Contractor Report ARAED-CR-91008

ANALYSIS OF NITROMETHANE

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Armament Engineering Directorate
Picatinny Arsenal, New Jersey

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MIGRAD SYSTEM IMPROVED SAFETY AND PRODUCIBILITY IN THE MANUFACTURING OF PYROTECHNIC MIXTURES

Component | Percent  
--- | ---  
Nitromethane | 98 or greater  
Nitroethane | 1.1 or less  
2-Nitropropane | 0.2 or less  
Water | 0.11 or less  
Metals | Trace (less than 10 ppb)  

Samples were taken at random from 60 barrels of nitromethane which were stored at Yuma Proving Grounds and sent to Southwest Research Institute for analyses. The nitromethane content was determined for each along with contaminate analyses for nitroethane, 2-nitropropane, water, and metals. The results indicated the following:
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1. INTRODUCTION

Originally, the Government had purchased and stored 60 barrels of nitromethane at the Yuma Proving Grounds for use in the TEXS system. This system required that the materials be housed in the all-purpose storage area. DOD has classified nitromethane as a Class 4, mass detonating material and not suitable for storage in the all-purpose area. This restriction resulted in the rejection of nitromethane as a candidate for the TEXS system.

These barrels have been exposed under varying degrees of environmental conditions and changes. Contamination and degradation to the nitromethane may have occurred during the storage period. An analysis is required to determine whether the material has deviated dramatically from the specifications furnished by the supplier. This analysis will determine whether the stored nitromethane is suitable for use in another application.

Samples of nitromethane were taken at random from the 60 barrels of stored nitromethane. These samples were taken from the top, middle, and bottom to ascertain the uniformity of nitromethane composition. Replicate samples of each were analyzed in the following manner for these components and contaminates that may be present:

<table>
<thead>
<tr>
<th>Component</th>
<th>Analytical Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitromethane</td>
<td>FTIR</td>
</tr>
<tr>
<td>Nitroethane</td>
<td>GC/Mass Spectroscopy</td>
</tr>
<tr>
<td>2-Nitropropane</td>
<td>GC/Mass Spectroscopy</td>
</tr>
<tr>
<td>Water</td>
<td>Karl Fischer</td>
</tr>
<tr>
<td>Metals</td>
<td>AA Graphite Furnace</td>
</tr>
</tbody>
</table>

FTIR - Fourier transform infrared  
GC - gas chromatography  
AA - atomic absorption
2. PROCEDURES AND RESULTS

Analysis of nitromethane was performed by FTIR. SwRI received a 99%+ sample of nitromethane that was certified by Angus Chemical. An FTIR analysis was performed and the results compared to the Chem Sources 98%+ sample used during the program. The results confirmed the purity level of the Chem Sources sample. The results are given in Table 1 and raw data are found in Appendix A.

| TABLE 1. FTIR ANALYSIS FOR PERCENT NITROMETHANE |
|------------------|------------------|
| Sample           | % Nitromethane   |
| Y1-B             | 99.6             |
| Y1-M             | 98.3             |
| Y1-T             | 100.0            |
| Y1-MM            | 99.3             |
| A1-B             | 99.3             |
| A1-M             | 99.9             |
| A1-MM            | 99.0             |
| N1-B             | 100.2            |
| N1-M             | 99.5             |
| N1-T             | 99.5             |
| Standard         | 98%              |

B  Bottom  
M  Middle  
T  Top  
MM  Middle mixed  

The FTIR spectra of the neat nitromethane samples were compared to that of the Mallinckrodt sample and found to be virtually identical. Computer subtraction of the Mallinckrodt sample from the other samples failed to show any gross contaminant. It was concluded that any impurities present were only in low concentration.

