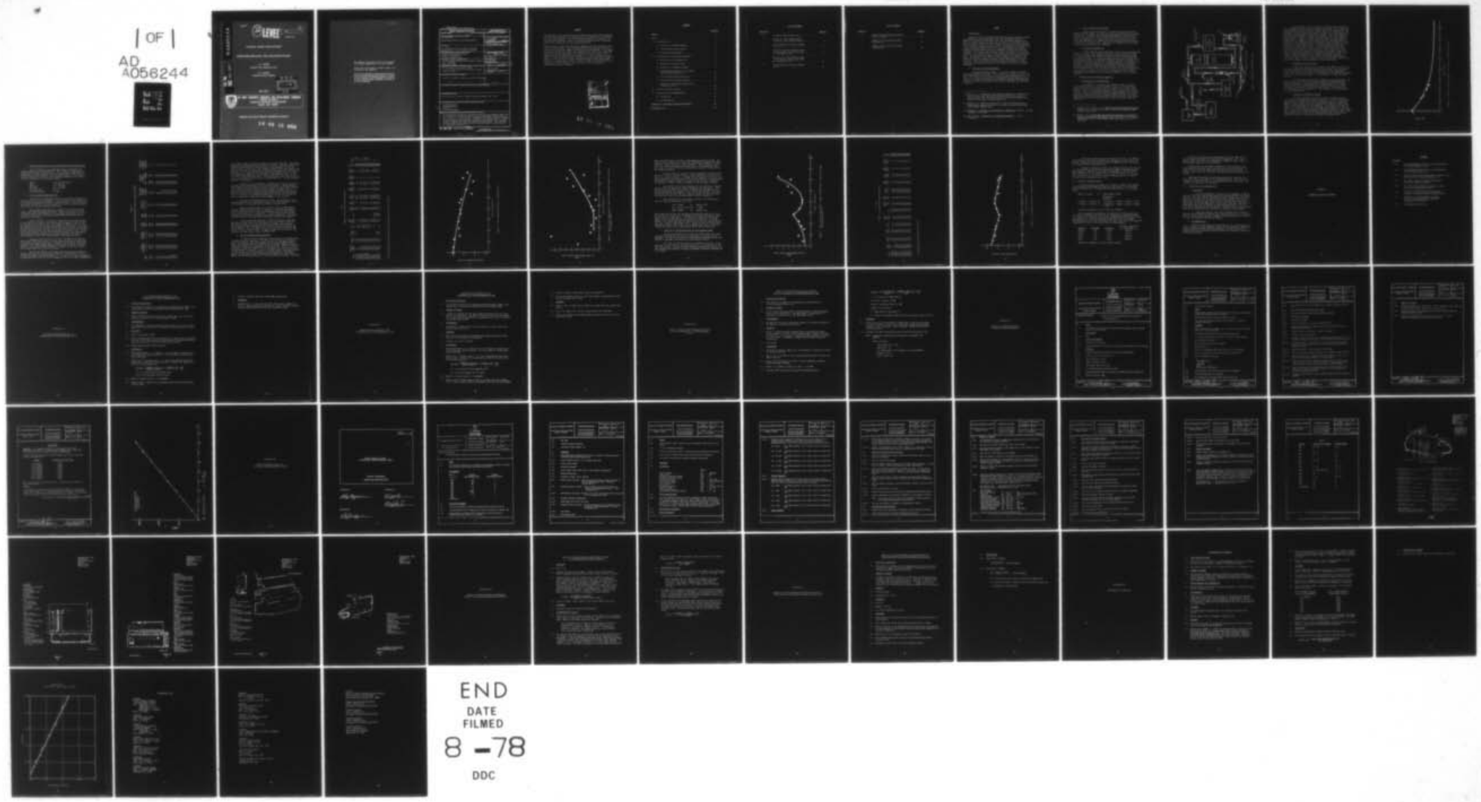
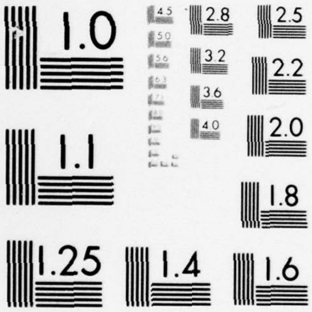
AD-A056 244 RADFORD ARMY AMMUNITION PLANT VA F/G 19/1
NITROFORM RECOVERY AND ISOLATION STUDIES.(U)
MAY 78 R A MUNDY, E E GILBERT
UNCLASSIFIED RAD-240.10 ARLCD-TR-78027 NL

1 OF 1
AD
A056244



END
DATE
FILMED
8 -78
DDC


1.0
4.5
5.0
5.6
6.3
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

(12) LEVEL II

AD

AD-E400 164

TECHNICAL REPORT ARLCD-TR-78027

# NITROFORM RECOVERY AND ISOLATION STUDIES

R. A. MUNDY
RADFORD ARMY AMMUNITION PLANT

E. E. GILBERT
ARRADCOM PROJECT ENGINEER

DDC
RECEIVED
JUL 17 1978
B

MAY 1978

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
WEAPON SYSTEMS LABORATORY
DOVER, NEW JERSEY

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

18 06 13 088

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

## REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

**1. REPORT NUMBER**
Technical Report ARLCD-TR-78027

**2. GOVT ACCESSION NO.**
(9)

**3. RECIPIENT'S CATALOG NUMBER**

**4. TITLE (*and Subtitle*)**
(6) NITROFORM RECOVERY AND ISOLATION STUDIES.

**5. TYPE OF REPORT ~~& PERIOD COVERED~~**
Final Report,
Decem~~ber~~ 1975 - Janu~~ary~~ 1978

**6. ~~PERFORMING ORG.~~ REPORT NUMBER**
PE-557 (RAD 240.10)

**7. AUTHOR(s)**
(10) R. A./Mundy, Radford Army Ammunition Plant
E.E./Gilbert, Project Engineer, ARRADCOM

**8. CONTRACT OR GRANT NUMBER(s)**
(14) RAD-240.10, PE-557

**9. PERFORMING ORGANIZATION NAME AND ADDRESS**
Radford Army Ammunition Plant
Hercules Incorporated
Radford, Virginia 24141

**10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS**
DA Project No. (16) 1T762720D048
~~Work Unit W-5~~

**11. CONTROLLING OFFICE NAME AND ADDRESS**
US Army Armament Research & Development Command
ATTN: DRDAR-TSS
Dover, NJ 07801

**12. REPORT DATE**
(11) May 1978

**13. NUMBER OF PAGES**
69 (12) 68p.

**14. MONITORING AGENCY NAME & ADDRESS (*if different from Controlling Office*)**
Energetic Materials Division, LCWSL
US Army Armament Research & Development Command
Dover, NJ 07801

**15. SECURITY CLASS. (*of this report*)**
Unclassified

**15a. DECLASSIFICATION/DOWNGRADING SCHEDULE**

**16. DISTRIBUTION STATEMENT (*of this Report*)**

Approved for public release, distribution unlimited.

(18) ARLCD, SBIE (19) TR-78027, AD-E400 164

**17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)**

**18. SUPPLEMENTARY NOTES**

This project was funded by Edgewood Arsenal, Aberdeen, MD 21010

**19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)**

Sodium Nitroform
Tetranitromethane
Nitroform
Pollution Abatement

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

An investigation was made to effectively remove tetranitromethane (TNM) from the effluent gas stream from trinitrotoluene (TNT) manufacturing operations and convert it to nitroform (NF). The TNM was efficiently removed by passing the gas through a column scrubber containing an aqueous solution of sodium carbonate ($Na_2CO_3$) and stabilized hydrogen peroxide ($H_2O_2$). The resulting sodium nitroform (SNF) solution can be vacuum distilled to obtain NF which is a marketable by-product.

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

407 057

JOB

# SUMMARY

Although TNM can be removed from a gas stream with sodium sulfite ($Na_2SO_3$) for pollution abatement, this approach does not produce NF for recovery in any appreciable quantity. The processes investigated are capable of TNT tail gas fume abatement as well as providing a source for NF, a material used in the manufacture of high energy propellants.

Under this study, short and long term scrubbing runs were conducted using a bench-scale scrubber. The scrubbing medium was an aqueous solution of either sodium hydroxide (NaOH) or $Na_2CO_3$ with stabilized $H_2O_2$. The results of these investigations showed that scrubbing will effectively reduce TNM from an air stream containing 750 to 1000 ppm to an exit level of considerably less than 100 ppm by converting it to soluble sodium nitroform (SNF). The SNF column scrubbing concentration can be increased to approximately 5-6 percent before column performance degrades when using $Na_2CO_3$ solutions. As previously reported, levels as high as 15-20 percent can be obtained with NaOH solutions. At these levels, NF is produced by neutralization and distillation.

# CONTENTS

# LIST OF FIGURES

# LIST OF TABLES

# STUDY

## I. INTRODUCTION

Previous work [1/] established that TNM could be effectively removed by scrubbing the TNT fume recovery tail gas with $Na_2SO_3$ solution. However, recovery of the NF salt, which has a potential market value, was not feasible because the salt was not stable in the $Na_2SO_3$ solution. Other scrubbing solutions [2/] were evaluated to establish the feasibility of economically achieving recovery of NF. A NaOH solution combined with caustic stabilized $H_2O_2$ (Albone "DS" peroxygen compound from DuPont) produced stable NF which could be recovered by neutralization and distillation. The fume recovery stream contains, in addition to 750-1000 ppm TNM, 2 to 5 percent each of carbon dioxide ($CO_2$) and carbon monoxide (CO). The $CO_2$ reacts with NaOH to produce $Na_2CO_3$, thus depleting the NaOH. The purpose of this study was to investigate the effect of $CO_2$ absorption from the fume gas stream by using a $Na_2CO_3$-$H_2O_2$ scrubbing solution. These data would also establish the feasibility of using $Na_2CO_3$ as the feed alkali which is less expensive and easier to handle than NaOH.

### A. Toxicity of Tetranitromethane

Tetranitromethane, $C(NO_2)_4$, is a toxic by-product produced during the manufacture of TNT. It is a heavy oily liquid (sp. gr. 1.65) which solidifies at 3°C and boils at 126°C without decomposition [3/]. It has a toxic hazard rating and the recommended personnel exposure level given by the American Conference of Government and Industrial Hygienist (ACGIH) is one part per million in air or 0.8 milligrams per cubic meter of air [4/].

---

[1/] Morris, J. A., Propellant Plant Pollution Abatement - Elimination of $NO_x$ in Process Tail Gas from TNT Manufactured by Absorption in Sulfuric Acid, Final Engineering Report on Production Engineering Project PE-352 (Phase I), RAAP, April 1973.

[2/] Mathes, C. D., Removal and Recovery of TNM from TNT Manufacture, Supplementary Engineering Report on Production Engineering Project PE-352, RAAP, October 1975.

[3/] Urbanski, T., Chemistry and Technology of Explosives, Volume 1, p. 588, Pergammon Press, 1964.

[4/] Sax, Irving N., Properties of Industrial Materials, p. 1151, 3d Edition.

## B. Present Fume Recovery System

During previous operation of the TNT Plant at Radford Army Ammunition Plant (RAAP), the fumes from nitrating operations were passed through water scrubbers which removed approximately 90 percent of the $NO_x$ but none of the TNM. This allowed 300 to 600 ppm (V/V) of TNM to reach the atmosphere. A separate stack venting the acid washer also discharged TNM and will be combined with the present fume gas stream on start up of the rebuilt lines. Emissions are estimated to be 750-1000 ppm when these two streams are combined.

## C. Previous Investigations

Cursory laboratory and bench-scale studies were conducted under PE-352 to evaluate three scrubber solutions for the abatement of TNM. The three solutions were $Na_2SO_3$, NaOH with stabilized $H_2O_2$ and $Na_2CO_3$ with stabilized $H_2O_2$ [5/]. All three solutions effectively removed TNM from the tail gases. The $Na_2SO_3$ scrubbing solution was eliminated from consideration because the SNF which formed decomposed very rapidly, i.e., NF could not be recovered from the scrubbing solution as a marketable by-product. Both the NaOH-$H_2O_2$ and $Na_2CO_3$-$H_2O_2$ systems effectively removed the TNM and the SNF could be converted to NF by neutralization and vacuum distillation of the solution, but no long term scrubbing data were available to assess the effect of $CO_2$ absorption. Also, little information was available on total SNF salt buildup in the scrubbing solution.

## II. INVESTIGATION OF OPERATING PARAMETERS

## A. Description of Scrubbing Unit

A schematic of the bench-scale system is shown in Figure 1. The scrubbing unit was a heavy wall glass column 1.5 m high with an inside diameter of 102 mm and packed to a depth of 0.9 m with ceramic saddles. The 0.9 m of packing contained a free volume of five liters. The entire system was maintained under a reduced pressure which was produced by a Thomas Industries, Incorporated Model 2727CA39, two stage diaphragm stainless steel pump attached to the exit side of the column. TNM in the exit gas was monitored with a Miran II infrared (IR) gas analyzer [6/].

---

5/ Gilligan, W. H., Hall, T. N., Removal of Tetranitromethane from Air Streams, Naval Surface Weapon Center, White Oak, Technical Report 75-128, October 1975.

6/ Murray, J. R., Monitoring and Controlling Systems for Tetranitromethane Pollutants in TNT Exhaust Gases, Final Report on Production Engineering Project PE-499, Radford Army Ammunition Plant, to be published.

