

UNCLASSIFIED

AD NUMBER

AD366610

CLASSIFICATION CHANGES

TO: unclassified

FROM: confidential

LIMITATION CHANGES

TO:
Approved for public release, distribution unlimited

FROM:
Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; AUG 1965. Other requests shall be referred to Naval Ordnance Test Station, China Lake, CA.

AUTHORITY

NOTS ltr dtd 29 Jul 1976; NOTS ltr dtd 29 Jul 1976

THIS PAGE IS UNCLASSIFIED

THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

SECURITY

MARKING

The classified or limited status of this report applies to each page, unless otherwise marked.

Separate page printouts MUST be marked accordingly.

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECTIONS 793 AND 794. THE TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

366610

DDC FILE COPY

CONFIDENTIAL

GROUP 4
Downgraded at 3-year intervals;
declassified after 12 years.

NAVWEPS REPORT 8788
NOTS TP 3882
COPY 63

20

6

**GAS CHROMATOGRAPHIC ANALYSIS OF HYDRAZINE,
MONOMETHYLHYDRAZINE AND WATER
IN MIXED HYDRAZINE FUELS (4)**

8

9 Technical publication

10

Richard M. Jones,
Propulsion Development Department

11

Aug 65

12 20p.

Qualified request for report direct from DDC.

14 NOTS-TP-3882

ABSTRACT. A gas chromatographic procedure is described for the analysis of a mixture of hydrazine, monomethylhydrazine (MMH) and water

17 RMMP 24 / 080 / 216 FCCY / 060 / 02

Analyses were obtained by the use of a Perkin-Elmer Vapor Fractometer Model 154-C with a Leeds and Northrup recorder and an Instron integrator. A column packed with 10 percent Dowfax 9N9 on Teflon 6 was used. The elution of the peaks required about 7 minutes and the peaks appeared in the order of water, MMH, and hydrazine. The composition analyses were duplicated within ± 0.5 percent of the amount of the individual components present in a synthetic mixture. The synthetic mixture was prepared from materials which had been analyzed by the acidimetric method.
(UNCLASSIFIED)

3

18 NAVWEPS

19 8788



U. S. NAVAL ORDNANCE TEST STATION

China Lake, California

August 1965

25/100

CONFIDENTIAL

CONFIDENTIAL

U. S. NAVAL ORDNANCE TEST STATION

AN ACTIVITY OF THE BUREAU OF NAVAL WEAPONS

J. I. HARDY, CAPT., USN
Commander

WM. B. McLEAN, Ph.D.
Technical Director

FOREWORD

During the applied research stage of the development of liquid propellant systems it was necessary to develop a rapid and accurate analytical procedure for the determination of the composition of mixed hydrazine fuels (hydrazine, MMH, and water).

There are many procedures for the analysis of mixtures of hydrazines but they were found to be inadequate when used for analysis of hydrazine-MMH compositions because they did not separate these components adequately for the accurate analysis required for use with rocket fuels.

The presented gas chromatographic procedure is simple, rapid, and accurate to within ± 0.5 percent.

This report was reviewed for technical accuracy by Dr. W. R. Carpenter and E. M. Bens. The work was performed under BuWeps Task No. RMMP-24-080/216-1/F009-060-02.

Released by
CRILL MAPLES, Head,
Quality Assurance Div.
30 July 1965

Under authority of
G. W. LEONARD, Head,
Propulsion Development Dept.

NOTS Technical Publication 3882
NAVWEPS Report 8788

Published by Propulsion Development Department
Collation Cover, 11 leaves, DD Form 1473, abstract cards
First printing 235 numbered copies
Security classification CONFIDENTIAL
Abstract alone UNCLASSIFIED
Title alone UNCLASSIFIED

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECTIONS 793 AND 794. THE TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.
REPRODUCTION OF THIS DOCUMENT IN ANY FORM BY OTHER THAN NAVAL ACTIVITIES IS NOT AUTHORIZED EXCEPT BY SPECIAL APPROVAL OF THIS STATION