Weighed quantities of each of the samples were dissolved in carbon tetrachloride to make 25 mL total volume. A solution prepared similarly from Chem Service nitromethane (98.0%) was utilized as a standard. This standard was used due to the higher degree of purity of the material. The nitromethane concentration of the samples was determined by comparing absorption intensities at 657 cm⁻¹ in a sealed liquid cell. The 657 cm⁻¹ absorption is specific for nitromethane and is unaffected by nitroethane and 2-nitropropane. The precision was estimated to be ca. ±1 nitromethane.
An overlay, offset comparison spectra of Y1-M and the Chem Service 98% standard is given in Appendix A. The two spectra are identical except for a few insignificant peaks in the 800-830 range. The spectra for all the samples are included in Appendix B.

Analysis of volatile compounds other than nitromethane was performed using GC/MS. The results for nitroethane and 2-nitropropane are given in Table 2 and raw data are found in Appendix C.

### TABLE 2. GC/MS ANALYSIS FOR VOLATILE CONTAMINANTS

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Composition</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitroethane</td>
<td>2-Nitropropane</td>
<td></td>
</tr>
<tr>
<td>Y1-B</td>
<td>0.9</td>
<td>~0.1</td>
<td></td>
</tr>
<tr>
<td>Y1-M</td>
<td>0.9</td>
<td>~0.1</td>
<td></td>
</tr>
<tr>
<td>Y1-T</td>
<td>0.8</td>
<td>~0.1</td>
<td></td>
</tr>
<tr>
<td>Y1-MM</td>
<td>0.9</td>
<td>~0.1</td>
<td></td>
</tr>
<tr>
<td>A1-B</td>
<td>~0.1</td>
<td>~0.1</td>
<td></td>
</tr>
<tr>
<td>A1-M</td>
<td>~0.1</td>
<td>~0.1</td>
<td></td>
</tr>
<tr>
<td>A1-MM</td>
<td>~0.4</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>N1-T</td>
<td>~0.1</td>
<td>~0.1</td>
<td></td>
</tr>
<tr>
<td>N1-M</td>
<td>~0.1</td>
<td>~0.1</td>
<td></td>
</tr>
<tr>
<td>N1-B</td>
<td>1.1</td>
<td>~0.1</td>
<td></td>
</tr>
</tbody>
</table>

See legend Table 1.

Analysis for semivolatile compounds was performed using GC/MS. Two samples were selected for analysis. The results are given in Table 3.

### TABLE 3. GC/MS ANALYSIS FOR SEMIVOLATILE CONTAMINANTS IN SELECTED NITROMETHANE SAMPLES

<table>
<thead>
<tr>
<th>Component</th>
<th>Sample Y1-M ppm</th>
<th>Sample N1-M ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraldehyde</td>
<td>70.0</td>
<td>38.0</td>
</tr>
<tr>
<td>2-Pentanone-4-methyl</td>
<td>42.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Total other unknowns</td>
<td>13.4</td>
<td>2.9</td>
</tr>
<tr>
<td>% Total Semivolatiles</td>
<td>0.01%</td>
<td>0.004%</td>
</tr>
</tbody>
</table>

See legend Table 1.
No single semivolatile contaminant was found to have a concentration >0.007%.

Karl Fischer analyses were performed to assay the water content of each of the samples. The results can be compared to standard 95% nitromethane sample from Mallinckrodt. The results are given in Table 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ppm H$_2$O</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>1,370</td>
<td>0.14</td>
</tr>
<tr>
<td>Y1-T</td>
<td>629</td>
<td>0.06</td>
</tr>
<tr>
<td>Y1-MM</td>
<td>697</td>
<td>0.07</td>
</tr>
<tr>
<td>Y1-M</td>
<td>1,077</td>
<td>0.11</td>
</tr>
<tr>
<td>Y1-B</td>
<td>693</td>
<td>0.07</td>
</tr>
<tr>
<td>N1-T</td>
<td>705</td>
<td>0.07</td>
</tr>
<tr>
<td>N1-M</td>
<td>506</td>
<td>0.05</td>
</tr>
<tr>
<td>N1-B</td>
<td>432</td>
<td>0.04</td>
</tr>
<tr>
<td>A1-M</td>
<td>549</td>
<td>0.05</td>
</tr>
<tr>
<td>A1-MM</td>
<td>589</td>
<td>0.06</td>
</tr>
<tr>
<td>A1-B</td>
<td>590</td>
<td>0.06</td>
</tr>
</tbody>
</table>

See legend Table 1.