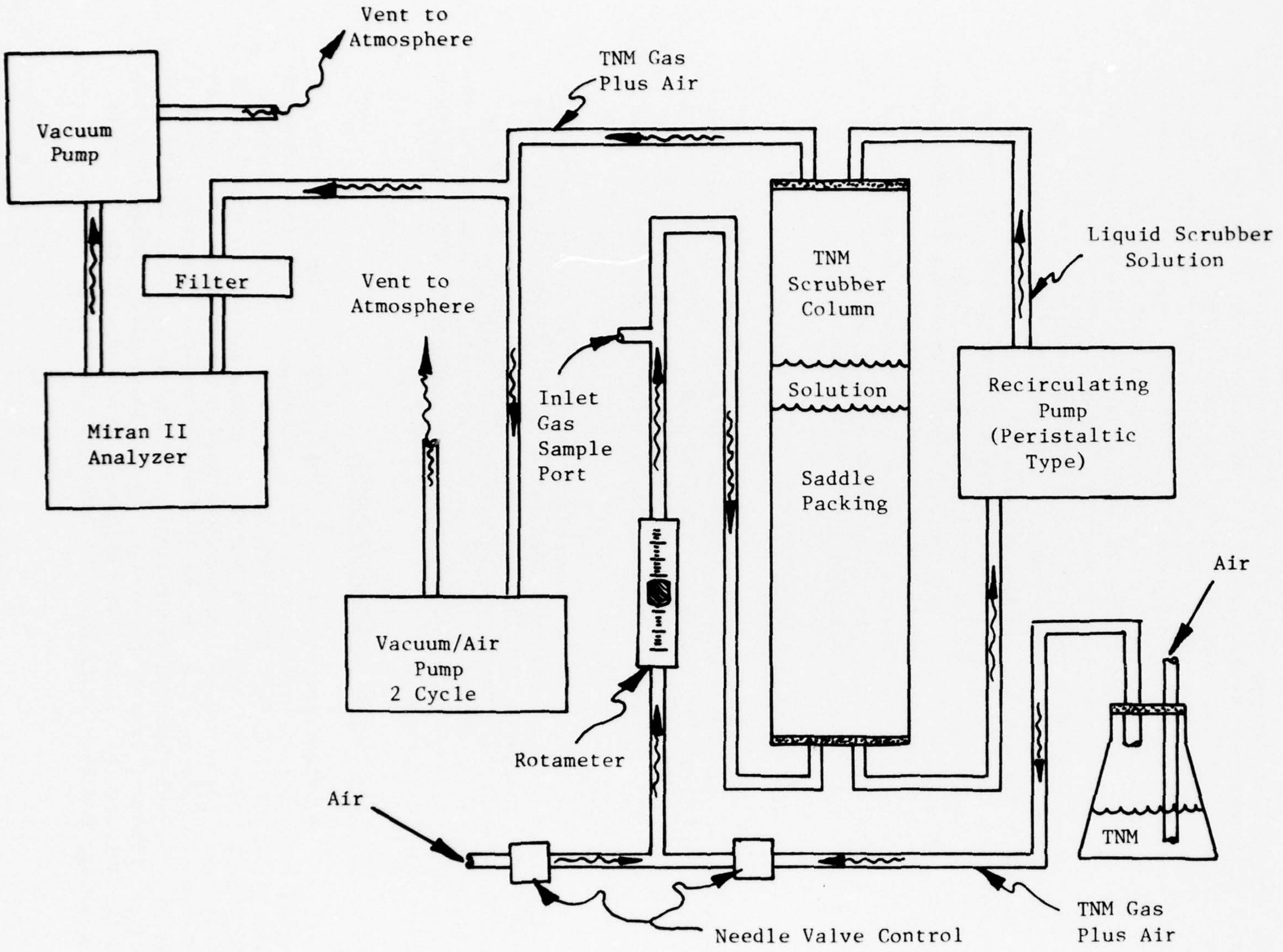


Figure 1. Diagram of TNM scrubber flows

Liquid TNM was placed in a 250 ml Erlenmeyer flask nebulizer. Air was bubbled through the liquid TNM and then mixed at the column inlet with additional air controlled by a needle valve. By adjusting the two air flows, the TNM concentration could be varied over a wide range. The Erlenmeyer flask was used as a nebulizer because of its large diameter flat bottom as compared to standard air bubblers. The flat bottom permitted a supply of TNM for a day's operation without a rapid change in liquid depth. A change in liquid depth would have required numerous changes in air to TNM vapor flows to maintain a constant TNM inlet concentration. The TNM stream was then passed through a flowmeter and into the bottom of the scrubber column. A 1500 ml filtration flask was inserted in the gas line at the exit of the column just prior to the vacuum pump to prevent any liquid carryover from reaching the vacuum pump. A tee was also mounted in the exit line to allow the gas to be pulled through the IR analyzer for continuous monitoring of TNM concentration. The liquid phase in the scrubber column was constantly circulated from the bottom to the top with a variable speed Monostat varistaltic pump. A tee was placed in the inlet and outlet lines to the pump to take samples or make additions to the liquid phase.

### B. Analysis of the Gas Stream

In the early portion of this project, the TNM in the inlet and exit gas streams was monitored using the IR analyzer. This was found to be unsatisfactory for the inlet stream because, at TNM concentration levels above 300 ppm, the slope of the absorbance versus TNM concentration curve is very flat and, therefore, is not sensitive to high TNM concentrations.

The inlet gas was, therefore, analyzed by several methods. One method used a Thermo Electron Corporation Model 10A Chemiluminescent NO-$NO_x$ Gas Analyzer. See Appendix A-2 for description of the method. A Hewlett-Packard Gas Chromatograph Model 5700A equipped with a flame ionization detector was also used for TNM analysis. A description of this method is shown in Appendix A-1. Both methods were found suitable for inlet TNM analysis.

### C. Stability of Hydrogen Peroxide

Hydrogen peroxide is not stable in basic solution unless a stabilizer such as magnesium sulfate is present. In order to determine the stability of DuPont Albone DS-50 stabilized $H_2O_2$ in a solution of $Na_2CO_3$, a known concentration was prepared and allowed to stand during which the $H_2O_2$ concentration was monitored. The original solution contained 1.04 percent $H_2O_2$ in a 0.45 N $Na_2CO_3$ aqueous solution. After 16 hours, the solution had spontaneously reduced in strength to 0.22 percent $H_2O_2$. Figure 2 is a graph showing $H_2O_2$ concentration versus time. These data indicate that if work is not being performed with the scrubbing solution, reactions continue thus consuming the residual $H_2O_2$.

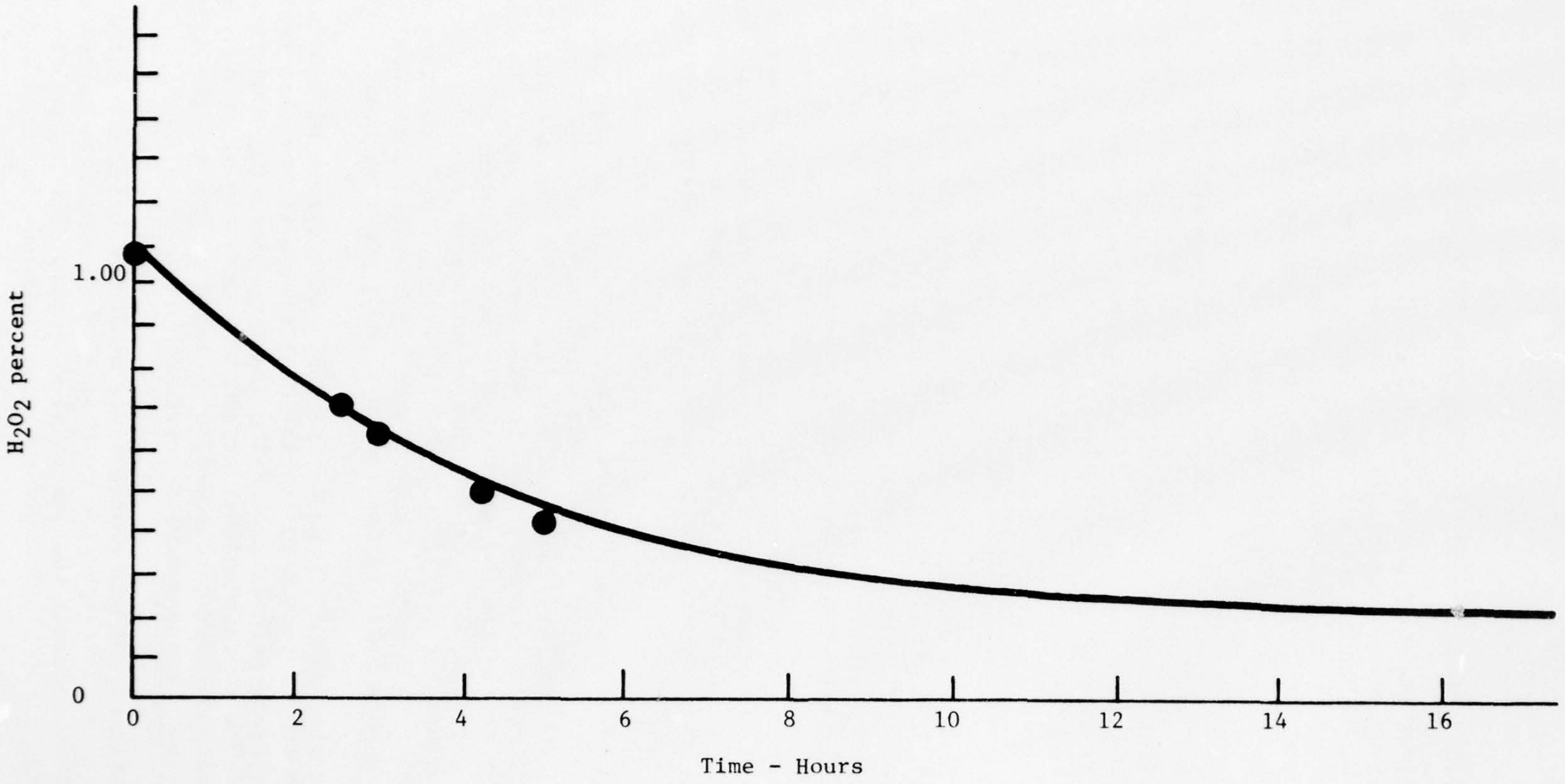


Figure 2. Albone DS - $H_2O_2$ concentration vs time in 0.45 N $Na_2CO_3$ solution

## D. Scrubbing Efficiencies at Low Sodium Nitroform Concentrations

The first phase of the investigation was to determine the optimum scrubber operating parameters. The variables considered were packing depth, $Na_2CO_3$ concentration, $H_2O_2$ concentration, TNM inlet concentration, gas flow rates and volume of liquid holdup in the column. From the data shown in Table 1, the following parameters were chosen as the most suitable for the scrubbing studies:

| | |
|---|---|
| $Na_2CO_3$ | 2.25 to 2.50 percent |
| $H_2O_2$ | 2.0 percent |
| TNM Inlet | 750 - 950 ppm |
| Gas Flow | 24 - 26 l/min |
| Packing Height | 0.9 m |
| Scrubbing Liquid | 4 liters |

## E. First Extended Column Operation

Four liters of scrubbing solution were prepared containing 1.82 percent $H_2O_2$ and 2.58 percent $NaCO_3$. This solution was then pumped into the column containing 0.9 m height of ceramic packing. This solution was circulated from the bottom of the column to the top at a rate of approximately one l/min using a variable speed pump.

The column was maintained at a pressure of 250 mm of mercury using a two-stage diaphragm vacuum pump. Room air was pulled into the column through the liquid TNM and the air makeup needle valve at a rate to produce a TNM inlet concentration between 700 and 1000 ppm and gas flow of 24 to 25 l/min.

During the first 12.25 hours of operation, an attempt was made to keep the level of $H_2O_2$ at 1.80 percent which required a total of 550 ml of additional 50 percent $H_2O_2$. The removal of TNM from the air flow was excellent with exit concentrations between 10 and 50 ppm. The column was operated only during the day and was shut down overnight and week-ends. During shutdown periods, the $H_2O_2$ concentration dropped to zero. It was noted during startup that the first few milliliters of $H_2O_2$ entering into the scrubbing solution immediately decreased the TNM in the effluent indicating that a much lower concentration of $H_2O_2$ might be used.

During the next 28 hours of the run, the addition of $H_2O_2$ was based on the TNM concentration in the effluent stream rather than trying to maintain a constant percentage. Using the same operating conditions, except the inlet TNM averaged higher at 900 ppm, only 268 ml of $H_2O_2$ was required. The effluent TNM concentration averaged 45 ppm and the $H_2O_2$ level ranged between zero and 0.05 percent.

The effluent TNM was continuously monitored using the Miran II analyzer and when the concentration reached 70 - 80 ppm, five to ten ml of $H_2O_2$ were added, reducing the TNM to 35 - 40 ppm. The higher consumption of $H_2O_2$ during the first 12.25 hours appeared to be due to rapid decomposition

# Table 1

Sodium carbonate/hydrogen peroxide column scrubbing

| Run | Sodium Carbonate, % | Hydrogen Peroxide, % | TNM Inlet, ppm | TNM Exit, ppm | Removal Efficiency, % | Flow Rate Through Column, l/min | Packing Height in Column, mm | | Scrubbing Liquid in Column, liters |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | mm | inches | |
| 4-1 | 1.40 | 0.76 | 325 | 55 | 83 | 34 | 559 | 22 | 4 |
| 4-2 | 1.40 | 0.76 | 275 | 75 | 73 | 34 | 559 | 22 | 2 |
| 4-3 | 1.40 | 0.76 | 275 | 160 | 42 | 34.5 | 559 | 22 | 1 |
| 5-1 | 2.53 | 1.29 | 540 | 15 | 97 | 25 | 914 | 36 | 4 |
| 5-2 | 2.53 | 1.29 | 580 | 15 | 97 | 25 | 914 | 36 | 3 |
| 5-3 | 2.53 | 1.29 | 640 | 18 | 97 | 30 | 914 | 36 | 2 |
| 5-4 | 5.24 | 1.25 | 760 | 21 | 97 | 24.5 | 914 | 36 | 4 |
| 5-5 | 5.24 | 1.25 | 760 | 16 | 98 | 25.5 | 914 | 36 | 2 |
| 5-6 | 5.28 | 1.80 | 250 | 12 | 95 | 23.8 | 914 | 36 | 4 |
| 5-7 | 4.23 | 0.95 | 395 | 12 | 97 | 24.6 | 914 | 36 | 4 |
| 5-8 | 4.32 | 0.55 | 465 | 18 | 96 | 24.3 | 914 | 36 | 4 |
| 5-9 | 4.32 | 0.49 | 540 | 26 | 95 | 24.6 | 914 | 36 | 4 |
| 5-10 | 0.52 | 0.78 | 720 | 15 | 98 | 24.6 | 914 | 36 | 4 |
| 5-11 | 0.26 | 0.81 | 720 | 18 | 97 | 24.6 | 914 | 36 | 4 |
| 5-12 | 2.22 | 0.25 | 950 | 24 | 98 | 24.8 | 914 | 36 | 4 |

of the $H_2O_2$ rather than being consumed in a reaction with TNM. The $Na_2CO_3$ concentration remained between 1.4 and 2.5 percent. The $H_2O_2$ addition was based on the TNM effluent concentration for the remainder of the run. After 49 hours of operation, the scrubbing solution color had changed from yellow to red and the consumption of $H_2O_2$ had increased four to five times. See Table 2 for comparison of the amount of $H_2O_2$ added per gram of TNM. This change was thought to have been due to the decrease in pH. A solution of 1.25 percent $Na_2CO_3$ and 0.1 percent $H_2O_2$ has a pH of 10.58 and the pH of the scrubbing solution after 53.5 hours was 9.21. The SNF concentration was 4.77 percent.

Operation of the column was continued for a total of 72 hours to determine if the consumption of $H_2O_2$ could be reduced. Adding $Na_2CO_3$ to the scrubbing solution resulted in short periods of reduced $H_2O_2$ consumption. Titration of the scrubbing solution after 59 hours with 0.3 N hydrochloric acid (HCl) using a pH meter showed the $Na_2CO_3$ concentration was not 2.45 percent as determined using the dead stop titration method but 1.21 percent. The difference between the 2.45 and 1.21 percent was due to 1.42 percent sodium bicarbonate ($NaHCO_3$) in the solution.

The run was terminated after 74 hours. The analysis of the scrubbing solution was 2.66 percent $Na_2CO_3$, 1.87 percent $NaHCO_3$, 4.65 percent nitrates, 2.43 percent nitrites, and 6.75 percent SNF.

Figure 3 shows the decline in the efficiency of TNM removal from the gas stream versus hours of operation. The graph presented in Figure 4 shows the ratio of $H_2O_2$ consumption per gram of TNM entering the column versus hours of operation. It can be seen that the column solution will provide an operation for 40 hours and produce a SNF concentration of only 5.5 percent before additional reactants are required.