CONTENTS

Introduction	1
Experimental	1
Apparatus	1
Column Preparation	1
Sample Preparation	3
Analytical Procedure	3
Calculations	5
Discussion	7
Conclusions	15
Appendixes:	
A. Procedure for Acidimetric Analysis of Hydrazines	16
B. Gas Chromatographic Procedure for Analysis of Mixed Hydrazine (Hydrazine and MMH) and Water	18
References	20

 Figures:

1. Gas Chromatograph and Equipment	2
2. Reciprocal Response Ratios of Water to Hydrazine	6
3. Resolution of a Typical Mixture of Hydrazines and Water by 15 Percent Triethanolamine on KOH Washed Chromosorb W	8
4. Resolution of a Typical Mixture of Hydrazines and Water by 10 Percent Dowfax 9N9 on Teflon 6	11
5. Resolution of MHF-3 Fuel by 10 Percent Dowfax 9N9 on Teflon 6	12

 Tables:

1. Percent Composition and Reciprocal Response Ratios of Water to Hydrazines	4
2. Retention Times of Hydrazines - Water Mixtures (110°C at 40 ml/min)	10
3. Reproducibility of Analysis	13

 NEGATIVE NUMBERS OF ILLUSTRATIONS

FIG. 1, LHL 106216; FIG. 2, LHL 105476; FIG. 3, LHL 105750;
 FIG. 4, LHL 105477; FIG. 5, LHL 105478.

ACKNOWLEDGMENT

The author is indebted to Dr. W. R. Carpenter and E. M. Bens of the Research Department for their assistance and advice in the development and evaluation of this chromatographic procedure.

INTRODUCTION

Hydrazine and monomethylhydrazine (MMH), being chemically similar and highly reactive compounds, have been difficult to analyze when present in the same mixture. There are many procedures available for the determination of water in hydrazines (Ref. 1, 2, and 3). There are a few gas chromatographic procedures in use for mixtures of hydrazine, MMH, and water; however, these procedures were found to be complicated and lengthy and without the accuracy required for the analysis of rocket fuels. The hydrazines, because they are strong bases and reducing agents, cause deterioration of the column material resulting in poor column stability.

The method of chromatographic separation of mixtures containing hydrazine, MMH, and water described in this report utilizes a column of 10 percent Dowfax 9N9, a product of Dow Chemical Company, Midland, Michigan, on Teflon 6, a product of E. I. duPont de Nemours and Company, Inc., Wilmington, Delaware. This procedure was adapted from a description of the separation of amines and amides with Dowfax 9N9 as the liquid phase (Ref. 4 and 5). This procedure as developed for analysis of mixed hydrazine fuels of hydrazine, MMH, and water proved simple, rapid, and accurate with excellent column stability.

EXPERIMENTAL

APPARATUS

All analyses were performed with a Fractometer (Perkin-Elmer Corp., Norwalk, Connecticut, Model 154-C Vapor Fractometer) using a dual chamber thermistor thermal conductivity cell. Chromatograms were recorded on a 5 millivolt (mv) full scale recorder (Leeds & Northrup Co., Philadelphia, Pennsylvania) at a chart speed of 1/2 inch per minute. An Instron integrator, two-counter model (Instron Engineering Corp., Canton, Massachusetts) was used to integrate the eluted peaks (Fig. 1).

COLUMN PREPARATION

The column materials were Dowfax 9N9 and Teflon 6. The chemical composition of Dowfax 9N9 is:

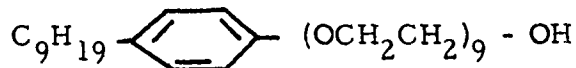




FIG. 1. Gas Chromatograph and Equipment.

The column was prepared by air drying a slowly stirred slurry of Dowfax 9N9 and Teflon 6 in methanol in amounts necessary to produce a 10 percent Dowfax 9N9 coating. The material was further dried in a vacuum oven at 100°C, chilled, screened through a 30-mesh sieve and carefully packed into a 6-foot stainless steel tube, 1/4-inch outside diameter (OD). The packing weight was about 22 grams. The column was then stabilized overnight at 150°C with a 20 milliliter (ml) per minute helium flow rate. The column was then conditioned to each day's use by one or more injections of about 10 μ l of hydrazine.