The average percent water of the samples was 0.06.

Metals contamination analysis was performed on a Perkin-Elmer 5000 graphite furnace atomic absorption spectrophotometer. Calibration standards were made up in methanol and samples were diluted 1:1 in methanol before analysis. A methanol blank was run with each sample set. No solvent contamination was observed.

The results are presented in Table 5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Standard</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Y1-T</td>
<td>8.2</td>
</tr>
<tr>
<td>Y1-MM</td>
<td>9.0</td>
</tr>
<tr>
<td>Y1-M</td>
<td>9.0</td>
</tr>
</tbody>
</table>
TABLE 5. METALS ANALYSIS OF NITROMETHANE SAMPLES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (ppb)</th>
<th>Fe (ppb)</th>
<th>Ni (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y1-B</td>
<td>6.6</td>
<td>&lt;4.0</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td>N1-T</td>
<td>6.6</td>
<td>&lt;4.0</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td>N1-M</td>
<td>6.6</td>
<td>&lt;4.0</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td>N1-B</td>
<td>5.8</td>
<td>&lt;4.0</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td>A1-MM</td>
<td>9.8</td>
<td>&lt;4.0</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td>A1-M</td>
<td>8.0</td>
<td>&lt;4.0</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td>A1-B</td>
<td>9.8</td>
<td>&lt;4.0</td>
<td>&lt;10.0</td>
</tr>
</tbody>
</table>

See legend Table 1.

A compendium of all the analytical results are given in Table 6.

TABLE 6. COMPUTATION OF VARIOUS ANALYSIS ON NITROMETHANE SAMPLES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitromethane</th>
<th>H₂O</th>
<th>Nitroethane</th>
<th>2-Nitropropane</th>
<th>Semivolatiles</th>
<th>Metal Contaminants (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y1-B</td>
<td>99.6</td>
<td>0.07</td>
<td>0.9</td>
<td>~0.1</td>
<td>&lt;0.1</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Y1-M</td>
<td>98.3</td>
<td>0.11</td>
<td>0.9</td>
<td>~0.1</td>
<td>0.01</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Y1-T</td>
<td>100.0</td>
<td>0.06</td>
<td>0.8</td>
<td>~0.1</td>
<td>&lt;0.01</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Y1-MM</td>
<td>99.3</td>
<td>0.07</td>
<td>0.9</td>
<td>~0.1</td>
<td>&lt;0.1</td>
<td>&lt;10</td>
</tr>
<tr>
<td>A1-B</td>
<td>99.3</td>
<td>0.06</td>
<td>~0.1</td>
<td>~0.1</td>
<td>&lt;0.1</td>
<td>&lt;10</td>
</tr>
<tr>
<td>A1-M</td>
<td>99.9</td>
<td>0.05</td>
<td>~0.1</td>
<td>~0.1</td>
<td>&lt;0.1</td>
<td>&lt;10</td>
</tr>
<tr>
<td>A1-MM</td>
<td>99.0</td>
<td>0.06</td>
<td>0.4</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>&lt;10</td>
</tr>
<tr>
<td>N1-B</td>
<td>100.2</td>
<td>0.04</td>
<td>1.1</td>
<td>~0.1</td>
<td>&lt;0.1</td>
<td>&lt;10</td>
</tr>
<tr>
<td>N1-M</td>
<td>99.5</td>
<td>0.05</td>
<td>~0.1</td>
<td>~0.1</td>
<td>&lt;0.01</td>
<td>&lt;10</td>
</tr>
<tr>
<td>N1-T</td>
<td>99.5</td>
<td>0.07</td>
<td>~0.1</td>
<td>~0.1</td>
<td>&lt;0.1</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

See legend Table 1.
3. DISCUSSION

A high degree of purity of nitromethane was found for all the samples. The FTIR analysis showed that all the samples had a concentration of 98% or greater nitromethane. This finding is based on the assumption that the Chem Service nitromethane standard used for comparison is of 98% purity. Other peaks in the FTIR spectra were of insufficient prominence to quantify, so alternate analytical techniques were utilized to identify the other compounds present.

