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TECHNICAL REPORT 8306

TERTIARY TREATMENT OF EFFLUENT FROM HOLSTON AAP  
INDUSTRIAL LIQUID WASTE TREATMENT FACILITY  
III. ULTRAVIOLET RADIATION AND OZONE STUDIES:  
TNT, RDX, HMX, TAX, AND SEX

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NOVEMBER 1983

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TECHNICAL REPORT 8306	2. GOVT ACCESSION NO. AD-A137 692	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) TERTIARY TREATMENT OF EFFLUENT FROM HOLSTON AAP INDUSTRIAL LIQUID WASTE TREATMENT FACILITY III. ULTRAVIOLET RADIATION AND OZONE STUDIES: TNT, RDX, HMX, TAX, AND SEX	5. TYPE OF REPORT & PERIOD COVERED Technical Report Sep 1982 - May 1983	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) W. DICKINSON BURROWS, Ph.D., P.E.	8. CONTRACT OR GRANT NUMBER(s)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS US Army Medical Bioengineering Research and Development Laboratory, ATTN: SGRD-UBG Fort Detrick, Frederick, MD 21701	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS  62720A 1L162720D048	
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Medical Research and Development Command ATTN: SGRD-RMS Fort Detrick, Frederick, MD 21701	12. REPORT DATE NOVEMBER 1983	
	13. NUMBER OF PAGES 21	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report)  UNCLASSIFIED	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) HMX   SEX Ozone    TNT Photolysis                                        TAX RDX   Wastewater		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) ✓ Destruction of TNT, RDX, HMX, TAX, and SEX by ultraviolet (UV) radiation and by ozone has been studied in the batch mode. Ultraviolet radiation alone is effective for removal of the nitramines, but not TNT, while ozone alone does not react readily with any of the munitions. Combined UV-ozone treatment is effective for destruction of TNT. An analysis of power requirements suggests that UV treatment in the tertiary mode may be useful for destruction of nitramines in wastewater, while combined UV-ozone may be suitable for removal of TNT from small, clean process streams. <i>n</i>		

PREFACE

The research reported herein was performed at the request of Large Calibre Weapons Systems Laboratory, US Army Armament Research and Development Center (ARDC), Dover, NJ, under R&D Project No. 1L162720D048, "Tertiary Treatment of Holston AAP Industrial Liquid Waste Treatment (ILWT) Effluent," Mr. Bossie Jackson, Jr., project officer, Energetic Systems Process Division. This study is part of the DARCOM Pollution Abatement and Environmental Control Technology Program, conducted by the US Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD. High performance liquid chromatography (HPLC) analyses were performed at US Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) by Mr. Ernst E. Brueggemann, and gas chromatography-mass spectrometry (GC-MS) analyses were carried out by Dr. Elizabeth P. Burrows.

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## INTRODUCTION

Holston Army Ammunition Plant (HSAAP) will produce 125 million gallons of wastewater per day at full mobilization. The current design of an MCA (Military Construction Army) project for the Industrial Liquid Waste Treatment Facility (ILWTF) at HSAAP does not provide a tertiary mode of treatment for the removal of pollutant chemicals which survive primary and secondary treatment. There is evidence that RDX, HMX, and TNT, as well as biproduct nitramines, such as hexahydro-1(N)-acetyl-3,5-dinitro-1,3,5-triazine (TAX) and octahydro-1(N)-acetyl-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX), will survive secondary biological treatment, at least in part, and may adversely affect aquatic organisms in receiving waters. A problem is foreseen in complying with proposed drinking water criteria of 0.049 mg/L for TNT and 0.035 mg/L for RDX/HMX<sup>1</sup> and ambient criteria of 0.06 mg/L for TNT and 0.3 mg/L for RDX/HMX for protection of aquatic life, based on studies by USAMBRDL.