SAMPLE PREPARATION

The known composition mixtures were prepared from hydrazine and MMH materials from Olin Chemical Co., Lake Charles, Louisiana. The hydrazines were purchased in accordance with Military Specifications (Ref. 6 and 7).

Samples of hydrazine and MMH were analyzed by the acidimetric method (Appendix A and Ref. 8). Analyses of 97.0 \pm 0.2 percent hydrazine and 90.9 \pm 0.2 MMH were obtained. These samples were used for the preparation of the first known composition mixtures. Later analyses were made of samples from a new supply; the results were 98.6 \pm 0.2 percent hydrazine and 99.4 \pm 0.2 percent MMH. These materials were used for the preparation of MHF-3, Bell Aero Fuels (BAF) (Bell Aero Systems, Inc., Buffalo, New York) and the typical mixture.

The known composition mixtures were prepared by adding different weighed amounts of water to hydrazine and to MMH and by mixing hydrazine, MMH, and water in various percentages (see Table 1).

ANALYTICAL PROCEDURE

The separation of hydrazine, MMH, and water was obtained by injection of a sample of approximately 5 μ l using a Hamilton 10 μ l microsyringe. The attenuation settings were determined from the estimated sample percent composition. A column temperature of 110°C and a helium flow rate of 40 ml per minute were maintained. All the peaks were eluted after about 7 minutes. An additional 10 minutes was allowed before the next analysis to let the baseline stabilize. The procedure is described in Appendix B.

TABLE 1. Percent Composition and Reciprocal Response Ratios of Water to Hydrazines

Sample	Percent component			Ratio H ₂ O = 1	
	MMH	H ₂ O	N ₂ H ₄	H ₂ O/MMH	H ₂ O/N ₂ H ₄
1	...	1.36	98.64	...	0.74 ^a
2	...	2.97	97.03	...	0.56 ^a
3	...	11.50	88.50	...	1.05 ^a
4	...	30.64	69.36	...	1.06 ^a
5	...	50.49	49.51	...	1.04 ^a
6	99.36	0.64	...	1.03 ^b	...
7	90.85	9.15	...	0.67 ^b	...
8	83.41	16.59	...	1.15 ^b	...
9	64.24	35.76	...	1.17 ^b	...
10	45.65	54.35	...	1.20 ^b	...
11	27.57	72.43	...	1.18 ^b	...
12	14.46	3.77	81.77	0.60	0.68
13	25.53	4.55	69.92	0.69	0.80
14	29.13	4.80	66.07	0.59	0.60
15	45.89	5.98	48.13	0.65	0.60
16	53.08	6.49	40.43	0.68	0.61
17	68.73	7.58	23.69	0.68	0.55
18	80.88	8.45	10.67	0.72	0.53
19	85.47	0.75	13.78	1.35	1.19
20	40.36	25.00	34.64	1.24	1.18
21	48.67	20.86	30.47	1.29	1.22

^aRatio of water to hydrazines for samples 1 through 5 were used in Fig. 2.

^bRatio of water to MMH for samples 6 through 11 were used in Fig. 2.

CALCULATIONS

The relative response ratio method of calculating percent composition of samples was used in this study. This method of determining percent composition was used because of its accuracy and property of being independent of variations in temperature, sample size, carrier gas flow rate and type of thermal conductivity detector used (Ref. 9 and 10).

The relative response of each component compared to water was determined from mixtures of known composition of the hydrazines and water. To simplify the calculation of reciprocal response ratios, the reciprocals of the relative response ratios were employed. These reciprocal response ratios were then used to calculate the composition of samples being analyzed. The reciprocal responses were calculated from the formula:

$$R = \frac{CA}{W}, \quad r_h = \frac{R_w}{R_h}, \quad r_m = \frac{R_w}{R_m}, \quad r_w = 1 \text{ by definition}$$

where:

- R = response
- C = integrator counts
- A = attenuation
- r = reciprocal response ratio
- h = hydrazine
- m = MMH
- w = water
- W = weight

The reciprocal responses are shown in Table 1 and Fig. 2. These ratios were determined from an average of at least three analyses. The percentage compositions were calculated by the following formula, which is given in this case, for hydrazine.

$$\% \text{ hydrazine} = \frac{C_h A_h r_h \times 100}{C_h A_h r_h + C_m A_m r_m + C_w A_w r_w}$$

Analogous formulas were used for other components.