A true conversion efficiency of TNM to SNF was not obtained because there were some fluctuations in the total scrubber volume and also some variance in the test for SNF at the higher concentration. The average estimated consumption efficiency of the first extended run was 65 percent. This was calculated on the basis that one mole of TNM reacts to form one mole of SNF. It does not take into account any side reaction that may involve either the TNM or SNF.

### F. Second Extended Column Operation

In order to better understand the operation of the TNM scrubber, a duplicate run was initiated. The four liters of starting scrubbing solution contained 2.66 percent $Na_2CO_3$ and 0.07 percent $NaHCO_3$ and no $H_2O_2$. The $H_2O_2$ was added as required and the $Na_2CO_3$, $NaHCO_3$ and pH were monitored in addition to parameters in the first run. After 4.5 hours of operation, the pH had dropped to 9.75, the $Na_2CO_3$ was 1.39 percent, and the $NaHCO_3$ was 0.57 percent. After 15.25 hours, the pH had again dropped to 9.45 and the solution contained 0.54 percent $Na_2CO_3$. Only small amounts of $H_2O_2$ were needed for each gram of TNM and the conversion of TNM to SNF was 83.04 percent with 2.52 percent SNF in solution. The yield

Table 2

Summary of first extended column scrubbing run

| Date | Operation Total Hours | $Na_2CO_3$, % | $NaHCO_3$, % | SNF, % | TNM Used per Day, g | pH | Inlet TNM, ppm | Exit TNM, ppm | TNM Removed, % | 50% $H_2O_2$ Added, ml | $H_2O_2$/TNM, ml/g | 60% NaOH Added, ml | $Na_2CO_3$ Added, g | Vol. in Col, ml | $H_2O_2$, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12-2-76 | 0 | 2.58 | (1) | - | - | | 760 | 5 | 99.34 | | | 0 | 0 | 4000 | 1.82 |
| 12-2-76 | 5 | 1.74 | | 0.65 | 39.2 | | 698 | 6 | 99.14 | 150 | 3.83 | 0 | 0 | 4000 | 1.83 |
| 12-7-76 | 10 | 1.65 | | 0.62 | | | - | - | | - | | 0 | 0 | 4000 | 0 |
| 12-8-76 | 12.25 | 1.63 | | - | 46.0 | | 719 | 10 | 98.61 | 400 | 8.70 | 0 | 0 | 4000 | - |
| 12-9-76 | 15.50 | 2.70 | | 2.22 | 46.0 | | 773 | 52 | 93.27 | 70 | 1.52 | 0 | 60.0 | 4000 | 0.03 |
| 12-13-76 | 22.00 | 2.36 | | 3.28 | 31.9 | | 856 | 50 | 94.16 | 45 | 1.41 | 0 | 32.0 | 4000 | 0 |
| 12-14-76 | 28.50 | 1.85 | | 4.23 | 38.0 | | 956 | 52 | 94.56 | 20 | 0.53 | 0 | 0 | 4000 | 0.01 |
| 12-15-76 | 35.50 | 1.90 | | 5.12 | 65.4 | | 889 | 64 | 92.80 | 63 | 0.96 | 0 | 40.0 | 4000 | 0.03 |
| 12-16-76 | 39.00 | 2.41 | | 5.70 | 35.4 | | 891 | 63 | 92.93 | 50 | 1.41 | 0 | 20.0 | 4000 | 0.07 |
| 2-3-77 | 39.00 | 3.10 | | 5.62 | - | | - | - | | - | | 0 | 0 | 3200 | - |
| 2-4-77 | 45.25 | 2.72 | | - | 68.3 | | 887 | 56 | 93.69 | 40 | 0.59 | 0 | 0 | 4000 | - |
| 2-8-77 | 48.75 | 1.97 | | - | 37.7 | | 878 | 71 | 91.91 | 65 | 1.72 | 0 | 0 | 4000 | - |
| 2-9-77 | 53.50 | 1.20 | | 4.77 | 18.9 | 9.21 | 641 | 115 | 82.06 | 50 | 2.65 | 0 | 70.0 | 4000 | 0 |
| 2-11-77 | 57.50 | 2.33 | | - | 30.0 | 9.30 | 701 | 88 | 87.45 | 140 | 4.67 | 0 | 45.0 | 3000 | 0 |
| 2-15-77 | 64.50 | 4.35 | 0.05 | | 34.7 | 10.43 | 718 | 138 | 80.78 | 200 | 5.76 | 0 | 60.0 | 3000 | - |
| 2-16-77 | 67.50 | 3.63 | 0.77 | | 17.6 | 9.85 | 811 | 79 | 90.26 | 50 | 2.84 | 0 | 0 | 3000 | - |
| 2-17-77 | 72.00 | 2.66 | 1.87 | 6.75 | 21.2 | 8.97 | 731 | 102 | 86.05 | 110 | 5.19 | 0 | 25.0 | 3000 | - |

(1) 12-2-76 through 2-11-77 analyzed for total alkalinity only and reported as $Na_2CO_3$.

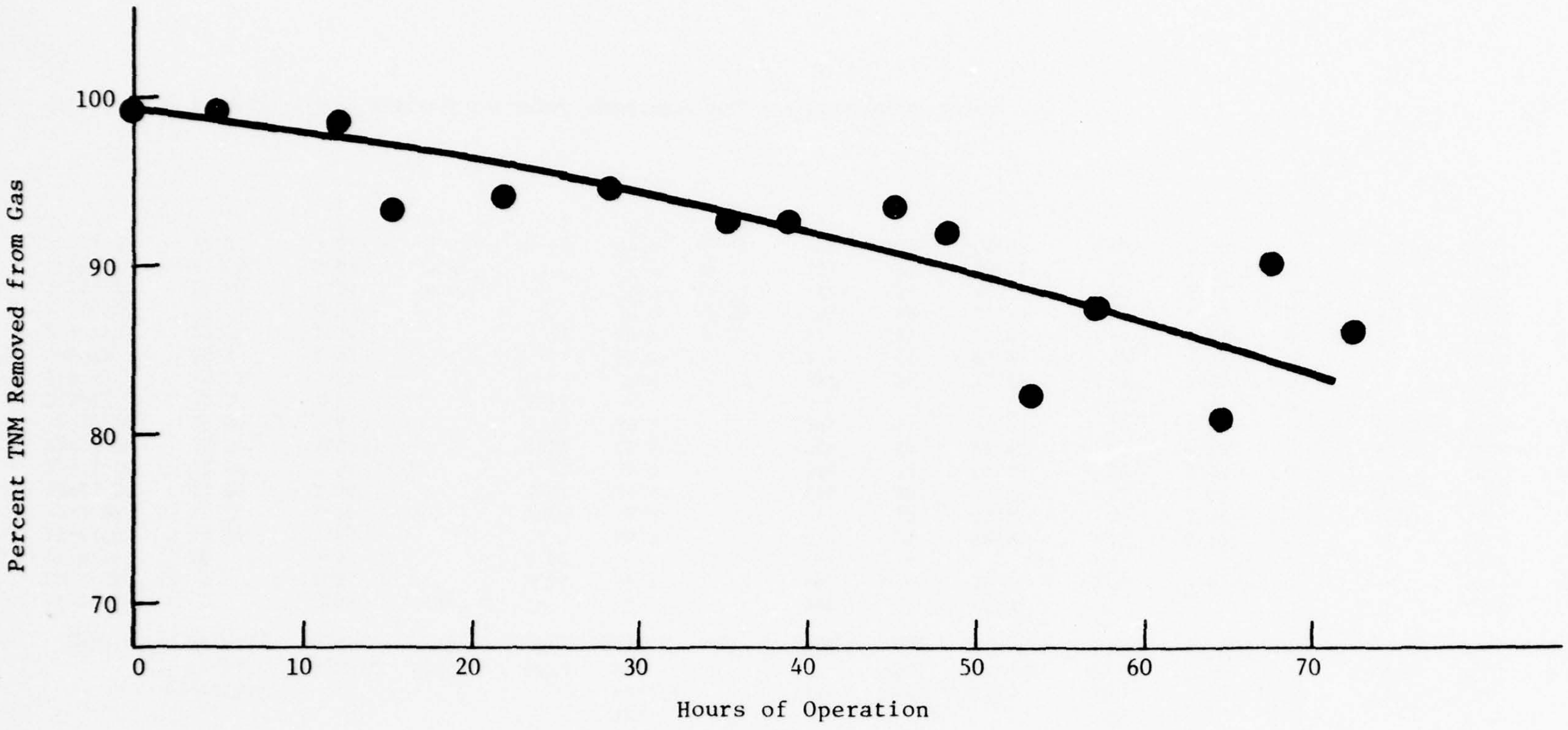


Figure 3. Gas scrubbing efficiency, extended run No. 1

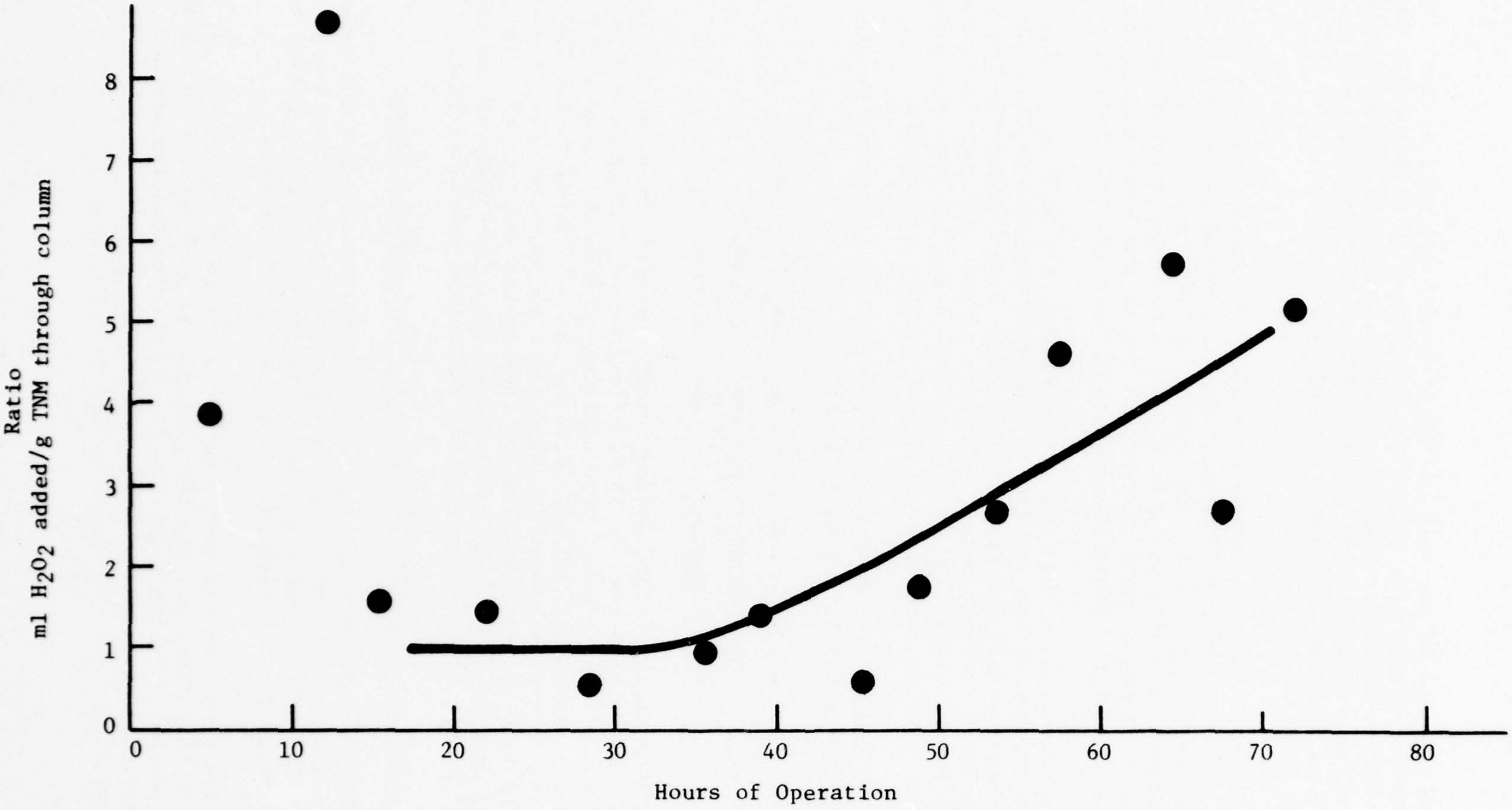


Figure 4. Ratio of ml of $H_2O_2$ added to grams of TNM through column versus time for extended run No. 1

was calculated based on one mole of TNM producing one mole of SNF. The number of moles entering the column was determined by weighing the TNM vaporizer, before and after a day's operation. After 28 hours of operation, the column contained 4.63 percent SNF but the consumption ratio (ml of $H_2O_2$ to grams of TNM) had increased by a factor of three and the pH steadily decreased.

Figure 5 shows an increase in $H_2O_2$ consumption through 28 hours and then a decrease through 43 hours. This condition was not noted for run No. 1 as seen in Figure 4. Throughout the remainder of the run, the $H_2O_2$ consumption increased steadily but could be reduced for short periods by addition of $Na_2CO_3$ or NaOH to increase the pH and lower the $NaHCO_3$ concentration. Table 3 shows the amounts of each reactant required.

As observed in the first extended run, the NaOH has a slightly greater effect in reducing the $H_2O_2$ consumption than the $Na_2CO_3$. This indicates that the main factors which increase $H_2O_2$ consumption are low pH and high $NaHCO_3$ concentration. The five percent $CO_2$ that is in the TNT process exit gas with TNM will lower the pH and increase the $NaHCO_3$ concentration, and in turn increase NaOH or $Na_2CO_3$ consumption.

The reactions that occur between the $CO_2$ in the TNT process exit gas, $Na_2CO_3$ and NaOH are as follows:

$$CO_2 + 2\,NaOH \rightarrow Na_2CO_3 + H_2O$$

$$CO_2 + Na_2CO_3 + H_2O \rightarrow 2\,NaHCO_3$$

$$NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$$

These equations indicate that during actual operation with two to five percent $CO_2$ in the exit gas, the $NaHCO_3$ content will increase and reduce the efficiency of TNM removal. The addition of NaOH will reduce the $NaHCO_3$ level, increase the pH and increase the efficiency of the TNM removal. The second extended run ended after 63 hours of operation when the ratio of $H_2O_2$ to TNM reached 5.85. During the run, the efficiency of TNM removal dropped from 94.88 to 88.06 percent (see Figure 6) and the overall efficiency of the conversion of TNM to SNF was 64 percent.

### G. Stability of Sodium Nitroform in the Scrubbing Liquid

During both extended runs, there were periods when the column operation was shut down due to lack of materials or a malfunction of equipment. The SNF concentration was monitored periodically during these periods to determine its stability in the scrubber solution.

The first run was shut down for a period of 44.5 days. At the beginning of this interval, the SNF content was 5.70 percent and at the end, 5.64 percent. During this time the $H_2O_2$ concentration was zero and the combined concentrations of $Na_2CO_3$ and $NaHCO_3$ calculated as $Na_2CO_3$ was 2.41 percent.