This, the third in a series of studies in tertiary treatment technologies,<sup>2,3</sup> concerns comparative removal rates for the five HSAAP munitions production wastewater contaminants by ultraviolet (UV) radiation and by UV radiation combined with ozone in the batch mode. Ozone in neutral water is a powerful, selective oxidizing agent capable of cleaving isolated carbon-carbon double bonds and even aromatic bonds of organic molecules, but it is most commonly inert or slightly reactive to saturated carbon bonds.<sup>4</sup> Under the influence of ultraviolet radiation, however, it decomposes rapidly, apparently to hydroxyl radicals (see Equations 1 and 2, where \* indicates an excited state).<sup>5</sup>



The hydroxyl radical is capable of abstracting a hydrogen atom from saturated carbon and other relatively stable molecules (Equation 3), thereby initiating a decomposition chain reaction.



The utility of UV and ozone or ozone alone as a wastewater treatment scheme is dependent not only on the reactivity of target molecules but on other substances in the wastewater which may participate in the decomposition reactions or which may defeat the treatment process through competitive absorption of UV radiation or chain termination. In this respect it is important to note that all experiments described herein utilized pure compounds in deionized water. These experiments address feasibility only and should not be considered a substitute for pilot studies on authentic wastewaters.

### OTHER MUNITION STUDIES

A number of studies have been carried out using UV radiation and ozone to treat Composition A5 (RDX) and Composition B (RDX/TNT) wastewaters for munitions removal. Fischer et al.<sup>6</sup> found UV-ozone treatment to be effective

in removal of RDX from Kansas Army Ammunition Plant wastewater and cost-competitive with activated carbon adsorption for small systems. (The authors acknowledge other studies demonstrating effective removal of TNT as well by this treatment.) Glover and Hoffsommer<sup>7</sup> found that aqueous RDX-<sup>14</sup>C treated with ozone under UV radiation produces carbon dioxide, ammonia, nitrate ion, and several organic nitro compounds; exposed to UV radiation in the absence of ozone, RDX produced nitrite ion, ammonia, some formaldehyde, and several organic nitrogen compounds. A solution of RDX first exposed to UV radiation, then allowed to react with ozone, produced carbon dioxide, cyanic acid, nitrate ion, and ammonia. In all three cases a major component was not isolated but was thought to be formic acid. The authors present evidence from mass spectral data that RDX subjected to UV radiation undergoes stepwise elimination of three moles of nitrous acid to form 1,3,5-triazine, and that 1,3,5-triazine and its precursors are cleaved to organic nitrogen compounds, such as formamidine and nitroformamidine, when further exposed to UV radiation and/or ozone. It seems reasonable to presume that analogous products are formed from HMX. Layne et al. studied the use of UV-ozone for treatment of pink wastewater at Iowa Army Ammunition Plant and found evidence for nearly complete mineralization of TNT.<sup>8</sup> They note that the combination of UV and ozone is much more effective than either agent alone.

## RESULTS AND DISCUSSION

### TREATMENT WITH OZONE

Rate data for disappearance of single munitions are presented in Appendix Tables A1-A5. Loss of TNT from solutions treated with ozone alone during 30 min was minor and variable and could be accounted for by air stripping alone. Air stripping of the nitramines was inconsequential, in agreement with the findings of Kobylinski and Burrows.<sup>3</sup> The presence of 0.6 percent of ozone in the air stream resulted in destruction of ca. five percent of TAX and SEX over a period of 20 to 30 min, but had no measurable effect on RDX or HMX concentrations. Under the conditions of these studies (ambient temperature and near-neutral pH), ozone alone is not effective in removal of TNT or the nitramines.

### EFFECT OF RADIATION

Ozone, promoted by UV radiation, reduced TNT concentrations in pure solution to detection limits within 30 min and nitramines in 10 min or less. First order rate constants are presented in Table 1. Correlations are not strong, and as shown in Figure 1 for a typical run, kinetics fall between zero and first order. The best explanation for this effect may be the increase in radiation density relative to the substrate concentration as the reaction proceeds. Thus:

$$\frac{dC}{dt} = \frac{-kC}{OD} \quad (4)$$

where OD, the optical density of the reacting solution, is proportional to the concentrations of substrate (C), products (C<sub>0</sub>-C), and any nonreacting materials present. We can write empirically (k, k', and K are constants)

$$\frac{dC}{dt} = \frac{-kC}{k'C + K} \quad (5)$$

When the substrate and products have the same absorbance ( $k'C \ll K$ ), the reaction is first order; when products are transparent ( $k'C \gg K$ ), the reaction is zero order. In integrated form ( $t_0 = 0$ ), Equation 5 becomes

$$a(C_0 - C) + b \ln \frac{C_0}{C} = kt \quad (6)$$

Division of Equation 6 by  $(C_0 - C)$  gives Equation 7 (where  $C \neq C_0$ ).