Analysis of other volatile and semivolatiles, especially nitroethane and 2-nitropropane, was accomplished utilizing GC/MS. It was ascertained that all the samples contained 1.1% or less of nitroethane and 0.2% or less of 2-nitropropane. All other peaks in the volatile analysis were significantly less prominent indicating much lower concentrations of any other volatile contaminants.

The semivolatile analysis yielded only trace quantities of contamination of the nitromethane. Only two samples were selected for analysis due to the similarity of the samples preceding analysis and the small percentage of unaccounted for components. Quantification of contaminants was accomplished by subtracting the effects of the nitromethane. It is possible that a higher percentage of paraldehyde is present due to the elution interference of the solvent, but the results of the prior analysis make this unlikely.

Karl Fisher water analysis yielded results of 0.11% water or less. This is consistent with the results of the metals analysis, which showed only trace amounts of metals contamination. For nitromethane to be corrosive to a steel container, the H₂O concentration must exceed 0.2%. The H₂O concentration was below this limit; hence, there was no or little interaction with the containers.

Sampling procedures did not accompany the samples. The method used to sample the barrels could have an effect on the analytical findings. It will be important in the future to ensure that a standard method of sampling is used, preferably a technique that yields a representative sample from each of the layers within a single drum of nitromethane.

It will also be necessary to establish a chain-of-custody record to ensure proper handling of the samples from the field to the analyst. Such a record could help to facilitate understanding any gross contamination that appears, that are not accounted for in future analysis.

Two possible explanations exist for the discrepancy between the original reported purity of the nitromethane, and the purity found in this program. First, during telephone conversations with Angus Chemical, the original shipment of nitromethane was certified at 96%+. This designation commonly results in product which is percentage points higher. Second, and most probable, if a point sampling procedure was utilized, as opposed to a cross-sectional sampling procedure, then a higher degree of homogeneity would result. Point sampling techniques miss any differences in product due to stratification.
APPENDIX A

FTIR COMPARISON SPECTRA
APPENDIX B

FTIR SPECTRA OF SAMPLES
LIBRARY SEARCH
DATA: C0621081 # 464
BASE M/Z: 207
CALI: C06150F1 # 3
RIC: 22815.

SAMPLE: VOA METHOD BLANK: 1UL MEOH PURGE
COND.: 300DEG 4MIN/4DEG/4MIN/FINAL 180 DEG
# 462 TO # 466 SUMMED - # 470 TO # 475 - # 432 TO # 443 X1.00

M WT 1993
B PK 207
RANK # 19993
PUR 874

M WT 244
B PK 207
RANK # 32875
PUR 820

C8.H22.O3.S12 DISILXONE, 1,3-DIETHOXY-1,1,3,3- TETRAMETHYL-
M WT 1983
B PK 207
RANK 3
PUR 664
LIBRARY SEARCH
DATA: C6621882 # 106
BASE M/Z: 51
CALI: CO615041 # 3
R111: 143593.

SAMPLE: B.H. 1UL (100UL/2ML MEOH) 50UL/10ML MEOH
COND.: 360DEG 4MIN/4DEG/MIN/FINAL 180 DEG
# 304 TO # 308 SUMMED - # 275 TO # 293 - # 333 TO # 363 X1.00

C3.02.H
MWT 61
BPK 56
RANK 1
# 126
PUR 588

C3.03.H
MWT 160
BPK 61
RANK 3
# 1671
PUR 682

M/2
40  60  80  100  120  140  150
LIEFARY SEARCH
06/22/90 0:22:00 + 7:15
SAMPLE: B.H.: 1UL (100UL/2ML MEOH) 50UL/10ML MEOH
CONDS.: 30DEG 4MIN/4DEG/1MIN/FINAL 180 DEG
# 434 TO # 439 SUMMED - # 448 TO # 456 - # 414 TO # 424 X1.00