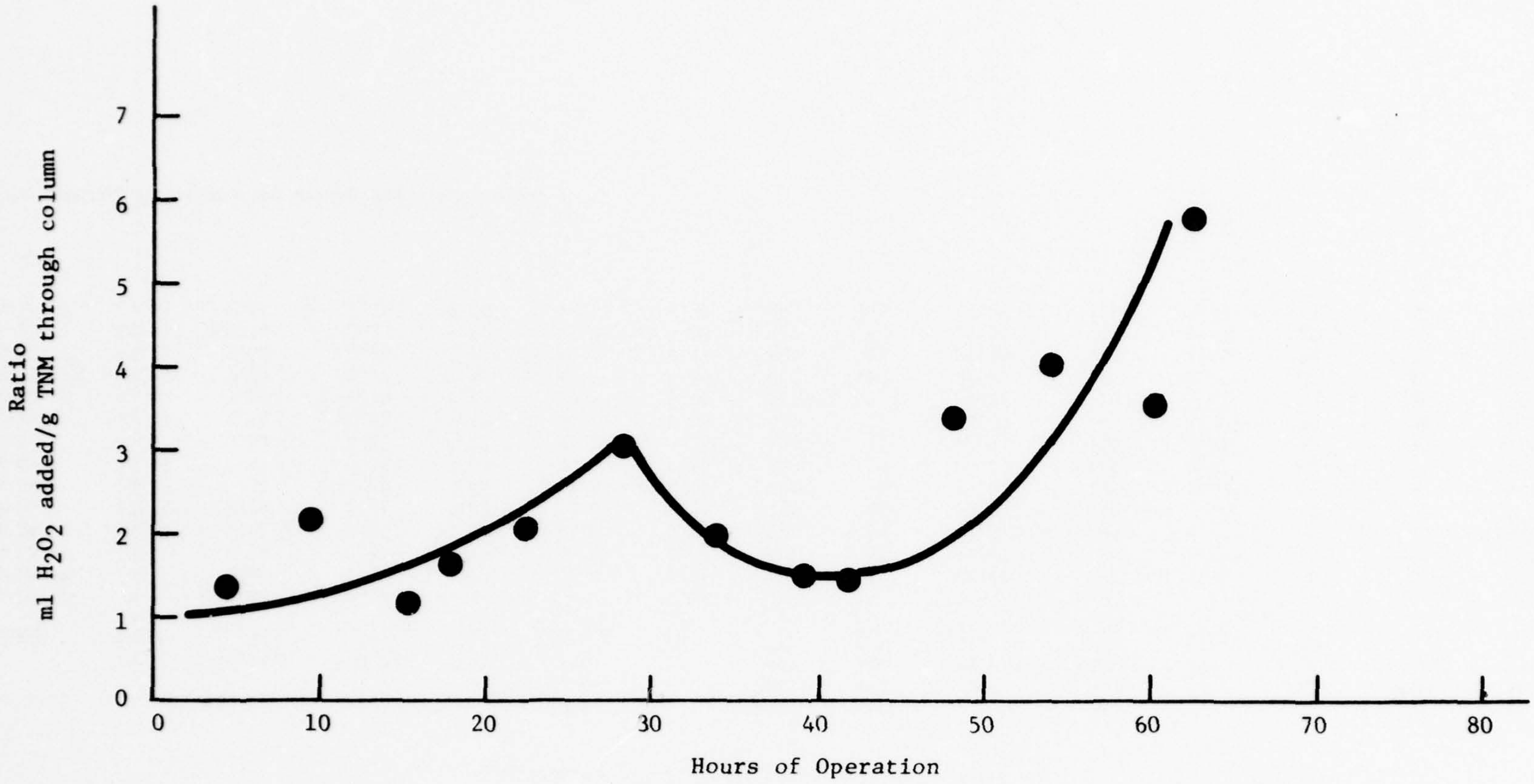


Figure 5. Ratio of ml of $H_2O_2$ added to grams of TNM through column versus time for extended run No. 2

Table 3

Summary of second extended column scrubbing run

| Date | Total Hours | $Na_2CO_3$, % | $NaHCO_3$, % | SNF, % | TNM Used per Day, g | pH | Inlet TNM, ppm (1) | Exit TNM, ppm (1) | TNM Removed, % | 50% $H_2O_2$ Added, ml | $H_2O_2$/TNM, ml/g | 50% NaOH Added, ml | $Na_2CO_3$ Added, g | Vol in Col, ml |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-18-77 | 0 | 2.66 | 0.07 | - | - | 10.95 | - | - | - | - | - | - | - | 4000 |
| 2-18-77 | 4.5 | 1.21 | 1.05 | 0.92 | 44.9 | 9.75 | 761 | 39 | 94.88 | 60 | 1.34 | 0 | 0 | 4000 |
| 2-25-77 | 9.5 | 1.39 | 0.57 | - | 36.6 | 10.05 | 807 | 59 | 92.69 | 80 | 2.19 | 17 | 0 | 4000 |
| 2-28-77 | 15.25 | 0.54 | 0.94 | 2.52 | 53.0 | 9.45 | 770 | 59 | 92.34 | 60 | 1.13 | 0 | 0 | 3950 |
| 3-2-77 | 17.75 | 0.29 | 0.86 | 2.85 | 24.4 | 9.30 | 770 | 66 | 91.43 | 40 | 1.64 | 0 | 0 | 3950 |
| 3-3-77 | 23.0 | 1.34 | 1.29 | 3.48 | 49.3 | 9.47 | 769 | 82 | 89.34 | 100 | 2.02 | 0 | 80 | 4000 |
| 3-4-77 | 28.25 | 0.97 | 1.18 | 4.63 | 48.9 | 9.45 | 740 | 85 | 88.51 | 150 | 3.07 | 0 | 0 | 4000 |
| 6-8-77 | 34.0 | 0.42 | 0.97 | 4.73 | 61.2 | 9.05 | 803 | 73 | 90.91 | 120 | 1.96 | 0 | 25 | 4000 |
| 6-9-77 | 39.25 | 0.74 | 0.97 | 5.57 | 61.0 | 9.65 | 880 | 67 | 92.39 | 90 | 1.48 | 30 | 20 | 4000 |
| 6-10-77 | 43.25 | 0.36 | 1.20 | 6.18 | 49.6 | 9.20 | 917 | 71 | 92.26 | 70 | 1.41 | 0 | 20 | 4000 |
| 6-13-77 | 48.25 | 1.75 | 0.77 | 7.42 | 62.6 | 9.65 | 872 | 92 | 89.45 | 210 | 3.35 | 30 | 40 | 3650 |
| 6-14-77 | 54.25 | 1.00 | 0.96 | 7.97 | 59.9 | 9.40 | 903 | 95 | 89.48 | 240 | 4.00 | 10 | 0 | 3350 |
| 6-21-77 | 60.50 | 0.54 | 0.83 | 9.42 | 68.7 | 9.06 | 889 | 95 | 89.31 | 245 | 3.57 | 20 | 0 | 2800 |
| 6-22-77 | 62.75 | 1.65 | 1.34 | 9.66 | 26.5 | 9.30 | 863 | 103 | 88.06 | 155 | 5.85 | 0 | 56 | 2800 |

(1) Average concentration during day's operation.

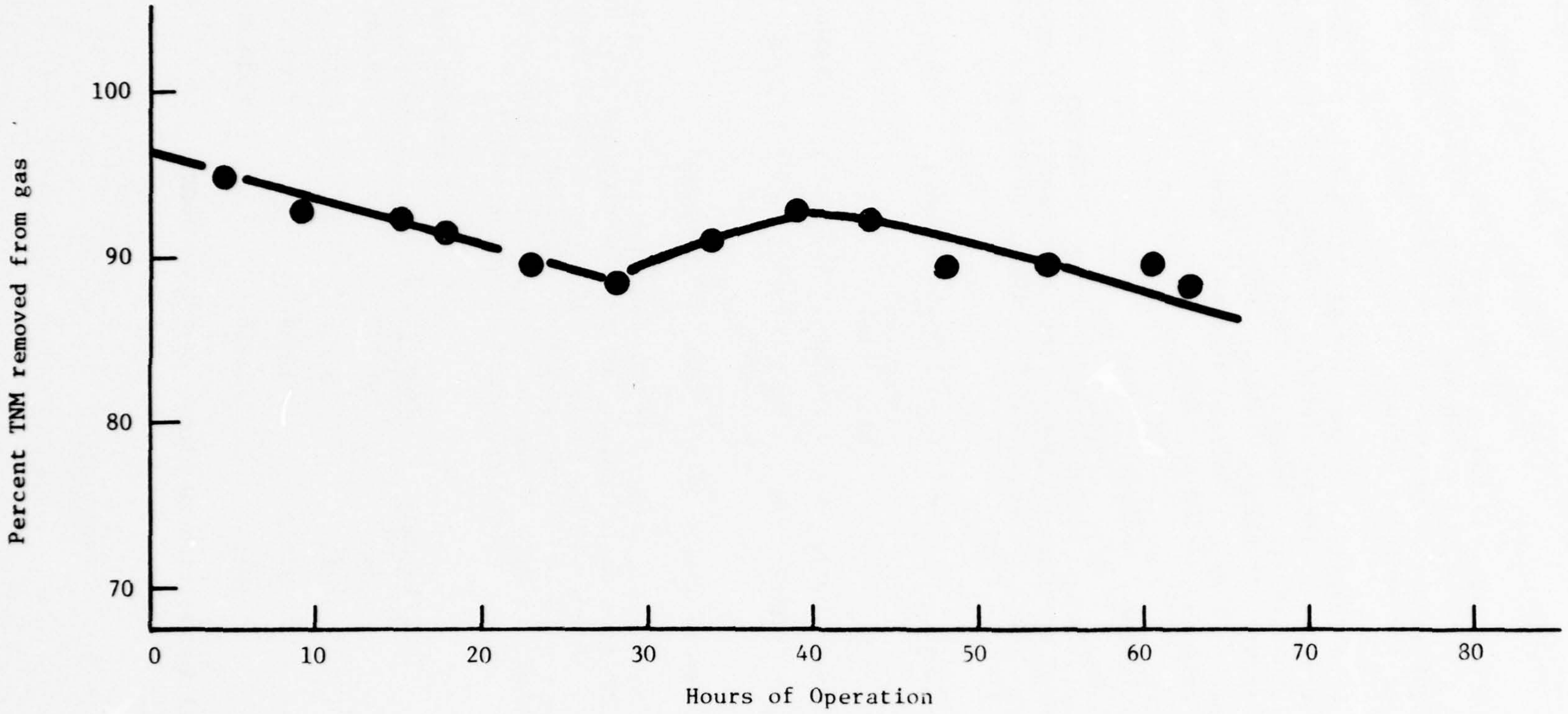


Figure 6. Gas scrubbing efficiency, extended run No. 2

The second extended run was shut down for 79 days. The SNF was 4.63 percent at the time of shutdown and 4.68 percent at the end of this period. The $Na_2CO_3$ was 1.18 percent and the $NaHCO_3$ was 0.97. These did not change during the shutdown period.

The above results show that the scrubbing solution can be stored for long periods of time without significant changes in the SNF content. This long-term stability is presumably attributable to the low level of $H_2O_2$ remaining in the scrubbing solution. Previous reports [5/] show that SNF is decomposed to form nitrite and presumably $Na_2CO_3$ in the presence of $H_2O_2$ for an extended period of time.

## III. POTENTIAL ECONOMIC ASPECTS

A cost analysis was performed on the usage of $Na_2SO_3$ versus $Na_2CO_3$-Albone DS $H_2O_2$ and NaOH-Albone DS $H_2O_2$ for the recovery of a relatively stable nitroform salt. The equations describing the reaction are shown below:

$$C(NO_2)_4 + Na_2SO_3 \rightarrow \underset{\text{Sulfonated* Nitroform}}{C(NO_2)_3SO_3Na} + NaNO_2$$

$$8\ C(NO_2)_4 + 9\ Na_2CO_3 \rightarrow 7\ NaC(NO_2)_3 + 7\ NaNO_3 + 4\ NaNO_2 + 10\ CO_2$$

$$3\ C(NO_2)_4 + 10\ NaOH \rightarrow 2\ NaC(NO_2)_3 + 4\ NaNO_2 + Na_2CO_3 + 2\ NaNO_3 + 5\ H_2O$$

*Further decomposition occurs with this compound.

The cost analysis was based on the manufacture of 204 kg per day (24 hours) of TNM from one nitration and purification building operating at a capacity of 454 Mg per day of TNT. Assuming entrained gases, CO, $CO_2$, NO, and $NO_x$ react with the scrubbing medium and column loss through vaporization result in only 50 percent efficiency, the cost of the essential ingredients for one day (24 hours) would be approximately:

| Chemical | Kilograms | Cost/kg, $ | Essential Ingredients Total Cost |
|---|---|---|---|
| $Na_2SO_3$ | 263 | 0.370 | $96.69 |
| $Na_2CO_3$ | 248 | 0.127 | $31.51 |
| NaOH | 278 | 0.384 | $103.67 |
| $H_2O_2$* | 1021 | 0.620 | $630.00 |

*Required in addition to either $Na_2CO_3$ or NaOH.

The $Na_2SO_3$ scrubbing system would remove 204 kg of TNM at a cost of $96.69 but no SNF would be available for conversion to NF. The $Na_2CO_3 + H_2O_2$ would remove the same amount of TNM at a cost of $661.51 and the NaOH - $H_2O_2$ at a cost of $733.67.

Assuming that all the TNM was converted to SNF according to the equations and that 90 percent of the SNF could be converted to NF, the cost per kg for essential ingredients would be $5.34 per kg using $Na_2CO_3$ - $H_2O_2$. The cost of NF from a foreign supplier was $26.50 per kg in 1975.

Additional processing cost would be incurred for utilities and labor but would be the same for all scrubbing systems. The cost of the conversion of SNF to NF has not been determined but the conversion would probably be performed by the purchaser.

## IV. CONCLUSIONS AND RECOMMENDATIONS

### A. Conclusions

1. The system NaOH-$H_2O_2$ is viable for the abatement of TNM and recovery of NF from a gas stream containing 750-1000 ppm TNM. The $Na_2CO_3$-$H_2O_2$ will also abate TNM but consumption of $H_2O_2$ increases drastically to maintain a 100 ppm level of TNM as the SNF salt concentration increases. This occurs because the high level of $CO_2$ in the fume gas stream reacts with $Na_2CO_3$ to produce $NaHCO_3$ which reacts slowly with TNM. Even with the NaOH system, $CO_2$ will be absorbed to produce $Na_2CO_3$ which in turn can react with additional $CO_2$ to form $NaHCO_3$. Therefore, NaOH is the preferred base and its consumption will increase over theoretical requirements.

2. Long-term stability tests have indicated that solutions of SNF with the concentration studied, were stable with little or no deterioration. Based on these results, shipment of these solutions to a purchaser for final processing to NF appears possible.

### B. Recommendations

Should the Army desire to recover NF for use in high energy propellant systems, on-line scrubbing studies would be required to determine control variables and SNF handling procedures. Further study of the neutralization and distillation areas would also be required if NF was the saleable end product.