$$\frac{a + b \ln C_0/C}{C_0 - C} = \frac{kt}{C_0 - C} \quad (7)$$

Although graphical solution of Equation 7 should be straightforward, in practice it gives a usable straight line only for the cases of RDX and TAX (Fig. 2). Equation 6 cannot in fact be solved for discrete values of  $a$ ,  $b$ , and  $k$ ; however, if  $(a + b)$  is set equal to unity, giving thereby the proportions of zero and first order character, the equation can then be solved by successive approximation, i.e., by seeking the (positive) values of  $a$  and  $b$  for which the left side of Equation 6 gives the best approximate linear correlation with time. These values are listed in Table 2, and correlations are much better than for the pure first order analysis (Table 1).

TABLE 1. FIRST ORDER RATE CONSTANTS FOR MUNITIONS DESTRUCTION

Munition	Init. Conc. (mg/L)	Conditions	$k^a$ $\text{min}^{-1}$	Correlation
TNT	18.23	UV/O <sub>3</sub>	0.127	0.9642
TNT	22.41	UV/O <sub>3</sub>	0.098	0.9683
RDX	18.61	UV/O <sub>3</sub>	0.419	0.9974
RDX	23.90	UV only	0.330	0.9943
HMX	2.67	UV/O <sub>3</sub>	0.649	0.9764
TAX	24.61	UV/O <sub>3</sub>	0.418	0.9824
TAX	22.94	UV only	0.348	0.9906
SEX	5.74	UV/O <sub>3</sub>	0.825	0.9755
SEX	4.95	UV only	0.762	0.9995

a. By linear regression least squares. The  $t_0$  point is included, but the line is not forced through the origin.



TABLE 2. MIXED ZERO ORDER AND FIRST ORDER RATE ANALYSIS  
FOR DESTRUCTION OF MUNITIONS

Munition	Init. Conc. (mg/L)	Conditions	Zero Order Fraction <sup>a</sup>	First Order Fraction <sup>a</sup>	k <sup>b</sup> min <sup>-1</sup>	Correlation
TNT	18.23	UV/O <sub>3</sub>	0.20	0.80	0.239	0.9980
TNT	22.41	UV/O <sub>3</sub>	0.25	0.75	0.278	0.9996
RDX	18.61	UV/O <sub>3</sub>	0.015	0.985	0.446	0.9976
RDX	23.90	UV only	0.05	0.95	0.453	0.9998
BMX	2.67	UV/O <sub>3</sub>	1.0	0.0	0.97	0.9986
TAX	24.61	UV/O <sub>3</sub>	0.10	0.90	0.645	0.9998
TAX	22.94	UV only	0.07	0.93	0.495	0.9997
SEX	5.74	UV/O <sub>3</sub>	0.50	0.50	1.31	0.9980
SEX	4.95	UV only	0.05	0.95	0.855	0.99999

a. Zero order and first order fractions which give best correlation.

b. By linear regression least squares. The t<sub>0</sub> point is included, but the line is not forced through the origin.

