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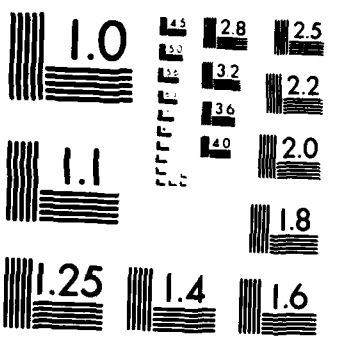

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TECHNICAL REPORT-8407

CHEMICAL CHARACTERIZATION OF DIMETHYLSULFOXIDE (DMSO) MUNITIONS RECRYSTALLIZATION PROCESS SAMPLES

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OCTOBER 1984

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: TECHNICAL REPORT 8407	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE *(and Subtitle)*: CHEMICAL CHARACTERIZATION OF DIMETHYLSULFOXIDE (DMSO) MUNITIONS RECRYSTALLIZATION PROCESS SAMPLES	5. TYPE OF REPORT & PERIOD COVERED: Technical Report June 1983-June 1984
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): ELIZABETH P. BURROWS, ERNST E. BRUEGGEMANN	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 21701-5010	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 61277A878 CA
11. CONTROLLING OFFICE NAME AND ADDRESS: US Army Medical Research and Development Command, ATTN: SGRD-RMS, Fort Detrick, Frederick, MD 21701-5012	12. REPORT DATE: October 1984
	13. NUMBER OF PAGES: 13
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)*

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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)*

Benzothiazole
Butylated hydroxytoluene
Diacetone alcohol
Dimethylsulfoxide
Gas chromatography/mass spectrometry
Health effects
High pressure liquid chromatography
Munitions compounds
Nitramines

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

As part of a program to assess possible adverse health effects to workers in a new nitramine munitions recrystallization process utilizing dimethylsulfoxide, pilot plant samples were analyzed qualitatively for trace organics by gas chromatography/mass spectrometry and quantitatively for nitramines by high pressure liquid chromatography. None of the variety of trace organics found was related to munitions manufacture or to breakdown of nitramines, and, except for the presence of diacetone alcohol, there was little overall consistency in trace organic content of the samples. Originator-supplied keywords.

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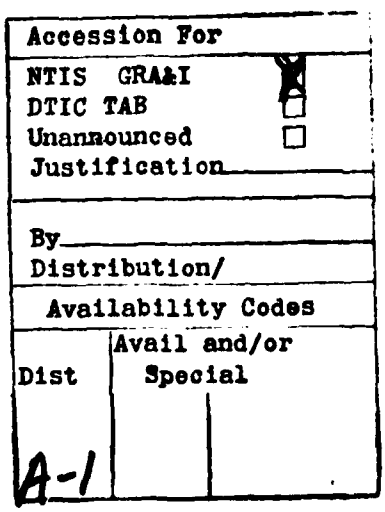
ACKNOWLEDGMENT

We thank MAJ David L. Parmer for providing information on the origin of the samples.



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INTRODUCTION

A pilot plant for the operation of a new munitions recrystallization process was set up at Holston Army Ammunition Plant (HSAAP) in 1979 and was operated for approximately 5 months. The new process involves recovery and recycling of dimethylsulfoxide (DMSO), in contrast to an older batch process utilizing acetone and cyclohexanone as recrystallization solvents. Though more efficient and cost effective, the DMSO process provoked concern over possible health hazards to workers due to the known rapid absorption of the solvent (along with any nitramine munition compounds, breakdown products or other trace organics in the solvent) into body tissues. Chemical characterization of the new process samples at HSAAP was limited to analyses of the nitramines hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 1-acetylhexahydro-3,5-dinitro-1,3,5-triazine (TAX), and 1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX) by high pressure liquid chromatography (HPLC).[1] The samples were tested for acute toxicity and mutagenicity by extramural laboratories and, when two of the process samples showed mutagenicity, US Army Medical Bioengineering Research & Development Laboratory (USAMBRDL) was tasked with chemical characterization and identification of any trace organics present in addition to the nitramines. Portions of the two samples, designated as evaporator sludge and recycle solvent, and a sample of unused DMSO were first received in June 1983, and the results of the analyses were described briefly in a Memorandum Report.[2] Additional portions of evaporator sludge and recycle solvent were received and analyzed in January 1984. An evaporator sludge sample which had not yet been tested for mutagenicity and a sample designated as recovered DMSO, as well as two river water samples, were received and analyzed in April 1984. The results are compared and contrasted with those of four samples from the older acetone/cyclohexanone process which were analyzed in June 1984.