C7.H11.02.N
BUTANOIC ACID, 2-CYANO-3-METHYL-, METHYL ESTER
M WT 141
B PK 43
RANK 1
# 5396
FUR 501

C3.H7.02.N
PROPANE, 1-NITRO-
M WT 83
B PK 43
RANK 2
# 777
FUR 500

C3.H7.02.N
PROPANE, 2-NITRO-
M WT 83
B PK 43
RANK 2
# 776
FUR 468
LIBRARY SEARCH
DATE: 06/22/90  01:22:00 + 7:50
SAMPLE: B.H. 11UL (100UL/2ML MEOH) 500UL/10ML MEOH
CONDS.: 30DEG 4MIN/4DEG/1MIN/FINAL 180 DEG
# 468 TO # 473 SUMMED - # 485 TO # 499 - # 434 TO # 448 X 1.00

[Graph showing mass spectra for three compounds:
- Cyclotrisiloxane, Hexamethyl-
- Arsenous Acid, Tris(trimethylsilyl) Ester
- Disiloxane, 1,3-Diethoxy-1,1,3,3-Tetramethyl-]
LIBRARY SEARCH
DATA: CO621802 # 306
06/22/90 0:22:00 + 5:06
CALI: CO6156F1 # 3
BASE N/2: 61
RIC: 143503.

SAMPLE: B.H.: 1UL (100UL/2ML MEOH) 50UL/10ML MEOH
COND.: 300DEG 4MIN/4DEG/MIN/FINAL 180 DEG
# 304 TO # 308 SUMMED - # 275 TO # 293 - # 333 TO # 363 X1.00

-------------------------------
SAMPLE
-------------------------------

METHANE, NITRO-

METHANAMINE, N-METHOXY-

1-NITRO-2-PROANOL

-------------------------------
LIBRARY SEARCH
06/22/90 0:22:00 + 7:50
SAMPLE: B.I.:1UL (100UL/2ML MEOH)50UL/10ML MEOH
COND. 30DEG 4MIN/4DEG/4MIN/FINAL 100 DEG
# 458 TO # 473 SUMMED - # 485 TO # 493 - # 434 TO # 448 X1.00

C6.H18.03.S13
CYCLOTIRISILXANKE, HEXANEKTEHPH-
H WT 222
B PK 267
RANK 1
# 19998
PUR 893

C3.H27.03.A5.S13
ARSENIC ACID, TRIS(TRIMETHYLSILYL) ESTER
H WT 342
B PK 207
RANK 2
# 32875
PUR 763

C8.H22.03.S12
DISPOXANE, 1,3-DIETHOXY-1,1,3,3-TETRAMETHYL-
H WT 222
B PK 267
RANK 3
# 20022
PUR 726

DATA: C0621002 # 470
CHL: C06150F1 # 3
RIP: 41471.
BASE M/Z: 207

M/Z 50 100 150 200 250 300
LIBRARY SEARCH
06/21/90 20:45:00 + 5:06
SAMPLE: 500G NITROMETHANE/2-NITROPROPRANE STD: 1UL PURGE
COND.: 300DEG 4MIN/4DEG/MIN/FINAL 180 DEG
# 304 TO # 303 SUMMED - # 315 TO # 321 - # 283 TO # 284 X1.00

METHANE, NITRO-

METHANAMINE, N-METHOXY-

1-NITRO-2-PROPA NOL

M/Z 30 40 50 60 70 80 90 100 110
LIBRARY SEARCH

SAMPLE: SONG NITROMETHANE/2-NITROPROPANE STD: 1UL FURGE
CONDS.: 300DEG 4MIN/4DEG/MIN/FINAL 180 DEG
# 437 TO #.439 SUMMED - # 442 TO # 451 - # 426 TO # 435 X1.00