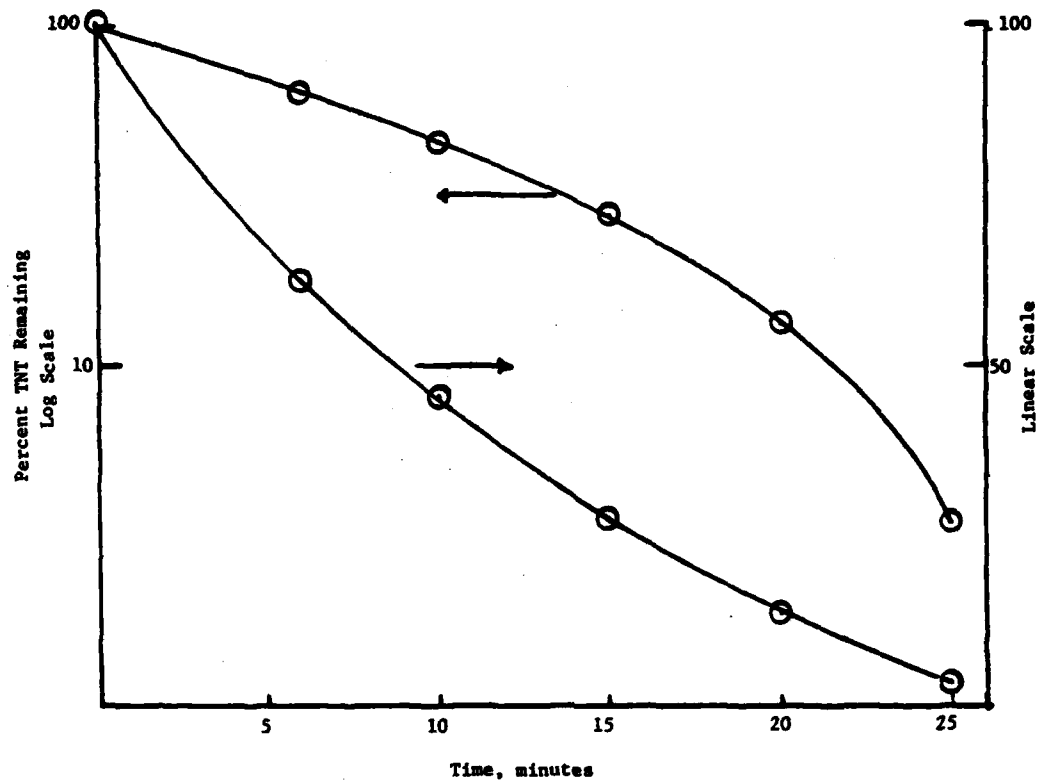


Figure 1. Destruction of TNT by UV-ozone, evaluated as zero and first-order processes. (Data from Table A-1, Run No. 2.)

