated.

- Sensitivities of 10^9 molecules translate into gas aliquot volumes of 1/3 liter to 300 liters for HE materials with a vapor pressure of 10^{-10} to 10^{-13} torr.

- Effective vapor pressures may be orders of magnitude less due to wrappings or short transfer times from one container to another. This orients the requirements for an HE detection system toward large gas aliquots.

- It is recommended that the NRC consider the installation of a centralized HE detection system at each nuclear facility. This system would monitor all the critical areas of the facility through a network of gas sampling tubes. This decision should be made in the near term since it will influence both sensor design and philosophy.

- Future LASL efforts should be directed toward optimizing sensitivity particularly in the use of Micellized solvent as a gas sampling and HE concentration mechanism.

- Continued funding of this feasibility program by the Safeguards Research Branch of the NRC is strongly recommended.

I. INTRODUCTION

Adversary implantation of High Explosive (HE) material within a nuclear facility is unfortunately a real possibility in the 1980s. It is important that appropriate government agencies, particularly the Nuclear Regulatory Commission (NRC), understand the dimension of this threat and develop appropriate countermeasures. HE material can be introduced into a facility by the employees, by visitors, or can even be attached to the various vehicles which daily enter the perimeter of a nuclear facility.

Predetonation detection schemes, therefore, must be developed in order to guarantee the safety of our nuclear facilities. A no-contact method is the most desirable, therefore a vapor detection technique must be developed. Unfortunately, the vapor pressure of HE materials is extremely low — 10^{-10} torr is typical. These concentrations strain the sensitivity limits of even the most sensitive analytical tools.

Four of these methods, which we can characterize as well as develop for predetonation detection of HE vapors, are summarized in Table 1. In order to establish a perspective of the sensitivity requirements for a useable HE detection scheme, it must be realized that there will be certain restrictions as to the amount of gas aliquot available for analysis. The size of the sample can vary considerably depending upon the type of system to be deployed. Portal detection, for example, may require that the aliquot size be limited to 1 to 10 liters, whereas a general facility sampling scheme may permit 10 to 10,000 liter aliquots. Even though these volumes may appear large, the total number of HE molecules available for analysis remains an infinitesimal quantity.

For example, a vapor pressure for HE of 10^{-10} torr translates to approximately 3.5×10^{9} molecules/liter of gas (STP). So in order to detect an average vapor pressure of HE, the sampling system will require a threshold sensitivity of less than 1 part in 10^{13} or $< 10^{-4}$ ppb. Table 1 reveals that 10^{-4} ppb exceeds the sensitivity limit for most of the so-called well-developed detection techniques. Obviously several orders of magnitude improvement in sensitivity will be required before we can reliably detect HE implants at nuclear facilities. The question to be addressed is: Can these sensitivities be achieved?

TABLE 1

CANDIDATE DETECTION TECHNIQUES FOR HE[*]

	Sensitivity (ppb)	Specificity	Measurement Time (sec)	Types of Vapors
Long Path Infrared Absorption	0.1 - 10	Moderate	100	All
Chemiluminescence	$1 - 10^{-3}$	Low-High	10-60	Most Nitro-Compounds
Electron Capture	10^{-4}	Low	15-120	Electronegative
Mass Spectrometry	$1 - 10^{-3}$	Moderate	10	All

II. CHEMILUMINESCENCE RESEARCH AT LASL

The Los Alamos Scientific Laboratory (LASL), with NRC Safeguards Research Branch funding, is developing a chemiluminescence (CL) HE detection technique which may provide an ultimate sensitivity of 10^{-8} ppb or 2×10^{5} molecules. Such a dramatic improvement in sensitivity would allow the detection of extremely low vapor pressure HE materials such as TATB (10^{-13} torr) using reasonably sized gas aliquots.

The specific CL reaction being explored and optimized by LASL is the liquid phase oxidation of luminol (5-amino-2.3-dihydrophthalazine-1,4-dione).

---

[*] Peter Jones, The Aerospace Corporation, private communication.

$$\text{Luminol} + \text{Base} + \text{Metal ion}^{+2} + \text{oxident}$$
$$\rightarrow \text{products} + h\nu\ (4400\text{Å})$$

Critical to the detection scheme are the first row transition metal catalyst ions. HE detection is accomplished through a coupling reaction which complexes the metal cations thereby starving the CL reaction of the catalyst. The result is a dimunition of output light intensity from the reaction whenever the metal ions are complexed by the presence of HE. Conversion of the HE nitro compounds to the complexing nitroso reagent occurs in solution by UV photolysis. This coupling reaction gives the method its molecular specificity while the luminol reaction provides the sensitivity.

III. MEASURED AND PROJECTED SENSITIVITIES

Projected sensitivities of 2×10^5 molecules have not yet been achieved. Demonstrated sensitivities range near 10^{12} HE molecules. This was accomplished in solution with HE concentrations of $\sim 10^{-3}$ ppb or a few parts per trillion. However, for these preliminary experiments, the apparatus was not optimized and substantial improvements in performance should be implemented during the second phase of this research effort.