# APPENDIX A

# LABORATORY ANALYSIS PROCEDURES

# CONTENTS

# Procedure A-1

## Gas Chromatographic Method for the Determination of Tetranitromethane in Air

# Gas Chromatographic Method for the Determination of Tetranitromethane in Air

## 1. SCOPE AND APPLICATION

1.1 This method is suitable for determining tetranitromethane (TNM) in gas streams with concentrations between 300 and 1200 ppm (v/v) TNM.

## 2. SUMMARY OF METHOD

2.1 Sample is taken directly from the gas stream using a gas syringe and injected directly into the chromatographic column.

## 3. INTERFERENCES

3.1 Any compounds in the gas stream that will elute from the gas chromatograph (GC) at the same time as the TNM will interfere with this test.

## 4. APPARATUS

4.1 1000 μl gas tight syringe.

4.2 Hewlett Packard Model 5750 GC equipped with a flame ionization detector and a 12 ft 1/8" stainless steel column packed with Chromosorb WHP 80-100 mesh coated with 10 percent UCW 98 silicone rubber.

4.3 Hewlett Packard Model 3370B Integrator.

## 5. CALIBRATION

5.1 Weigh approximately 4 g of TNM into a 25 ml volumetric flask which is half filled with carbon disulfide. Fill the flask to the mark with carbon disulfide.

5.2 Using a 25 μl syringe, inject 5 μl into a gas sampling tube with a known volume. Calculate the concentration of TNM in the sample tube using the following equation:

$$\text{PPM TNM} = \frac{\text{g TNM/25 ml } CS_2 \times V_1}{25{,}000 \times 196.03} \times \frac{0.08205 \times 293}{1} \times \frac{10^6}{V_2}$$

$V_1$ = μl injected into gas sample tube

$V_2$ = vol of gas sample tube in liters

5.3 Repeat 5.2 using 10 and 15 μl standards.

5.4 Inject a 500 μl sample from each sample tube into the GC and record the peak areas.

5.5 Prepare a graph of peak area versus TNM concentration.

## 6. PROCEDURE

6.1 Withdraw 500 μl of gas from the inlet side of the scrubber in a 1000 μl syringe and inject into the GC. Record the peak area and determine TNM concentration from the calibration graph.

## Procedure A-2

## Chemiluminescence Method for the Determination of Tetranitromethane in Air

# Chemiluminescence Method for the Determination of Tetranitromethane in Air

## 1. SCOPE AND APPLICATION

1.1 This method is suitable for measuring tetranitromethane (TNM) in gas streams with concentrations between 100 ppm and 1500 ppm TNM.

## 2. SUMMARY OF METHOD

2.1 A sample is removed from the gas stream and injected into the inlet side of the instrument. The TNM is converted to NO in the instrument and the resulting chemiluminescence generated with ozone is a measure of the TNM concentration.

## 3. INTERFERENCE

3.1 Any NO, $NO_2$ or material that can be converted to these species will interfere with this test.

## 4. APPARATUS

4.1 Model 10A self-contained chemiluminescent NO-$NO_x$ Gas Analyzer manufactured by Thermo-Electron Corporation.

4.2 Suitable strip chart recorder.

## 5. CALIBRATION

5.1 Weigh approximately 4 g of TNM into a 25 ml volumetric flask which is half filled with carbon disulfide. Fill the flask to the mark with carbon disulfide.

5.2 Using a 25 $\mu$l syringe, inject 5 $\mu$l into a gas sampling tube with a known volume. Calculate the concentration of TNM in the tube using the following equation:

$$\text{PPM TNM} = \frac{\text{g TNM/25 ml } CS_2 \times V_1}{25{,}000 \times 196.03} \times \frac{0.08205 \times 293}{1} \times \frac{10^6}{V_2}$$

$V_1$ = $\mu$l injected into gas sampling tube

$V_2$ = vol of gas sample tube in liters

5.3 Repeat 5.2 using 10 and 15 $\mu$l standards.

5.4 Inject a 500 $\mu$l sample using a 1000 $\mu$l syringe from each standard into the gas stream entering the instrument and record the peak height.

5.5 Prepare a graph of peak height versus concentration.

5.6 Set the instrument controls so that peak height is approximately three quarters maximum chart travel.

## 6. PROCEDURE

6.1 Remove a 500 µl sample using a 1000 µl syringe from the scrubber gas stream.

6.2 Inject the sample into the gas stream entering the instrument.

6.3 Measure peak height and determine TNM concentration directly from the calibration curve.

## Procedure A-3

## Miran II Infrared Spectrophotometric Method for the Determination of Tetranitromethane in Air

# Miran II Infrared Spectrophotometric Method for the Determination of Tetranitromethane in Air

## 1. SCOPE AND APPLICATION

1.1 This method is suitable for determining the concentration of tetranitromethane (TNM) in air.

## 2. SUMMARY OF METHOD

2.1 An air stream containing TNM is passed through the Infrared Analyzer which absorbs radiation at a set wavelength. The absorption of radiation is proportional to the TNM concentration.

## 3. INTERFERENCES

3.1 Any material in the gas stream that absorbs at the same wavelength as the TNM will interfere with the test.

## 4. APPARATUS

4.1 Miran II infrared analyzer equipped with a variable path length 20 meter sample cell with filters transmitting at 798 cm$^{-1}$ for TNM and 2564 cm$^{-1}$ as a reference. Windows are silver bromide and mirrors are gold coated. Instrument is manufactured by Wilks Scientific Corporation.

4.2 Vacuum pump

## 5. CALIBRATION

5.1 The Miran II analyzer sample cell is evacuated to an absolute pressure of 250 mm of mercury.

5.2 Inject one $\mu$l of TNM into the closed system and allow one minute for TNM to vaporize.

5.3 Slowly open the sample cell valve to reach atmospheric pressure. Record absorbance reading.

5.4 Repeat 5.1 through 5.3 using 2, 3 and 4 $\mu$l of TNM.

5.5 Determine TNM concentration using the following equation:

$$\text{PPM TNM} = \frac{\mu l \times 1.639\ \text{g/ml}}{196.03} \times \frac{0.08205 \times (273 + T)}{1\ \text{atm}} \times \frac{10^3}{V}$$

$\mu l$ = microliters of TNM injected

1.639 g/ml = density of TNM

196.03 g = molecular weight of TNM

0.08205 = gas constant

T = temperature of instrument °C

V = volume of instrument sample cell and connecting tubing in liters

## 6. PROCEDURE

6.1 Attach inlet side of instrument to sample port on exit side of column and allow a portion of exit gas to be flushed through the instrument by means of the vacuum pump. When instrument readings become steady, record absorbance.

6.2 Determine the TNM concentration directly from the calibration curve.

NOTE: Instrument settings must be the same for standards and samples.

Typical settings:

Path Length Dial = 9.05

Expansion = 1X

Zero Suppression = As necessary to zero instrument

Response = Fast

Meter = Diff, 0-1

# Procedure A-4

## Analysis of Sodium Nitroform by Ultraviolet Spectrophotometry

**HERCULES**
**POWDER COMPANY**

| | | | |
|---|---|---|---|
| HERCULES POWDER COMPANY | PROCEDURE MANUAL<br>Chemical Laboratories | Procedure No.<br>L- 102 | Policy No.<br>5 |
| | | Function No.<br>2.1.2 | Issue<br>1 |
| Radford Army Ammunition Plant<br>Radford, Virginia | Technical and Quality<br>Assurance Department | Page 1 of 6 | Date<br>12-18-74 |

**Statement of Function:** Analysis of Sodium Nitroform Salt By Ultraviolet Spectrophotometry

1. SCOPE

1.1 This document establishes the procedure for determining sodium nitroform content in liquid samples.

2. REQUIREMENTS

2.1 None

3. APPLICABLE DOCUMENTS

3.1 Laboratory Safety Manual

3.2 Operating Manual for Beckman DK-2 Ultraviolet spectrophotometer or equivalent

4. MATERIALS

4.1 Instrument Model DK-2 Beckman Ultraviolet spectrophotometer

4.2 Pipettes sizes 1 ml through 10 ml

4.3 100 ml volumetric flasks

4.4 1000 ml volumetric flasks

4.5 "Blue label" UV cells for DK-2

4.6 2 % sodium hydroxide solution (in water)

4.7 Tetranitromethane (TNM) for standards from Hummel Chemical Corporation)

4.8 Hydrogen peroxide (50%)

Approved: B. A. Walker Jr.
Chemical Laboratories Area Supervisor

W. T. Bolleter
Technical Director

4.9 125 microliter syringe

5. SAFETY

5.1 Safety glasses, flame resistant lab coats or coveralls, and conductive safety shoes shall be worn at all times.

5.2 Rubber gloves shall be worn when working with TNM.

5.3 All sampling of tetranitromethane shall be done in a hood with adequate ventilation.

6. OPERATION

6.1 Turn on instrument and tungsten lamp. Make sure knob is on TUNGSTEN LAMP and not on HYDROGEN LAMP.

6.2 Turn knobs beside cell holders on photomultiplier (IX).

6.3 Fill sample and reference cell with 2 % sodium hydroxide solution.

6.4 Set wavelength to 500A mμ

6.5 Open reference light and sample light.

6.6 Turn range to 0 - 1.

6.7 Turn to % T and adjust 100 % base line knob to 100 % reading.

6.8 Turn to A and adjust 0 % base line with zero adjust knob.

6.9 Set up instrument as follows:

A
Time Constant 0.1
0 % Adj:
100 % Adj:
Range 0 - 1
Do not adjust sensitivity.

6.10 Place sample in cell holder nearest front of instrument.

6.11 Place recording paper in instrument.

6.12 Set recorder pen to extreme right side and lower pen.

Approved:

Chemical Laboratories Area Supervisor

Technical Director

6.13 Set scan time on 2X, scale expansion to 1X from N and motors from N to IN.

6.14 Turn switch below wavelength knob to ON.

6.15 Let run until top of first peak comes off (near 340).

6.16 Turn scan switch OFF.

6.17 Turn motors to OUT.

6.18 Turn scale expansion to N and lift recording pen.

6.19 Replace sample with a new sample and start at 6.12 above, but this time only lower the pen.

6.20 Repeat as often as required to analyze all samples.

6.21 Preparation of Standard Curve.

6.21.1 Prepare a 100 ml volumetric flask containing approximately 75 ml of a 2 % NaOH solution and 0.5 % $H_2O_2$. Accurately weigh to nearest milligram.

6.21.2 Add 60 microliters of pure TNM to the flask. Perform all operations with TNM in a well ventilated hood. The solution will assume a lemon yellow coloration.

6.21.3 Reweigh accurately to get the weight of TNM added.

6.21.4 Make up the flask to 100 ml volume with a 2 % NaOH/0.5 % $H_2O_2$ solution.

6.21.5 Pipette 10 ml of the solution prepared into a 100 ml volumetric flask to get a 1:10 volumetric dilution. Mix thoroughly.

6.21.6 Prepare 100 ml volumetric flasks to contain each, 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 6 ml, 7 ml, 8 ml, 9 ml and 10 ml of the solution prepared in 6.21.5 above. Make up to the mark using 2 % NaOH solution.

6.21.7 These flasks contain the standards for preparing the Standard curve. Proceed to 6.1 above and measure absorbance with the Beckman DK-2 ultraviolet spectrophotometer.

6.21.8 A Standard curve (below) is used to measure sodium nitroform content in samples.

6.22 Analysis of Samples

6.22.1 Pipette and weigh 1 ml of sample into a 1000 ml volumetric flask. Make up to volume with 2 % NaOH. Use directly in sample cells.

6.22.2 Analyze the sample by the Beckman DK-2 ultraviolet spectrophotometer, starting in Step 6.1 above.

6.22.3 Measure the absorbance value obtained and determine the sodium nitroform concentration from the calibration curve.

**Approved:**

Chemical Laboratories Area Supervisor

Technical Director

## CALCULATIONS

Standards 60 µl weighed accurately is approximately 0.1033 gram
With 0.1033 g in 100 ml the concentration is 0.001033 g/ml. This sample is further diluted 10 ml to 100 ml to give 0.0001033 g/ml.

Aliquots are taken and diluted to 100 ml volume with 2 % NaOH to give the following concentrations:

| Aliquot | Concentration X $10^{-6}$ g/ml |
|---|---|
| 1 ml contains | 1.033 |
| 2 ml contains | 2.066 |
| 3 ml contains | 3.099 |
| 4 ml contains | 4.132 |
| 5 ml contains | 5.165 |
| 6 ml contains | 6.198 |
| 7 ml contains | 7.231 |
| 8 ml contains | 8.264 |
| 9 ml contains | 9.297 |
| 10 ml contains | 10.330 |

These concentrations are used to construct a standard curve of absorbance versus concentration.

Samples

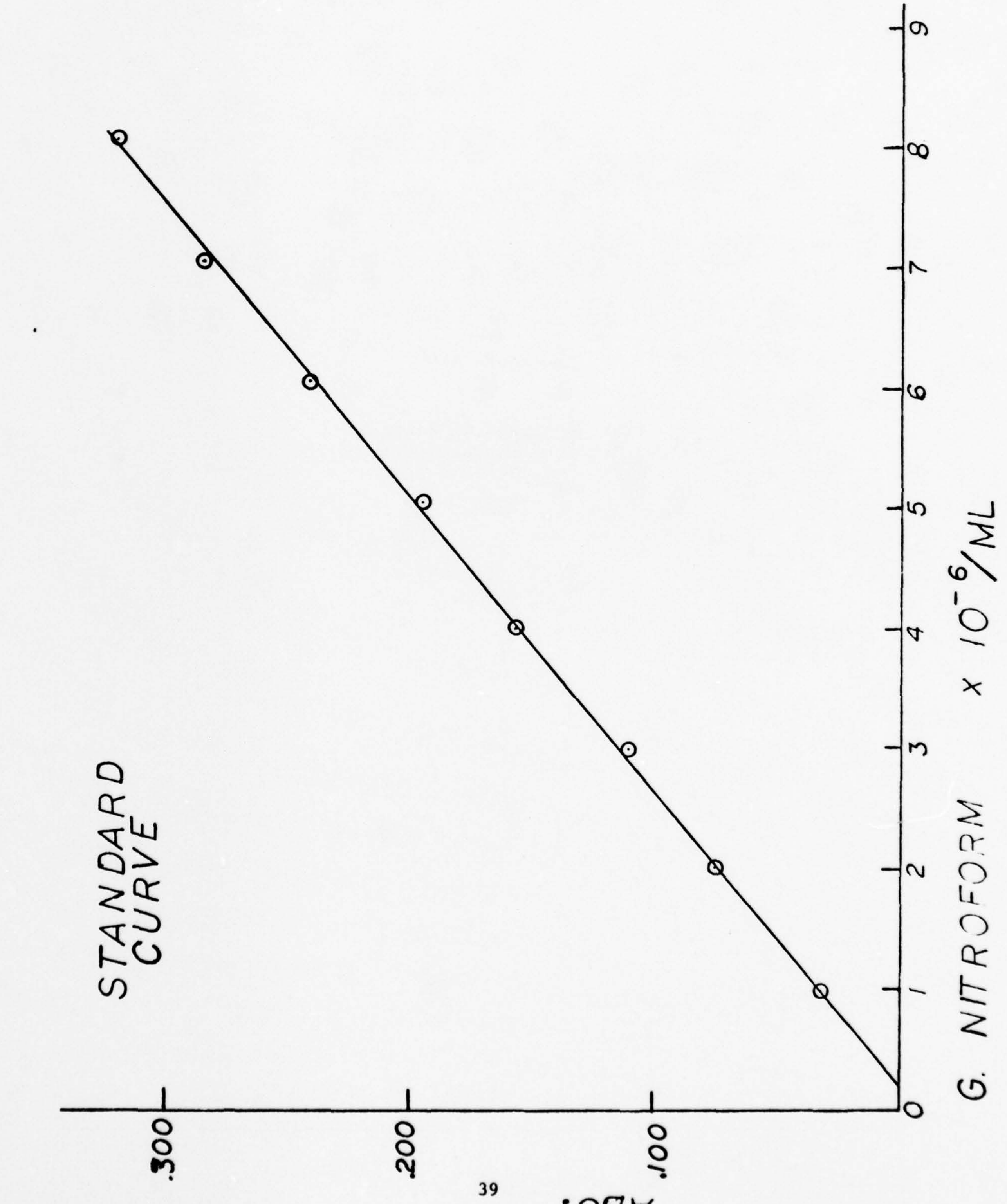
A 1 ml sample is accurately weighed and diluted to 1000 ml in a volumetric flask using 2 % NaOH. If the sample does not fall within the concentration range of the standard curve, other dilutions will be required. The absorbance is used to determine nitroform concentration on the standard curve.