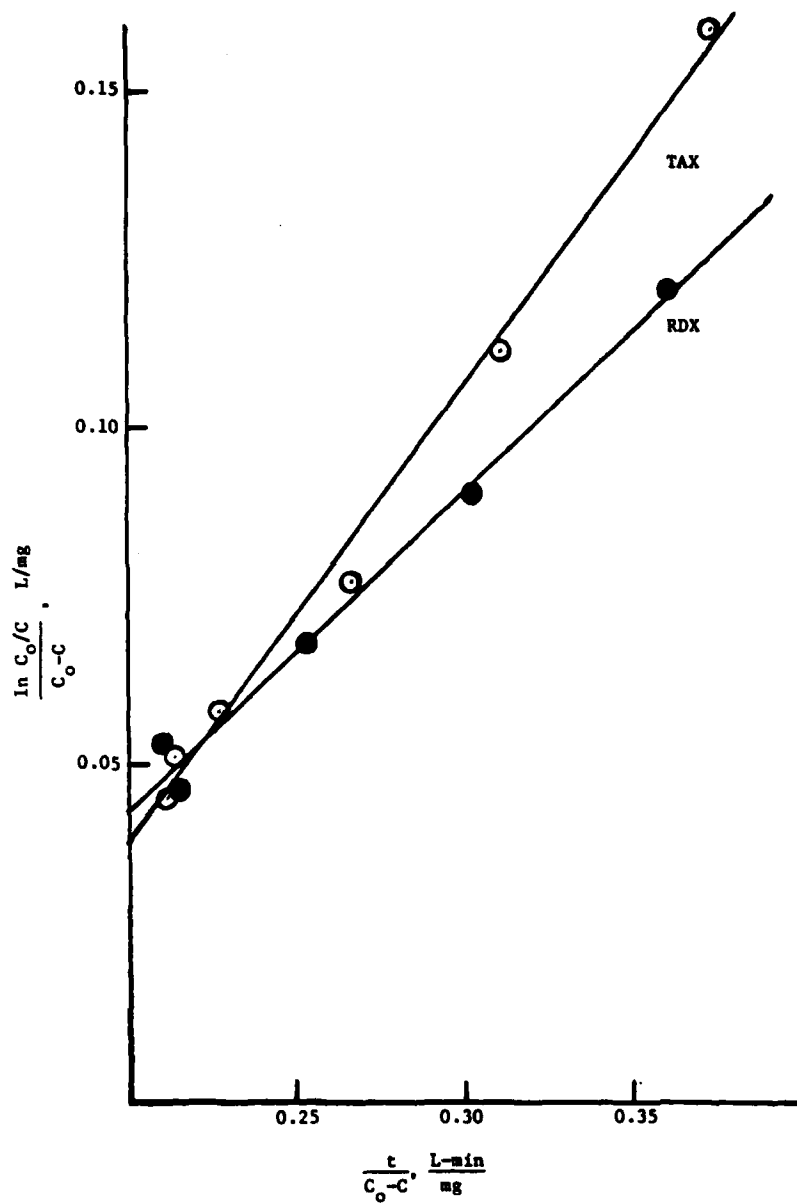


Figure 2. Destruction of RDX by UV radiation and TAX by UV-ozone, both evaluated as combined zero and first-order processes.

In the absence of ozone, a solution of TNT exposed to UV radiation turned rapidly pink, but disappearance of TNT after 30 min was less than 10 percent. This demonstrates that the intermediate photolysis products of ozone (hydroxyl radical, e.g.) are necessary for destruction of TNT in aqueous solutions containing no other substances. For nitramines, however, there was no substantial difference in photolysis rates with ozone present. The role of ozone is presumably limited to destruction of primary photolysis products, and the slight rate enhancement is accounted for if ozone-treated solutions become more transparent, relative to nonozonized solutions, as the reaction proceeds.

Destruction of munitions in mixture by UV-ozone (Tables 3 and A-6) was much slower because of the greater initial optical density of the solution. It is of interest, moreover, that the specific rate depression was twofold for TNT but 5- to 15-fold for the nitramines, reflecting the differences in reaction mechanisms. This explains the findings of Layne et al., that HMX is actually more slowly decomposed than TNT by combined UV-ozone in pink water.<sup>8</sup>

TABLE 3. FIRST ORDER RATE CONSTANTS FOR DESTRUCTION OF MIXED MUNITIONS BY UV RADIATION AND OZONE

Munition	Init. Conc. (mg/L)	$k^a$ min <sup>-1</sup>	Correlation
TNT	24.05	0.051	0.9939
RDX	24.39	0.081	0.9808
TAX	25.84	0.084	0.9884
SEX	5.60	0.070	0.9806
HMX	3.82	0.044	0.9712

a. By linear regression least squares. The  $t_0$  point is included, but the line is not forced through the origin.

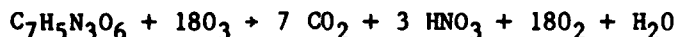
#### PRODUCTS

2,4,6-Trinitrobenzoic acid was detected by GC-MS as an intermediate in UV-ozonolysis of TNT but was not present after 30 min of treatment. The absence of any other extractable products provides strong evidence for destruction of the aromatic ring of TNT, in agreement with Layne et al.<sup>8</sup> No single, readily identifiable products were detected in methylene chloride extracts from UV-ozonolysis of the nitramines. In consideration of the detailed studies of RDX by Glover and Hoffsommer,<sup>7</sup> no further effort was made to identify products from the nitramines.

## SUMMARY AND CONCLUSIONS

Evaluation of UV radiation as treatment technology for Composition B process waters must be based on authentic wastewater, since energy requirements will, as noted earlier, depend on optical density. A wastewater containing suspended material, e.g., will be more efficiently treated for munitions removal if filtered before radiation. A 10 min exposure in the batch treatment unit, sufficient to reduce 25 mg/L of nitramines to detection limits in laboratory studies, corresponds to a 54 kw power requirement for a 1 million gallon per day (mgd) wastewater loading. On the basis of reaction rate, there is no significant advantage to adding ozone for photolytic destruction of nitramines. However, the reaction products are different in the presence of ozone,<sup>7</sup> and the toxicity (if any) of the product wastewater may also be different.