EQUIPMENT AND METHODS

HIGH PRESSURE LIQUID CHROMATOGRAPHIC (HPLC) ANALYSES

A Waters liquid chromatographic system (Waters Associates, Milford, MA) consisted of the following components: two Model 6000A solvent delivery systems, a Model 721 programmable systems controller, a Model 730 data module, a Lambda-max Model 480 LC spectrophotometer, and a Model 710B Waters intelligent sample processor (WISP). A Zorbax C_8 reverse phase stainless steel column (25 cm x 4.6 mm ID, particle size 6 µm, DuPont Instruments, Wilmington, DE) was used. The nitramines were eluted using a linear gradient program in which pump A contained 1:4 methanol/water and pump B contained 4:1 methanol/water, and the methanol/water composition was changed from 95:5 A/B to 50:50 A/B in 25 min at a flow rate of 1.2 mL/min. The effluent was monitored at 254 nm, 0.05 absorbance units full scale (AUFS). Standard solutions were prepared as described previously.[3]

GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC (GS/MS) ANALYSES

GC/MS analyses were performed with a Hewlett Packard 5985B system equipped with a 25 m x 0.2 mm ID fused silica capillary column (cross-linked OV-1, 0.11 μm thick) interfaced directly to the source (source temperature 200°C). Injection temperature was 150° or 250°C, and the GC oven was programmed from 60° to 250° at 20°C per minute with an initial hold of 1 minute. The data system was upgraded to RTE-VI and included a data base of 70,000 spectra.

PREPARATION OF SAMPLES

For HPLC analyses, 1 mL of liquid was made up to 100 mL in distilled deionized water; further dilutions were made when necessary. A 4 mL portion of each solution was passed through a 0.45 μm Millex-SR filter into a WISP sample vial. Weighed amounts of solid samples were dissolved in acetonitrile (5 mL) and made up to 100 mL in distilled deionized water and treated as above.

For GC/MS analyses, liquid samples containing DMSO and munitions compounds (5 mL) were diluted with water (10-50 mL), filtered when necessary to remove any precipitated munitions compounds, and extracted with methylene chloride (CH_2Cl_2, 5-10 mL). The CH_2Cl_2 extracts were washed with three 25 to 50 mL portions of water, dried, and evaporated, and the residues were dissolved in acetone for injection. The DMSO pilot plant water samples and the RDX and HMX system filtrates from the earlier acetone/cyclohexanone recrystallization process (100-200 mL) were extracted with CH_2Cl_2 and the extracts were dried and treated as above. The used acetone sample was partially evaporated and the resulting aqueous suspension was extracted with CH_2Cl_2 and treated as above. A small portion (0.2 mL) of the used cyclohexanone was taken to dryness under N_2 and redissolved in acetone for analysis.

RESULTS AND DISCUSSION

Chemical characterization of evaporator sludge and recycle solvent samples included qualitative analysis for trace organics by GC/MS and quantitative analysis for nitramine munitions by HPLC.[3] Results of sample analyses in June 1983 and January 1984 are summarized in Tables 1 and 2.