$$\text{\% Nitroform salt} = \frac{\text{(conc. from curve) (dilution factor)(100)}}{\text{(Sample wt)}}$$

Approved:

Chemical Laboratories Area Supervisor

Technical Director


STANDARD
CURVE
ABS.
.300
.200
.100
0
1
2
3
4
5
6
7
8
9
G. NITROFORM x $10^{-6}$/ML

# Procedure A-5

# Nitrate Analysis of Water by Ultraviolet Spectrophotometric Method

L-101
November 14, 1974

# NITRATE ANALYSIS OF WATER BY ULTRAVIOLET SPECTROPHOTOMETRIC METHOD

**HERCULES INCORPORATED**

**RADFORD ARMY AMMUNITION PLANT**

**Prepared By:**

W. D. Wygal

**Reviewed By:**

R. A. Mundy

P. A. Walker, Jr.

**Approved By:**

T. G. Grady

HERCULES
POWDER COMPANY

| | | | |
|---|---|---|---|
| HERCULES POWDER COMPANY<br>Radford Army Ammunition Plant<br>Radford, Virginia | PROCEDURE MANUAL<br>Chemical Laboratories | Procedure No.<br>L-101 | Policy No.<br>5 |
| | | Function No.<br>2.1.2 | Issue<br>1 |
| | Technical and Quality<br>Assurance Department | Page 1 of 14 | Date<br>11/14/74 |

Statement of Function:

Nitrate Analysis of Water by Ultraviolet Spectrophotometric Method

## 1. SCOPE

1.1 This document establishes the procedure for determining nitrates in outfall water using the Ultraviolet Spectrophotometric Method.

## 2. REQUIREMENTS

| Outfall | Maximum mg/l Nitrates as N | Maximum mg/l Nitrites as N |
|---|---|---|
| 004 | 18 | - |
| 005 | 516 | - |
| 006 | 38 | - |
| 007 | 260 | 6 |
| 009 | - | 4 |
| 012 | 159 | 6 |
| 013 | - | 3 |
| 018 | 2,036 | 4 |
| 019 | 270 | - |
| 020 | 271 | - |
| 026 | - | - |
| 028 | - | - |
| Incinerator | - | - |

## 3. APPLICABLE DOCUMENTS

3.1 Instruction Manuals for Beckman Spectrophotometers Models DU and DK

3.2 Standard Methods for the Examination of Water and Wastewater, Method 133B

3.3 Authorization to Discharge Under the National Pollutant Discharge Elimination System, Permit No. Va 0000248

3.4 DUP 3786

3.5 Laboratory Safety Handbook

3.6 Laboratory Safety Manual, L-6

## 4. MATERIALS

4.1 Spectrophotometer Beckman Model DU, DK or equivalent w/photomultiplier attachment and hydrogen lamp source

4.2 Cells, matched silica, 1 cm or longer light path

4.3 Outfall water sample

4.4 Analytical balance

4.5 Filter paper, Glass fiber Type A, 47mm, Gelman Instrument Co.

4.6 Demineralized water

4.7 Volumetric flasks, 50 ml, 1000 ml

4.8 Stock nitrate solution: 721.8 mg potassium nitrate ($KNO_3$) dissolved in 1000 ml demineralized water = 100 mg/l = 100 ppm $NO_3$ as N

4.9 Standard nitrate solution: 100 ml of $KNO_3$ stock solution diluted to 1000 ml with demineralized water. 1 ml = 10 ppm $NO_3$ as N

4.10 Hydrochloric acid (HCl) solution, 1 N = 10 ml concentrated HCl diluted with 110 ml demineralized water

4.11 Aluminum hydroxide ($Al_2O_2.H_2O$)

4.12 Graph paper (20 x 20 to the inch)

4.13 Standard nitrite solution: 303.95 mg potassium nitrite ($KNO_2$) dissolved in 1000 ml demineralized water = 50 mg/l = 50 ppm $NO_3$ as N

4.14 Lens paper

4.15 DK recorder paper

5. SAFETY

5.1 Safety glasses, flame resistant coats or coveralls shall be worn at all times.

5.2 Use only undamaged glassware.

5.3 If acid is spilled on skin or clothing, wash off immediately with water.

5.4 Allow pipets to drain freely; never force solutions from pipets.

5.5 Use rubber suction bulb for drawing solutions into pipets.

6. OPERATION

6.1 DU Settings

Fig. 1

| | | | |
|---|---|---|---|
| Source Selector | (1) | - | Hydrogen |
| Power Switch | (14) | - | ON |
| Filament Temperature Switch | (15) | - | 2 |
| Photomultiplier Gain Switch | (16) | - | 4 |
| Phototube Selector | (3) | - | 700 - 900 |
| Lead Resistor Switch | (4) | - | Photomultiplier |
| Screen Bias Switch | (18) | - | 3 |
| Slit Control | (9) | - | 1.825 |
| Wavelength Selector | (13) | - | 220 mu, 275 mu |
| Function Switch | (12) | - | 0 - 100 |
| Tungsten Lamp Switch | (2) | - | ON |
| Transmittance-Absorbance Control | (11) | - | 0 - 100 |

6.2 Firing Hydrogen Lamp

6.2.1 Turn the Filament Temperature Switch to Warm-Up for about 30 seconds; then turn the switch to Position 1. After lamp is fired, turn the switch to the highest number at which the lamp is stable (Position 2 for this procedure). The lamp is fired when it emits a purple glow. If the lamp does not fire, turn the switch back to Warm-Up for a longer interval and try Position 1 again. Allow an hour for full stabilizing warm-up.

6.3 Preparation of Standards

6.3.1 Nitrate Standards

6.3.1.1 Prepare nitrate standards by diluting three or more volumes of the standard nitrate solution, plus 1 ml of 1 N HCl to 50 ml with demineralized $H_2O$. Use buret for measuring standard nitrate solution.

(a) Blank - 0 ml $KNO_3$ solution, 1 ml 1 N HCl, dilute to volume with $H_2O$

(b) 0.4 ppm - 2 ml $KNO_3$ solution, 1 ml 1 N HCl, dilute to volume with $H_2O$

(c) 0.8 ppm - 4 ml $KNO_3$ solution, 1 ml 1 N HCl, dilute to volume with $H_2O$

(d) 1.2 ppm - 6 ml $KNO_3$ solution, 1 ml 1 N HCl, dilute to volume with $H_2O$

(e) 2.0 ppm - 10 ml $KNO_3$ solution, 1 ml 1 N HCl, dilute to volume with $H_2O$

(f) 3.0 ppm - 15 ml $KNO_3$ solution, 1 ml 1 N HCl, dilute to volume with $H_2O$

6.3.2 <u>Nitrite Standards</u>

6.3.2.1 Prepare nitrite standards by diluting three or more volumes of the standard nitrite solution, plus 1 ml 1 N HCl to 50 ml with demineralized $H_2O$. Use buret for measuring standard nitrite solution.

(a) Blank - 0 ml $KNO_2$ solution, 1 ml 1 N HCl, dilute to volume with $H_2O$

(b) 1 ppm - 1 ml $KNO_2$ solution, 1 ml 1 N HCl, dilute to volume with $H_2O$

(c) 2 ppm - 2 ml $KNO_2$ solution, 1 ml 1 N HCl, dilute to volume with $H_2O$

(d) 3 ppm - 3 ml $KNO_2$ solution, 1 ml 1 N HCl, dilute to volume with $H_2O$

(e) 4 ppm - 4 ml $KNO_2$ solution, 1 ml 1 N HCl, dilute to volume with $H_2O$

6.3.3 <u>Other Standards</u>

6.3.3.1 When anionic surfactants or hexavalent chromium are known to be present in the sample, prepare correction curves for each of these substances at 2 mg/l intervals up to 10 mg/l. Use potassium dichromate ($K_2Cr_2O_7$), and linear alkylate sulfonate with demineralized water.

6.3.3.2 Measure the absorbances given by each substance at a wavelength of 220 mu against demineralized water and plot a separate curve for each.

### 6.4 Preparation of Standard Nitrate Curve

6.4.1 Rinse the reference cell several times with the nitrate blank; fill the cell with the blank.

6.4.2 Dry the cell with lens paper.

6.4.3 With the shutter closed, mount the cell in the sample positioner. (Always have the shutter closed when opening the sample compartment.)

6.4.4 Adjust the Dark Current Control to balance null meter. If the needle pegs left, turn the control clockwise; if the needle pegs right, turn the control counterclockwise. This sets the zero percent transmission level.

6.4.5 Turn the shutter switch to open and adjust the Sensitivity Control to balance the null meter as above. This sets the 100 percent transmission level.

6.4.6 With the sample positioner, place each nitrate standard, in turn, in the beam.

6.4.7 Turn the shutter switch to open.

6.4.8 Balance the null meter with the Adjust Transmittance-Absorption Control.

6.4.9 Read the absorbance of each nitrate standard at a wavelength of 220 mu.

NOTE: If the Dark Current is reset, the Sensitivity Control generally will require re-adjustment, and vice versa.

6.4.10 Plot the ppm nitrate as N against the absorbance at 220 mu.

### 6.5 Preparation of Nitrite Curve

6.5.1 Repeat steps 6.4.1 through 6.4.9 using the nitrite standards and blank.

6.5.2 Plot the ppm nitrite as N against absorbance at 220 mu.

6.6 Analysis of Sample

6.6.1 To approximately 100 ml of sample, add a small amount (dip stirring rod into bottle) of aluminum hydroxide.

6.6.2 Mix sample and filter through Glass fiber filter paper.

6.6.3 Pipet the required quantity of the sample into a 50 ml volumetric flask. (Use Table I as a guide.)

6.6.4 Add 1 ml of 1 N HCl solution to the sample.

6.6.5 Make the sample to volume with demineralized water and thoroughly mix.

6.6.6 Measure the absorbance at a wavelength of 220 mu to obtain the nitrate reading and at a wavelength of 275 mu to obtain the interference due to dissolved organic matter.

6.6.7 Subtract 2 times the absorbance reading at 275 mu from the absorbance reading at 220 mu.

6.6.8 Using the nitrite standard curve. convert the ppm nitrite (which has been determined by another method), if present, to absorbance at 220 mu, and subtract this value from the absorbance of the sample at 220 mu. Using this corrected absorbance, read the nitrate concentration from the nitrate standard curve. Correct for other known interferring materials in the same manner using the appropriate standard curve.

ppm Nitrate as N = net ppm Nitrate as N x dilution factor
ppm Nitrate as $NO_3$ = ppm Nitrate as N x 4.43

6.7 DK-2 Settings

| | | | | |
|---|---|---|---|---|
| Main Power Switch | (1) | Fig. V | - | ON |
| Detectors | (4) | Fig. IV | - | Photomultiplier and 20X |
| Hydrogen Lamp | (1) | Fig. V | - | ON |
| Operating Range Control | (13) | Fig. III | - | 0 - 100 |
| Sensitivity Control | (8) | Fig. III | - | 11 |
| Time Constant Selector | (10) | Fig. III | - | .6 |
| Wavelength Motor Control | (2) | Fig. II | - | Out |
| Scale Expansion Selector | (11) | Fig. II | - | Neutral |
| Scanning Time Selector | (3) | Fig. II | - | 5 |
| Wavelength Selector | (1) | Fig. II | - | 220 |
| Operation Selector | (9) | Fig. III | - | Absorbance |

6.7.1 Allow an hour for full stabilizing warm-up time.

6.8 Preparation of Standard Curves

6.8.1 Using standard nitrate and nitrite solutions as prepared in paragraphs 6.3.1 and 6.3.2 scan at 220 mu as follows:

6.8.2 When other interferring materials are known to be present, prepare standards according to Paragraph 6.3.3, measure the absorbance at 220 mu and plot a separate curve for each.

6.8.3 Make certain both sample and reference knobs are in off position anytime the sample compartment is opened.

6.8.4 Fill both cells with the blank or reference solution; rinse cell three times.

6.8.5 Dry the cells with lens paper.

6.8.6 Turn the wavelength to 220 mu.

6.8.7 Open the reference control; set the pen at zero on the chart with the zero knob.

6.8.8 Then open the sample control and set the pen at 100% on the chart with the 100% knob.

6.8.9 Repeat the zero and 100% setting operation.

6.8.10 Close both the sample and reference controls.

6.8.11 Fill the front cell with the standard material rinsing three times. Dry cell with lens paper.

6.8.12 Place the cell in position (front) and close the sample compartment.

6.8.13 Turn the wavelength control to 245 mu.

6.8.14 Open both the sample and the reference controls at the same time (prevents bumping of the pen at either extreme).

6.8.15 Turn the Scale Expansion to 1X; Wavelength Motor Control to In.

6.8.16 Set the pen on the chart.

6.8.17 Turn the switch to scan, and scan from 245 mu to 220 mu.

6.8.18 Lift the pen at exactly 220 mu.

6.8.19 Turn scan switch to stop and lift pen.

6.8.20 Close both the sample and reference at the same time.

6.8.21 Plot the ppm nitrate as N against the absorbance for each standard solution.

6.9 Analysis of Sample

6.9.1 Prepare sample according to Paragraph 6.6.

6.9.2 Measure the absorbance at a wavelength of 220 mu to obtain the nitrate reading and at a wavelength of 275 mu to obtain the interference due to dissolved matter.