Power requirements for ozone generation cannot be estimated directly from this study because ozone was always in excess. If one assumes the following stoichiometry for destruction of TNT:



and if the efficiency of ozone generation is assumed to be that of the bench scale generator (i.e., 0.58 percent ozone, 20 SCFH at 250 w), then removal of 25 mg/L of TNT from 1 mgd of wastewater imposes a power requirement of 887 kw (exclusive of compressor hp) for ozone alone; UV generation, based on 30 min exposure in the batch unit, requires an additional 162 kw. It must be emphasized that these calculations, based on a hypothetical clean wastewater, provide minimum energy requirements. Each additional mg/L of ozone-reactive COD in the wastewater will draw an additional 28 kw.

The power requirements for UV treatment alone are at least manageable. The use of combined UV-ozone in the tertiary mode imposes what could be unacceptable power requirements in consideration of the large volume of effluent to be treated. On the other hand, treatment of a small process stream for TNT removal would be acceptable provided that the stream did not carry a heavy ozone demand due to other organics (formaldehyde, e.g.).

The conclusions from this study are that UV radiation is a promising technique for destruction of RDX, HMX, SEX, and TAX, and that combined UV-ozone may be suitable for TNT destruction if applied to a small and relatively clean process stream. As an alternative to granular activated carbon, UV or UV-ozone treatment has a logistical advantage; spent carbon must be either regenerated or disposed of as a hazardous waste. UV-ozone treatment may also be more economical for wastewaters containing TNT and nitramines, for which carbon is not very efficient.<sup>2</sup> This would have to be established through comparative testing of authentic wastewater on a pilot scale.

## EXPERIMENTAL PROCEDURES

### MATERIALS

1,2,3,4,5,6-Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,2,3,4,5,6,7,8-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) were provided by HSAAP and were of washed, crude quality (Table 4). Both were air-dried to constant weight before use. 1-Acetyl-1,2,3,4,5,6-hexahydro-3,5-dinitro-1,3,5-triazine (TAX) and 1-acetyl-1,2,3,4,5,6,7,8-octahydro-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX) were prepared by SRI International by methods described previously<sup>9,10</sup> and were used as received (Table 4). 2,4,6-Trinitrotoluene (TNT) was synthesized at USAMBRDL and recrystallized from ethanol. Granular activated carbon (GAC; Calgon F300) was pulverized and screened to -200 mesh. A single batch was used for all experiments.

TABLE 4. CONSTITUENTS OF TEST SUBSTANCES

Substance	Purity % (dry basis)	Other Constituents, %
TNT	est. >99	
RDX	88.61	HMX, 11.39
HMX	98.76	RDX, 1.24
TAX	99	
SEX	96.7	HMX 2.4, DADN <sup>a</sup> 0.9

a. 1,5-Diacetyloctahydro-3,7-dinitro-1,3,5,7-tetrazocine.

The reactor described previously by Kobylinski and Peterman was used.<sup>11</sup> The stainless steel reactor column (Fig. 3) is 6.6 inches in diameter and 78 inches tall, with an effective volume of 39 L. A sintered stainless steel gas sparger, having a mean pore size of 5 microns, is located approximately 2 inches above the base of the reactor. An 80-watt UV lamp (estimated 34-watt output), encased in a 1-inch quartz tube and running vertically through the center of the column, emits radiation at a wavelength of 253.7 nm. The reactor is capable of batch or continuous operation. With gas flow rates of 20 SCFH and above, the reactor contents are completely mixed. Mixing may also be achieved by recirculating the contents at a flow rate of approximately 3 L/min. Ozone is provided by a W.R. Grace & Co. Model CG-2-L2 corona generator.