TABLE 1. HPLC ANALYSES OF MUNITIONS FROM DMSO RECRYSTALLIZATION PROCESS SAMPLES

Compound	Retention Time (min)	Evaporator Sludge Jan 1984 Amt (ppm)[a]	Recycle Solvent Jun 1983 Amt (ppm)	Recycle Solvent Jan 1984 Amt (ppm)
SEX	7.3	64	150	412
HMX	9.1	1,750	3,500	41,900
TAX	11.2	2,400	580	648
RDX	15.7	403	5,500	39,900

a. Relative amounts in June 1983 sample were TAX > RDX > HMX >> SEX.

The observed discrepancies in nitramine content between the two sets of analyses (Table 1) may be attributed to inconsistent sampling or sampling errors, due to inhomogeniety of the mixtures and/or temperature differences at the time of sampling.

No impurities were found in the unused DMSO. Of the trace organics found in the recrystallization process samples (Table 2), all except DDBH and trans-4-chlorocyclohexanol were commercially available compounds. Diacetone alcohol is formed by aldol condensation of acetone, and dimethylsulfone is an obvious oxidation product of DMSO. The genesis of DDBH, found in three of four samples, is obscure. A literature survey revealed few citations: the compound was first reported as the end product of a synthesis requiring six steps from commercially available chemicals,[4] but was recently found as one of many trace organics in highly polluted rivers in Japan[5] and in volatile constituents of certain fungi.[6]

This finding of a variety of trace organics unrelated to the munitions manufacture process or to possible decomposition or transformation of the nitramines prompted an investigation of the organic constituents of samples of water from the Holston River, which had been used in the pilot plant process. In addition, another sample of evaporator sludge which had not yet been tested for mutagenicity and a sample designated as "recovered DMSO" were analyzed for trace organics and munitions compounds; the results are summarized in Tables 3 and 4.

TABLE 2. GC/MS IDENTIFICATION OF TRACE ORGANICS PRESENT IN DMSO RECRYSTALLIZATION PROCESS SAMPLES[a]

Retention Time (min)	Compound	Evaporator Sludge	Recycle Solvent
	June 1983		
2.4	Diacetone alcohol	+	-[b]
4.1	Dimethylsulfone	-	+
4.9	Benzothiazole	+	+
6.7	1,5-Di-t-butyl-3,3-dimethyl-bicyclo(3.1.0)hexan-2-one (DDBH)	-	+
	January 1984		
2.5	Diacetone alcohol	+	+
2.6	1,4-Dithiane	+	-
3.4	trans-4-Chlorocyclohexanol	+	+
4.9	Benzothiazole	+	+
6.8	1,5-Di-t-butyl-3,3-dimethyl-bicyclo(3.1.0)hexan-2-one (DDBH)	+	+
7.0	2,6-Di-t-butyl-4-methylphenol (BHT)	+	+

a. +, present; -, not detected.
b. Not detected because of DMSO interference, but believed to be present.

TABLE 3. HPLC ANALYSES OF MUNITIONS IN NEW DMSO RECRYSTALLIZATION PROCESS SAMPLES, APRIL 1984

Compound	Retention Time (min)	Evaporator Sludge[a] Amt (ppm)
SEX	7.6	66
HMX	10.2	1,940
TAX	12.5	2,540
RDX	18.5	410

a. Munitions in "recovered DMSO" were below detection limit (<0.3 ppm).

TABLE 4. TRACE ORGANIC CONTENT OF RIVER WATER AND DMSO RECRYSTALLIZATION PROCESS SAMPLES, APRIL 1984[a]