6.9.3 Subtract 2 times the absorbance reading at 275 mu from the absorbance reading at 220 mu.

6.9.4 Using the nitrite standard curve, convert the ppm nitrite (which has been determined by another method), if present, to absorbance at 220 mu, and subtract this value from the absorbance of the sample at 220 mu. Using this corrected absorbance, read the nitrate concentration from the nitrate standard curve. Correct for other known interferring materials in the same manner using the appropriate standard curve.

ppm Nitrate as N = net ppm Nitrate as N x dilution factor
ppm Nitrate as $NO_3$ = ppm Nitrate as N x 4.43

## Table I

| Outfall | Dilution, ml of Sample | Dilution Factor |
|---|---|---|
| 004 | 25 - 50 | 2 - 1 |
| 005 | 10 | 5 |
| 006 | 25 - 50 | 2 - 1 |
| 007 | 1 | 50 |
| 009 | 25 - 50 | 2 - 1 |
| 012 | 1 | 50 |
| 013 | 1 - 5 | 50 - 10 |
| 018 | 10 - $NO_3$, 50 - $NO_2$ | 5 - 1 |
| 019 | 10 | 5 |
| 020 | 1 - 5 | 50 - 10 |
| 026 | 10 | 5 |
| 028 | 25 | 2 |
| Incinerator | 25 | 2 |

**NOTE**

To prevent noise and ensure *optimum performance, always* turn Photomultiplier Gain Switch to OFF position when using red-sensitive phototube.

Beckman Instruments, Inc.
Fullerton, California
September 1964 14TW602

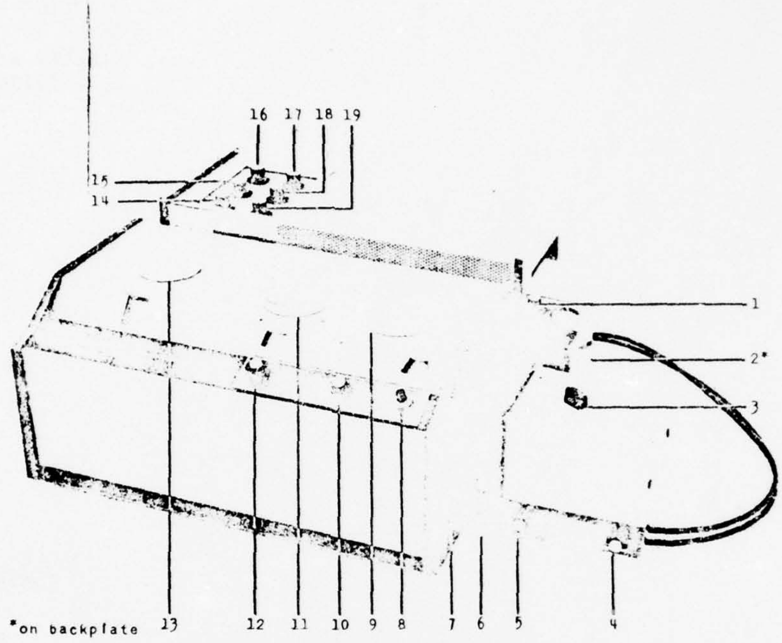


Figure I. Operating Controls

1. SOURCE SELECTOR
Selects either tungsten or hydrogen lamp source.

2. TUNGSTEN LAMP SWITCH
Turns tungsten lamp on and off.

3. PHOTOTUBE SELECTOR
Moves either blue-sensitive or photomultiplier or red-sensitive phototube into beam.

4. LOAD RESISTOR SWITCH
Selects proper load resistor for phototube.

5. SHUTTER SWITCH
Blocks beam from striking phototube.

6. SAMPLE POSITIONER
Positions sample and reference cells in beam.

7. FILTER POSITIONER
Positions filter or open aperture in beam.

8. SENSITIVITY CONTROL
Changes voltage across transmittance slidewire.

9. SLIT CONTROL
Selects spectral bandwidth.

10. DARK CURRENT CONTROL
Balances current flow in phototube when no energy is falling on cathode. Sets zero reference for transmittance-absorbance scale.

11. TRANSMITTANCE-ABSORBANCE CONTROL
Provides readout of spectral analyses. Controls electrical null-balance system of instrument.

12. FUNCTION SWITCH
Selects either of three ranges full scale and circuit functions.

13. WAVELENGTH SELECTOR
Selects desired wavelength. Scroll range: 185-2000 millimicrons. Normal operating range: 190-1000 millimicrons.

14. POWER SWITCH
Turns power supply on and off.

15. FILAMENT TEMPERATURE SWITCH
Controls power and varies filament temperature on hydrogen or mercury lamps.

16. PHOTOMULTIPLIER GAIN SWITCH
Adjusts sensitivity on photomultiplier tube.

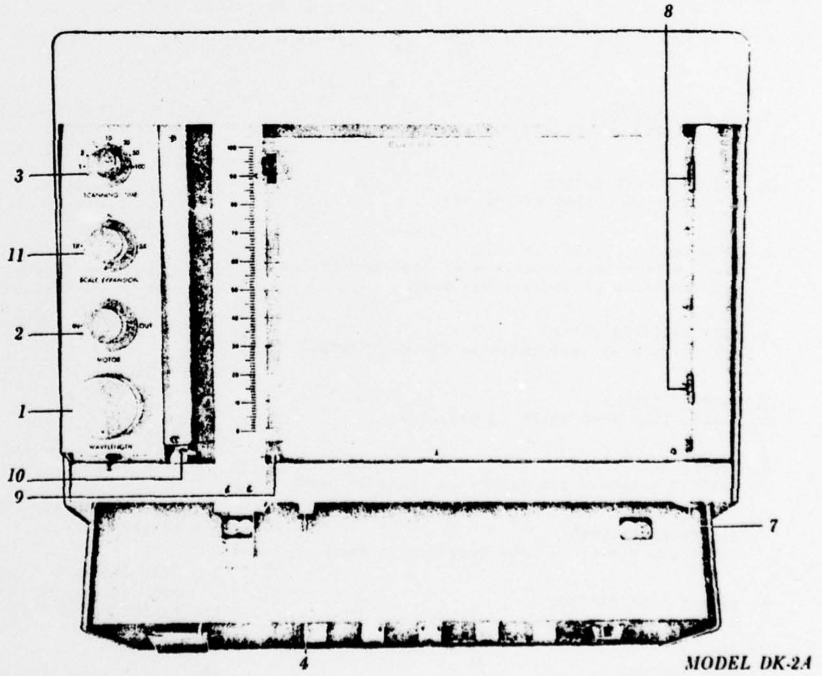
17. ZERO SUPPRESSION SWITCH
Applies bucking voltage to compensate for background energy effects in flame, fluorescence or reflectance measurements.

18. SCREEN BIAS SWITCH
Controls screen voltage on 2532 tube in spectrophotometer amplifier.

19. SOURCE CIRCUIT SWITCH
Selects correct circuit for either hydrogen or mercury lamps.

**Figure I**

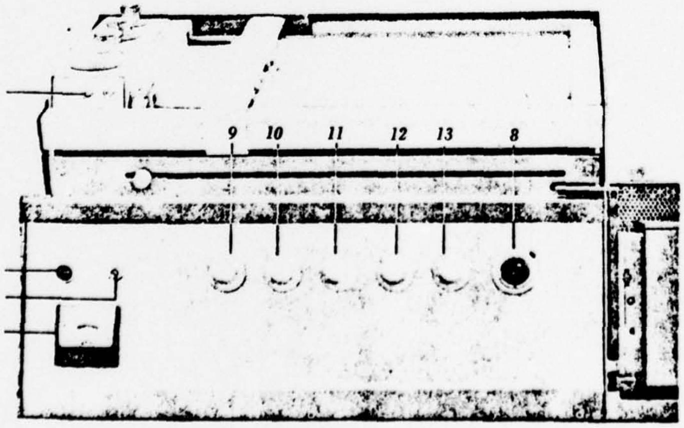
1. *WAVELENGTH SELECTOR*
   *Permits manual selection of wavelength.*
2. *WAVELENGTH MOTOR CONTROL*
   *Engages and disengages automatic wavelength drive.*
3. *SCANNING TIME SELECTOR*
   *Selects different scanning times.*
4. *SCAN LIMIT CONTROL*
   *Automatically stops scan at predetermined wavelength.*
5. *WAVELENGTH DRIVE SWITCH*
   *Turns off and reverses wavelength drive.*
6. *SLIT SERVO CONTROL*
   *Engages and disengages slit servo motor.*
7. *MANUAL SLIT CONTROL*
   *Enables manual selection of slit width.*
8. *CHART PAPER CLIP*
   *Holds right end of chart paper.*
9. *PEN LIFT LEVER*
   *Raises pen from chart.*
10. *CHART PAPER RETAINER*
    *Retains left end of chart paper.*
11. *SCALE EXPANSION SELECTOR*
    *Disengages wavelength drive from pen carriage drive; permits wavelength expansion and contraction of recorded spectral regions.*



Top Panel Controls

Figure II

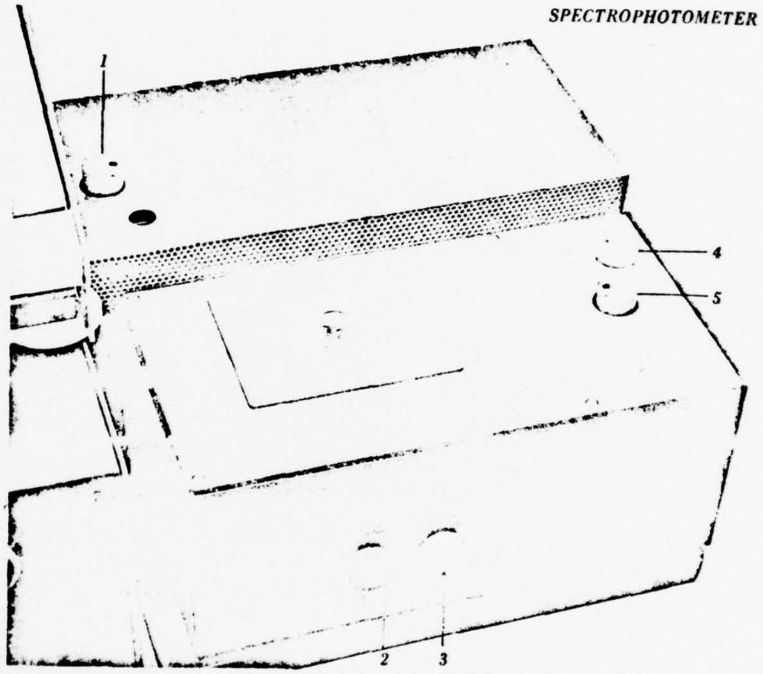
1. *REFERENCE*
   *ENERGY METER*
   *Shows reference channel and slidewire current; indicates operation of slit servo system during transmittance or absorbance scan.*
2. *MAIN*
   *POWER SWITCH*
   *Turns on and off all instrument power.*
3. *POWER*
   *INDICATOR LIGHT*
   *Glows when instrument is receiving power.*
4. *SCAN*
   *SWITCH*
   *Turns on and off the wavelength drive and recording system.*
5. *RECORDER*
   *POWER SWITCH*
   *Not shown, behind door; controls power to recorder.*
6. *CHART*
   *DRIVE SWITCH*
   *Starts and stops chart drive.*
7. *CHART*
   *DRUM KNOB*
   *Permits manual rotation of chart drum.*
8. *SENSITIVITY*
   *CONTROL*
   *Determines slit width for transmittance or absorbance operation; determines gain of system for energy operation.*
9. *OPERATION*
   *SELECTOR*
   *Determines operating mode: absorbance, transmittance or energy.*
10. *TIME CONSTANT*
    *SELECTOR*
    *Controls response time to change in signal level; settings of 0.1, 0.2, 0.6 and 2.0 are approximately equivalent to periods (in seconds) of 1.5, 2.0, 4.0 and 11.0, respectively.*
11. *ZERO*
    *ADJUST CONTROL*
    *Permits setting recorder pen to zero.*
12. *100%*
    *ADJUST CONTROL*
    *Permits setting recorder pen to 100%.*
13. *OPERATING*
    *RANGE CONTROL*
    *Controls ordinate expansion of signal—transmittance or absorbance.*



***MODEL DK-2A***

**Front Panel Controls**

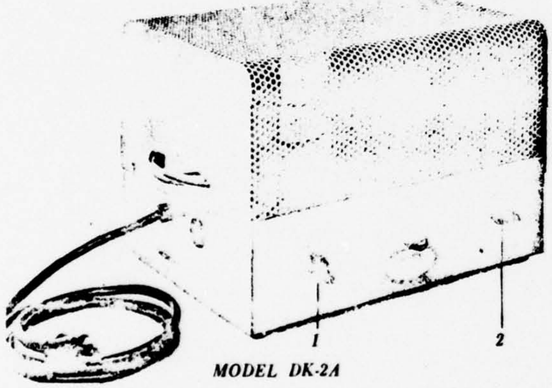
**Figure III**



1. *SOURCE*
   *SELECTOR*
   *Controls mirror for selection of sources.*
2. *SAMPLE*
   *SHUTTER CONTROL*
   *Blocks sample beam for setting zero base line.*
3. *REFERENCE*
   *SHUTTER CONTROL*
   *Blocks reference beam for setting rotating mirror in correct position for energy operation.*
4. *DETECTOR*
   *CIRCUIT SELECTOR*
   *Switches into circuit the lead sulfide cell or photomultiplier tube (two sensitivity settings).*
5. *DETECTOR*
   *BEAM SELECTOR*
   *Controls mirror to direct beam onto lead sulfide cell or onto photomultiplier tube.*
6. *TUNGSTEN*
   *LAMP SWITCH*
   *Controls power to tungsten lamp.*
7. *SLIT HEIGHT MASK*
   *AND*
   *FILTER CONTROL*
   *Used to adjust exit slit height and to interpose filter in exit beam.*

Lamphouse and Photometer Controls

**Figure IV**



1. *HYDROGEN LAMP POWER SWITCH*
   *Turns on and off all power to the unit (WARM setting of three-position switch is used when starting lamp).*
2. *HYDROGEN LAMP INTENSITY CONTROL*
   *Controls filament temperature of hydrogen lamp.*
3. *HYDROGEN LAMP STARTER BUTTON*
   *Starts arc in hydrogen lamp.*
4. *POWER INDICATOR LAMP*
   *Glows when power is supplied to unit.*

**Hydrogen Lamp Power Supply Controls.**
**On late-model instruments, the transistorized unit replaces the vacuum tube power supply.**

**Figure V**

## Procedure A-6

## Analysis of Sodium Carbonate and Hydrogen Peroxide in Sodium Nitroform Scrubber Solution

## Analysis of Sodium Carbonate and Hydrogen Peroxide in Sodium Nitroform Scrubber Solution

1. SOLUTIONS

1.1 HCl, 1/3 N

1.2 Hydrogen peroxide 1/10 strength. Dilute one part Albone DS 50 percent hydrogen peroxide with nine parts water (need not be exact).