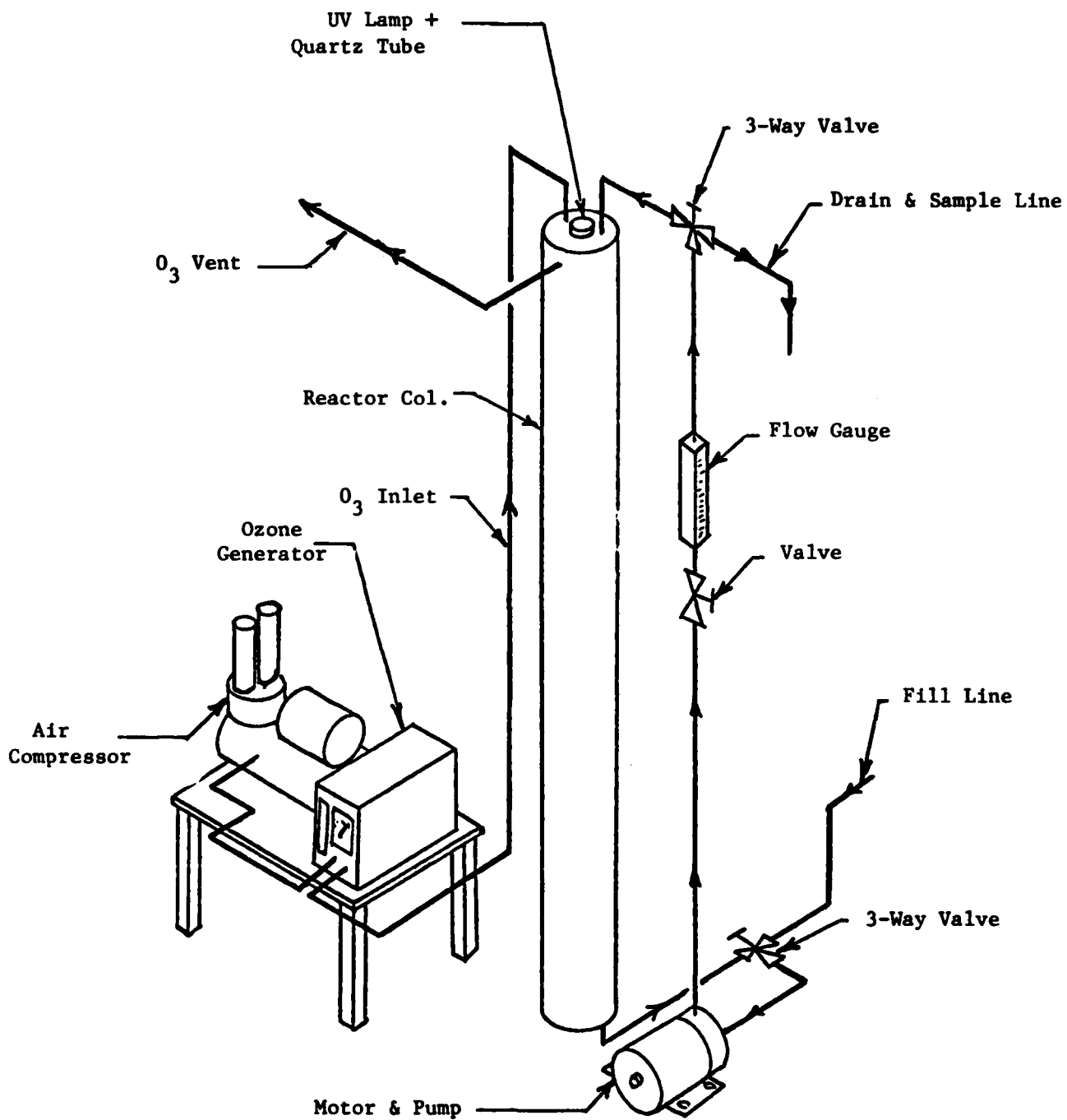


Figure 3. UV-ozone reactor schematic.

## PROCEDURE

Munitions were made up to desired strength by adding to 18 L of deionized water at an initial temperature of 40-50°C and stirring overnight. Solutions were then pumped into the reactor and treated at ambient temperature (21 to 24°C). Compressed air was passed through the reactor at a constant 20 SCFH and 10 PSIG. Using a 250 W power setting on the corona generator, the exit gas stream from tap water was found to contain 0.58 percent by weight of ozone. Thereafter, these instrument settings were used for all experiments with ozone, and (except as noted) ozone was always detectable in the exit stream. Samples were collected by drawing off about 100 mL of reactor contents into a tared bottle which, for ozone experiments, contained 5.0 mL of 0.1 N sodium thiosulfate and a few drops of 20 percent potassium iodide.