What we will try to assess here is what gains are possible in the fully optimized system vs. those sensitivity improvements which are likely to be attained in the near term. Table 2 breaks down this disparity of 10^7 between projected ultimate sensitivity and laboratory demonstrated sensitivities, and also reveals where these gains are expected to be realized.

It is anticipated that for the near term an improvement of 10^3 in sensitivity is a reasonable expectation for the LASL CL detection system. This will provide for the detection of $\sim 10^9$ molecules of HE per gas aliquot. At 10^{-10} torr vapor pressure this amounts to 1/3 of a liter of sample, certainly adequate for portal detection schemes or for remote suitcase operations. On the other hand, extremely low vapor pressure materials such as

TABLE 2

SOURCES OF SENSITIVITY IMPROVEMENT

Factor	Ultimate Gain in Sensitivity	Expected Near Term Gain
Quantum Efficiency	20	3
Photocell Sensitivity	5	2
Electronic S/N Enhancement	20	5
Photon Collection Efficiency	5	3
Concentration of Reactants (Micelle Solvent Concentration)	1000	20
Total Gain	1×10^7	1.8×10^3

TATB (10^{-13} torr) will require considerably larger aliquots (~ 300 liters). This volume is much too large for a portal detector or a remote suitcase system. In fact, as one analyzes the realistic sensitivities for an HE detection system, it becomes apparent that reasonably large volumes (10^2 - 10^4 liters) will most likely be required to properly detect HE implants. We have been calculating sensitivities based on ideal vapor pressures. In the real world, an HE implant loosely wrapped in plastic or even placed in a paper bag, may have an effective vapor pressure which is several orders of magnitude lower than the published literature value. Large volume aliquots require new thinking about the type of HE detection scheme which should be implemented.

IV. CONSIDERATIONS FOR THE NRC

Projected sensitivities of 2×10^5 molecules or ~ 10^{-8} ppb mean that an HE material which exhibits a vapor pressure of 10^{-13} torr could be detected in a gas aliquot of only 30 milliliters. This sensitivity couples well with a nuclear facility security system design which deploys small, compact, and inexpensive detection monitors at portals and other predetermined critical operation areas. Unfortunately the super sensor is still far into the future. Nevertheless it appears that in the near term the detection of low vapor pressure materials (10^{-13} torr), or higher vapor pressure HE which are loosely wrapped, will require aliquot samples of several hundred liters.

In order to facilitate the handling of these large samples and the subsequent analysis, a centralized detection scheme should be considered. In Figure 1 we show a schematic of a centralized detection system. One or more CL detection monitors would be connected to a system of gas sampling tubes which are run to all the critical areas of a facility. This could include storage rooms, portals, loading facilities and fuel rod storage and handling areas. Gas sampling tubes would be small bore tubing which could be incorporated into existing return air ducting or separate runs as required.

This centralized approach to a security system design has three distinct operational advantages over the multiple sensor concept. First, the ability to handle larger gas samples immediately establishes a system with maximum sensitivity. Second, the cost of the system should be significantly reduced since only one or two sensors are required, as opposed to one at each portal and critical area. This approach also eliminates the need for miniaturization of the sensors and associated gas handling and photolysis equipment which further reduces cost and improves sensitivity and reliability. Third, the system is easily checked out and calibrated by carrying a small HE sample from one area to another throughout the facility.

Perhaps a fourth advantage is that any detection system can be easily adapted to this facility. If a new system with better sensitivity or molecular specificity is developed, it could be incorporated into the existing gas handling system without major design changes in the overall installation.

Obviously the basic system design will have a strong influence on the sensor sensitivity and operational constraints. At this point it appears that the centralized concept offers several clear advantages over a dispersed sensor concept. A decision on the type of system to be deployed will strongly influence the next phase of LASL's CL research program.

V. FUTURE LASL EFFORTS

Improved sensitivity should be the main thrust of LASL's effort. Hardware improvements should be incorporated during the next phase of this program. Better photocells, improved light collection and electronic S/N enhancement should be implemented as quickly as possible. These modifications will permit an early assessment of the basic sensitivity gains to be expected from these hardware modifications.

Quantum yield and micelle solvent concentration are the remaining areas which affect the ultimate detection capability of the system. Micelle concentration offers the largest single area for gain in sensitivity and should be pursued as the major effort in the next phase of this program. Concentration enhancement is an unknown factor and could range from 10 to 10^4. The higher the concentration effect, the more sensitive the system. Of course this sensitivity can also be traded off for smaller aliquot size, if desired.

Searching for chemiluminescent reactions which significantly improve the quantum efficiency over the current value of 4% should be given less priority in this investigation. It is likely that only a factor of two or three is to be gained and this search may require considerable time and effort.