1.3 Sodium arsenite, 0.25 N. Dissolve 16.24 g $NaAsO_2$ in water, add 20 ml 50 percent NaOH and dilute to one liter. To standardize, pipet exactly one ml of five percent hydrogen peroxide and titrate with $NaAsO_2$ solution as described in paragraph 3. Then pipet exactly one ml of the same hydrogen peroxide solution into a flask containing 50 ml water, 20 ml 1:1 $H_2SO_4$, 5 g KI, and three drops ammonium molybdate solution [2.5 g $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$ in 25 ml water, filtered if cloudy]. Stopper, swirl, let stand for five minutes and titrate with 0.2 N $Na_2S_2O_3$ to starch endpoint.

$$\text{N NaAsO}_2 = \frac{\text{ml Na}_2\text{S}_2\text{O}_3 \times \text{N Na}_2\text{S}_2\text{O}_3}{\text{ml NaAsO}_2 \text{ to titrate one ml H}_2\text{O}_2}$$

1.4 10 percent NaOH. Dilute 200 ml of 50 percent NaOH to one liter.

2. EQUIPMENT

2.1 Precision Scientific Company Auto-Aquatrator

3. DETERMINATION OF $Na_2CO_3$

3.1 Pipet two ml (or any suitable volume) of the sample into an aquatrator vessel which is about half full of water. Add two ml of five percent $H_2O_2$. Make the following instrument settings:

> With electrodes dry, set knob to "Direct Adjust" and adjust black needle to 20 $\mu$A. (Needs to be checked only occasionally.) Turn knob to "Direct Titrate." Set end point hold for 30 seconds. Set Burette Selector to Left Burette. Fill left burette with standard HCl.

3.2 Put sample under burettes, start stirrer, and be sure electrode wires are covered. Set red needles at 0 and 20 for the beginning of the titration. As the black needle moves down scale, reset the right-hand red needle to about two $\mu$A higher than the lowest point reached. For example, if the $\mu$A readout is 20→1 — 4, set the right-hand red needle at three. The actual settings will be determined by experience.

when the "START" light illuminates, read the burette and calculate $Na_2CO_3$ percent.

$$\% \; Na_2CO_3 = \frac{\text{ml HCl x N HCl x 5.3}}{\text{ml of sample}}$$

4. DETERMINATION OF $H_2O_2$

4.1 Pipet two ml (or any suitable volume) of the sample into an Aquatrator vessel which is about half full of water. Add 10 ml 10% NaOH. Make the following instrument settings:

> With electrodes dry, set knob to "Back Adjust" and adjust black needle to 20 $\mu$A. (Needs to be checked only occasionally.) Turn knob to "Back Titrate." Set Burette Selector to right Burette. Fill right burette with $NaAsO_2$ solution.

4.2 Put sample under burettes, start stirrer, be sure electrode wires are covered. Set red needles as necessary. (Try three and 14 to begin with.) The end point is reached when the black needle gives a low reading (probably below five $\mu$A) and has no tendency to revert to a higher reading between drops of titrant.

4.3 On back-titration the instrument adds titrant more slowly (in the region between the red needles) than it does in direct titration. The end point hold does not work in the back-titration mode; when the black needle moves to the left of the left red needle, the titration stops. The $H_2O_2$ percentage can be calculated as shown below:

$$\% \; H_2O_2 = \frac{\text{ml } NaAsO_2 \text{ x N } NaAsO_2 \text{ x 1.70}}{\text{ml of sample}}$$

# Procedure A-7

# Analysis of Tetranitromethane Scrubbing Solution for Sodium Carbonate and Sodium Bicarbonate Concentration

# Analysis of Tetranitromethane Scrubbing Solution for Sodium Carbonate and Sodium Bicarbonate Concentration

## 1. SCOPE AND APPLICATION

1.1 This method is suitable for the determination of sodium carbonate ($Na_2CO_3$) and sodium bicarbonate ($NaHCO_3$) concentrations in tetranitromethane (TNM) scrubber solutions.

## 2. SUMMARY OF METHOD

2.1 A sample of scrubber solution is diluted with distilled water and titrated using 0.3 N hydrochloric acid. The acid is added in small increments and after each add the pH is recorded. A plot of ml of acid versus pH is prepared and from the ml at the two points of inflection the concentrations of $Na_2CO_3$ and $NaHCO_3$ can be calculated.

## 3. REAGENTS

3.1 Distilled water

3.2 Standardized 0.3 N HCl

## 4. APPARATUS

4.1 pH meter

4.2 Magnetic stirrer

4.3 5 ml buret graduated in 0.02 ml

## 5. PROCEDURE

5.1 Pipet three ml of scrubber solution into 100 ml distilled water in a 250 ml beaker.

5.2 Place beaker on stirrer and position pH electrodes in sample.

5.3 Add 0.3 N HCl in 0.2 ml increments and record pH after each addition. As the end point is approached, allow more time between additions for the pH to stabilize.

5.4 When a pH of 3.5 is obtained, stop the titration.

5.5 On a standard graph paper, plot ml of HCl versus pH and draw a titration curve.

5.6 Determine the ml of HCl at the two inflection points.

## 6. CALCULATIONS

### 6.1 Calculation of $Na_2CO_3$

$$\frac{V_1 \times N \times 10.6}{3} = \text{Percent } Na_2CO_3$$

### 6.2 Calculation of $NaHCO_3$

$$\frac{(V_2 - 2V_1) \times N \times 8.4}{3} = \text{Percent } NaHCO_3$$

$V_1$ = Vol of HCl at first point of inflection (highest pH)

$V_2$ = Total vol of HCl at second point of inflection (lowest pH)

N = Normality of HCl solution

# Procedure A-8

# Determination of Nitrites

# Determination of Nitrites

## 1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of nitrite in drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The method is applicable in the range from 0.01 to 1.0 mg $NO_2$ as N/l.

## 2. SUMMARY OF METHOD

2.1 The diazonium compound formed by diazotation of sulfanilamide by nitrite in water under acid conditions is coupled with N-(1-naphthyl)-ethylenediamine to produce a reddish-purple color which is measured in a spectrophotometer at 540 nm.

## 3. SAMPLE HANDLING AND PRESERVATION

3.1 Samples should be analyzed as quickly as possible. They may be stored for 24 to 48 hours at 4°C.

## 4. INTERFERENCES

4.1 There are very few known interferences at concentrations less than 1,000 times that of the nitrite; however, the presence of strong oxidants or reductants to the samples will readily affect the nitrite concentrations. High alkalinity ($>$600 mg/1) will give low results due to a shift in pH.

## 5. APPARATUS

5.1 Spectrophotometer equipped with 1 cm or longer cells for use at 540 nm.

5.2 Nessler tubes, 50 ml or volumetric flasks, 50 ml.

## 6. REAGENTS

6.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.

6.2 Buffer-color reagent: To 250 ml of distilled water, add 105 ml conc. hydrochloric acid, 5.0 g sulfanilamide and 0.5 g N-(1-naphthyl) ethylenediamine dihydrochloride. Stir until dissolved. Add 136 g of sodium acetate ($CH_3COON_a \cdot 3H_2O$) and again stir until dissolved. Dilute to 500 ml with distilled water. This solution is stable for several weeks if stored in the dark.

6.3 Nitrite stock solution: 1.0 ml = 0.10 mg $NO_2$-N. Dissolve 0.4926 g of dried anhydrous sodium nitrite (24 hours in desiccator) in distilled water and dilute to 1000 ml. Preserve with 2 ml chloroform per liter.

6.4 Nitrite standard solution: 1.0 ml = 0.001 mg $NO_2$-N. Dilute 10.0 ml of the stock solution (6.3) to 1000 ml.

## 7. PROCEDURE

7.1 If the sample has a pH greater than 10 or a total alkalinity in excess of 600 mg/l, adjust to approximately pH 6 with 1:3 HCl.

7.2 If necessary, filter the sample through a 0.45 $\mu$ pore size filter using the first portion of filtrate to rinse the filter flask.

7.3 Place 50 ml of sample, or an aliquot diluted to 50 ml, in 50 ml Nessler tube; hold until preparation of standards is completed.

7.4 At the same time prepare a series of standards in 50 ml Nessler tubes as follows:

| ml of Standard Solution 1.0 ml = 0.001 mg $NO_2$-N | Conc., When Diluted to 50 ml, mg/l of $NO_2$-N |
|---|---|
| 0.0 (Blank) | 0.0 |
| 0.5 | 0.01 |
| 1.0 | 0.02 |
| 1.5 | 0.03 |
| 2.0 | 0.04 |
| 3.0 | 0.06 |
| 4.0 | 0.08 |
| 5.0 | 0.10 |
| 10.0 | 0.20 |

7.5 Add 2 ml of buffer-color reagent (6.2) to each standard and sample, mix and allow color to develop for at least 15 minutes. The color reaction medium should be between pH 1.5 and 2.0.

7.6 Read the color in the spectrophotometer at 540 nm against the blank and plot concentration of $NO_2$-N against absorbance.

## 8. CALCULATION

8.1 Read the concentration of $NO_2$-N directly from the curve.

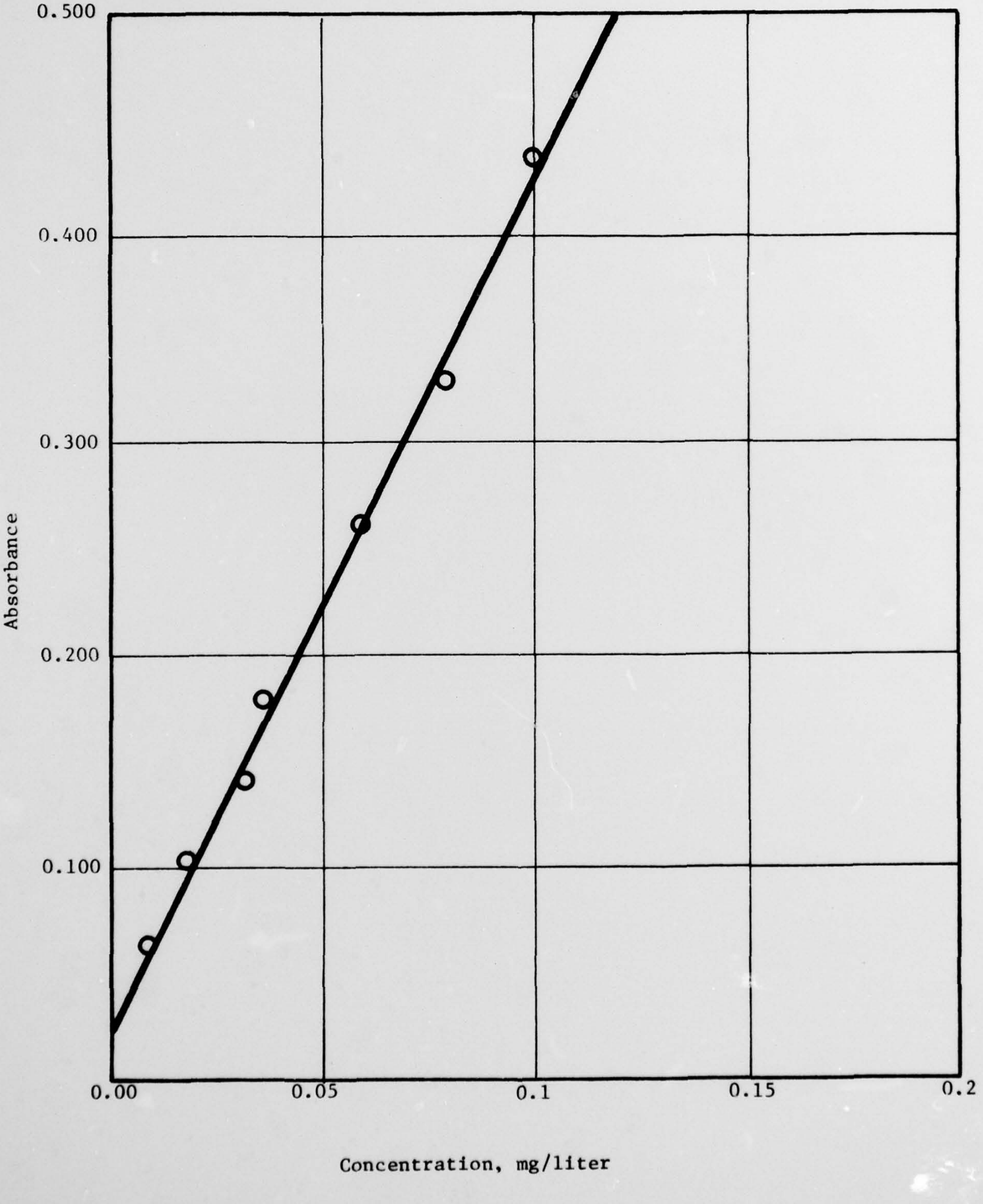
8.2 If less than 50.0 ml of sample is taken, calculate mg/l as follows:

$$NO_2\text{-N, mg/l} = \frac{\text{mg/l from standard curve} \times 50}{\text{ml sample used}}$$

## 9. PRECISION AND ACCURACY

9.1 Precision and accuracy data are not available at this time.

Nitrate Test
Spectrmic 20, Wave Length - 540 nm



# DISTRIBUTION LIST

Commander
US Army Armament Research
and Development Command
ATTN: DRDAR-LCE (15 cys)
DRDAR-TSS (5 cys)
DRDAR-LCM-E, R. Wolff
DRDAR-LCM-S, I. Forsten
Dover, NJ 07801

Commander
Naval Ammunition Depot
ATTN: R. Klausmeir
Crane, IN 47522

Commander
US Army Armament Materiel
Readiness Command
ATTN: DRSAR-RDM, G. Cowan
DRSAR-LEP-L
Rock Island, IL 61299

Commander
Radford Army Ammunition Plant
ATTN: W.T. Bolleter (15 cys)
Radford, VA 24141

Commander
Naval Surface Weapons Center
ATTN: T.N. Hall (4 cys)
White Oak Laboratory
Silver Spring, MD 20910

Commander
Naval Weapons Center
ATTN: A.T. Nielsen (2 cys)
China Lake, CA 93555

Commander
Naval Sea Systems Command
ATTN: A. Amster, SEA-0332
Washington, DC 20300

Commander
Chemical Systems Laboratory
ATTN: A. Hilsmeier (2 cys)
L. Schiff
Aberdeen Proving Ground, MD 21010

Commander
Army Medical Bioengineering
R&D Laboratory
ATTN: D. Rosenblatt
Fort Detrick, MD 21701

Commander (3 cys)
Volunteer Army Ammunition Plant
Chattanooga, TN 37401

Commander (3 cys)
Joliet Army Ammunition Plant
Joliet, IL 60436

Commander
US Army Armament Materiel Readiness Command
ATTN: DRCPM-PBM
Dover, NJ 07801

Commander
US Army Research Office
ATTN: G. Wyman (2 cys)
P.O. Box 12211
Research Triangle Park, NC 27709

John Brown Associates
ATTN: J. Brown
P.O. Box 145
Berkeley Heights, NJ 07922

Defense Documentation Center (12 cys)
Cameron Station
Alexandria, VA 22314

Director
US Army TRADOC Systems Analysis Activity
ATTN: ATAA-SL (Tech Library)
White Sands Missile Range, NM 88002

Weapon System Concept Team/CSL
ATTN: DRDAR-ACW
Aberdeen Proving Ground, MD 21010

Technical Library
ATTN: DRDAR-CLJ-L
Aberdeen Proving Ground, MD 21005

Technical Library
ATTN: DRDAR-TSB-S
Aberdeen Proving Ground, MD 21010

Technical Library
ATTN: DRDAR-LCB-TL
Benet Weapons Laboratory
Watervliet, NY 12189