Preliminary experiments were performed in order to bracket desired times of exposure and frequency of sampling and also to assess the contribution of air sparging to disappearance of the munition. An example of such an experiment is presented in Table 5 for RDX. In this example the ozone generator was turned on immediately after the first sample was taken. After 30 min, ozone and air were shut off, and the system was left under 10 psig air pressure for an additional 27 min, then was sparged with air for 5 min (to establish whether excess ozone was present). After sample 4 was taken, ozone and the UV lamp were turned on for the remainder of the experiment. For most experiments 1-2 L of reactor contents were expended in the course of sampling.

TABLE 5. PRELIMINARY EXPERIMENT WITH RDX

Time (min)	Sample	Air	Ozone	UV	RDX (mg/L) <sup>a</sup>
0	1	on	on	off	23.4
15	2	on	on	off	24.2
30	3	off	off	off	23.0
57		on	off	off	
62	4	on	off	off	21.8
64		on	on	on	
74	5	on	on	on	<0.6
84	6	on	on	on	<0.6

a. Corrected for dilution by thiosulfate.

## ANALYSIS

Munitions analyses were carried out by high performance liquid chromatography (HPLC) using a UV absorption detector, as described by Brueggemann.<sup>12</sup> Ozone in the reactor exit stream was estimated by passing the stream for a measured time through two gas washing cylinders in series, each containing a known volume of 20 percent potassium iodide solution. The solutions were then strongly acidified with 1N sulfuric acid and titrated with 0.100 N sodium thiosulfate to a starch end point.



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APPENDIX A  
TIME AND CONCENTRATION DATA

TABLE A-1. DECOMPOSITION OF TNT BY  
UV RADIATION AND OZONE

Time (min)	Conc. (mg/L)		
	UV-Ozone (Run No. 1)	UV-Ozone (Run No. 2)	UV Only
0	18.23	22.41	24.87
5		17.57	24.51
6	11.39		
10	8.28		24.22
10.25		12.46	
15	5.05	8.32	23.95
20	2.50	4.66	23.63
25	0.64	1.77	23.19
30	<0.60	<0.60	22.81

TABLE A-2. DECOMPOSITION OF RDX BY  
UV RADIATION AND OZONE

Time (min)	Conc. (mg/L)	
	UV-Ozone	UV Only
0	18.61	23.90
1	13.93	19.27
2	9.51	14.44
4	3.87	8.18
6	1.41	4.03
8	0.76	1.66
10	<0.72	<0.75

TABLE A-3. DECOMPOSITION OF HMX BY  
UV RADIATION AND OZONE

Time (min)	Conc. (mg/L)
0	2.67
1	1.79
2	0.73
3	<0.58

TABLE A-4. DECOMPOSITION OF TAX BY  
UV RADIATION AND OZONE

Time (min)	Conc. (mg/L)	
	UV-Ozone	UV Only
0	24.61	22.94
1	19.87	19.02
2	15.26	14.36
3	11.39	10.92
5	5.82	5.87
7	1.99	2.69
9	0.53	0.96

TABLE A-5. DECOMPOSITION OF SEX BY  
UV RADIATION AND OZONE

Time (min)	Conc. (mg/L)	
	UV-Ozone	UV Only
0	5.74	4.95
1	3.91	2.41
2	1.65	1.08
3	0.49	<0.53
4	<0.48	

TABLE A-6. DECOMPOSITION OF MIXED MUNITIONS  
BY UV RADIATION AND OZONE

Time (min)	Concentration (mg/L)				
	TNT	RDX	TAX	SEX	HMX
0	24.05	24.39	25.84	5.60	3.82
1	23.12	23.26	24.16	5.36	3.62
2	22.11	21.80	22.92	5.04	3.51
3	21.26	20.61	21.88	4.90	3.50
4	20.34	19.52	20.64	4.68	3.43
5	19.56	18.72	19.52	4.54	3.32
7	17.95	17.16	17.43	4.16	3.17
10	15.63	14.33	14.28	3.57	2.89
15	11.96	10.46	9.90	2.64	2.38
20	8.76	6.48	6.11	1.84	1.88
25	6.17	4.03	3.77	1.16	1.51
30	4.10	1.70	1.77	0.60	0.84

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