Perhaps it is not too early in this study to begin thinking about a lab bench simulation of the full analysis sequence. This would include a gas sampling pump, gas liquid bubblers, photolysis cell and CL detection cell. Several steps are involved in the total scheme and actually only the last two have been investigated. Total HE detectability may in fact be limited by wall effects (e. g., absorption, catalysis poisoning) or a general accumulation of inefficiencies from all the steps in the sampling/detection scheme.

VI. CONCLUSION

In general, the CL technique appears to hold the promise for the kind of sensitivities needed for nuclear facility predetonation HE detection. The work by LASL so far has been an excellent feasibility study and it is certainly recommended that the Safeguards Research Branch of the NRC continue to fund this program.

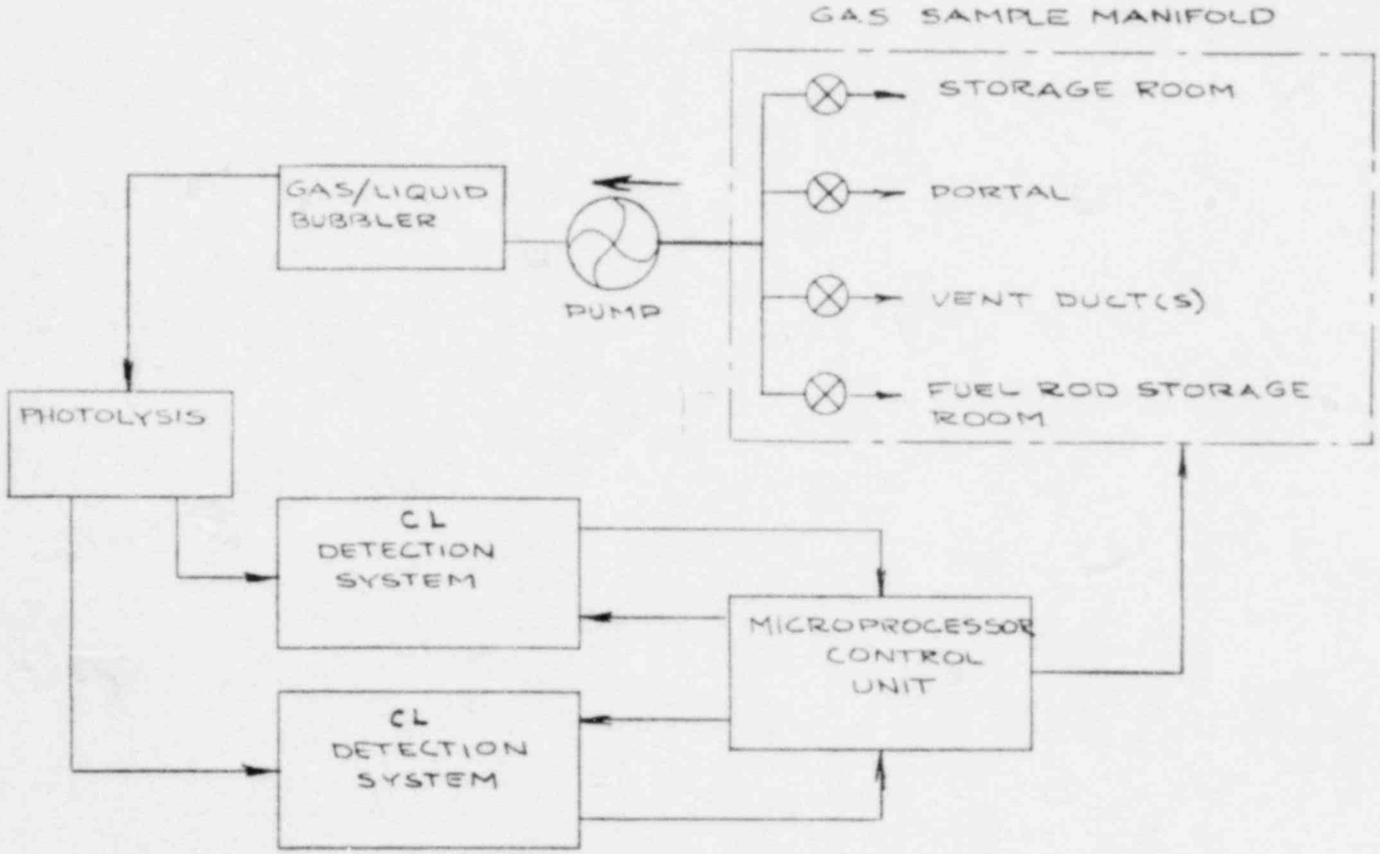


FIGURE 1 A CENTRALIZED HE VAPOR DETECTION SCHEME

DISTRIBUTION

	Copies
Nuclear Regulatory Commission, RS, Bethesda, Maryland	318
Technical Information Center, Oak Ridge, Tennessee	2
Los Alamos National Laboratory, Los Alamos, New Mexico	50
	370