Sample	Retention Time (min)	Compound
River water, single	2.5	Diacetone alcohol
	6.4	p-Hydroxyacetanilide
	7.6	Unidentified, MW 213[b]
River water, composite[c]	2.5	Diacetone alcohol
	6.4	p-Hydroxyacetanilide
	7.3	Diphenyloxazole[d]
	7.6	Unidentified, MW 213[b]
Evaporator sludge	10.9	Acetyl tri-n-butyl citrate (Citroflex A, citrate plasticizer)
Recovered DMSO	2.5	Diacetone alcohol
	7.0	2,6-di-t-Butyl-4-methylphenol (BHT)
	7.7	3,4'-Dimethyldiphenylmethane
	8.9	N-Butylbenzenesulfonamide
	12.1	Octadecanamide

a. In addition to phthalates.
b. Mass spectrum below m/z 135 identical to that of p-methoxystyrene.
c. Composite consisted of 4 aliquots taken at 6 hr intervals.
d. Mass spectrum indicated 4,5-isomer rather than the commercially available 2,5-isomer.

Comparison of the results for the April 1984 evaporator sludge with those of the January 1984 sample (Tables 1 and 2) showed good consistency for the nitramines, but the trace organic content of the two samples was quite different. Furthermore, except for the consistent presence of diacetone alcohol (found in six of eight samples), the trace organic content in the river water samples was different from the process sludge and solvent samples. Significantly, benzothiazole, a suspect mutagen present in the four samples of sludge and solvent analyzed in June 1983 and January 1984, was not found in any of the samples analyzed later. The difference in organic content between "recycle solvent" DMSO and "recovered" DMSO may be attributable to the fact that the samples were taken at different stages of the process. The former was a composite taken from a storage tank and decanted from precipitated munitions; the latter was taken after separation of process DMSO from munitions and water.

Trace organic content of the four samples from the acetone/cyclohexanone process was low. Diacetone alcohol was found in the RDX filtrate and the used acetone samples, but not in the HMX filtrate. It was not possible to detect trace organics in the presence of the enormous quantity of cyclohexanone, and its relative insolubility in water precluded concentration of possible trace organics by liquid/liquid extraction procedures. No trace organics were identified in the residue after evaporation of the cyclohexanone to dryness, but volatile compounds such as diacetone alcohol would also have been removed by the evaporation.

CONCLUSION

It must be emphasized that none of the trace organics identified can be attributed either to the munitions manufacture process or to breakdown or transformation of the munitions compounds. Only dimethylsulfone clearly originated from reaction of the solvent, DMSO. Diacetone alcohol could have been a solvent-derived product in the acetone/cyclohexanone recrystallization process, but not in the DMSO process. The wide variety and lack of consistency (except for the presence of diacetone alcohol) of trace organics found in the latter process samples suggest river water used in the process as the source. While trace organic contents of the single and 24 hr composite river water samples taken in 1984 were similar, and different from that of any of the 1979 pilot plant samples (again, except for the presence of diacetone alcohol), variation of the nature of organic pollutants in the river over extended time periods is not unexpected. The observed variation in organic content of the evaporator sludge samples (Tables 2 and 4), however, is not readily explained.

REFERENCES

1. Hunter, B.A. and R.A. Jackson. 1979. Analytical Methods Development: HPLC for Nitramines and TNT. Technical Report HDC-51-79. Holston Defense Corporation, Kingsport, TN.

2. Burrows, E.P. 1983. GC/MS and HPLC Analysis of Munition-Contaminated Dimethylsulfoxide (DMSO) Samples. Memorandum Report 13-83. US Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD.

3. Brueggemann, E.E. 1983. HPLC Analysis of SEX, HMX, TAX, RDX, and TNT in Wastewater. Technical Report 8206, AD A127348. US Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD.

4. van Tamelen, E.E. and T.H. Whitesides. 1971. Valence tautomers of heterocyclic aromatic species. J. Amer. Chem. Soc. 93:6129-6140.

5. Yasuhara, A., H. Shiraishi, M. Tsuji, and T. Okuno. 1981. Analysis of organic substances in highly polluted river water by mass spectrometry. Environ. Sci. Technol. 15:570-573.

6. Seifert, R.M. and A.D. King, Jr. 1982. Identification of some volatile constituents of Aspergillus clavatus. J. Agr. Food Chem. 30:786-790.

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