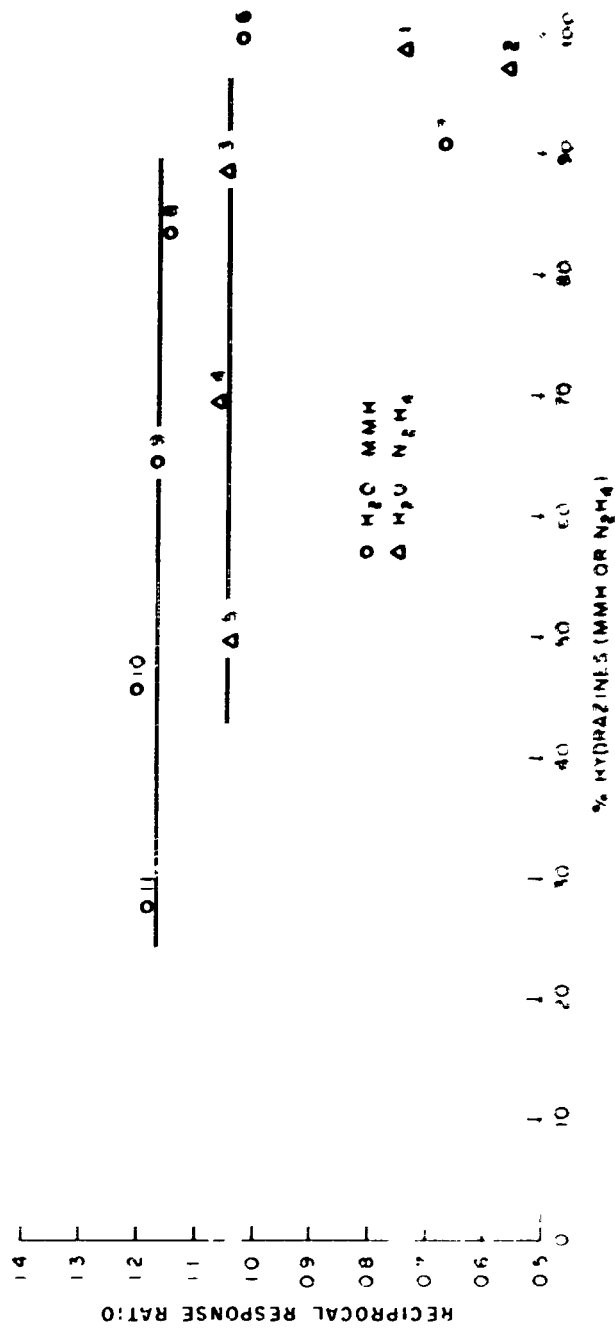


FIG. 2. Reciprocal Response Ratios of Water to Hydrazine.

The calculated responses were based on prepared mixtures of known composition and depend on the acidimetric analysis of the hydrazine and MMH which is accurate to about ± 0.2 percent.

DISCUSSION

An acidimetric analysis was used for the assay of the original hydrazine and MMH materials because the procedure is simple, rapid and the degree of accuracy is adequate, if impurities which are basic in reaction are not present in significant amounts. The iodimetric method (Ref. 8) was used as a check of the acidimetric procedure to determine the level of basic nonreducing impurities, which would interfere with the calculations. Since this method duplicated the acidimetric analysis of the hydrazine and gave values of 3 to 4 percent higher in the MMH analysis, it indicated that the basic nonreducing impurities were not present in significant amounts. The gas chromatographic analysis indicated that the acidimetric analysis of MMH was more accurate than the iodimetric method.

In Table 1 and Fig. 2 the reciprocal response ratios showed only slight variations with changes in water down to the 10 percent level. Below this, small errors in the calculated amount of water created large errors in the calculated reciprocal response ratios.

It is apparent that in the region of from 2 to 10 percent water the reciprocal response ratios for both hydrazine and MMH are low; however, below 2 percent water these ratios become higher. Nevertheless, these values still give calculated percent compositions which compare favorably with acidimetric analysis because errors involved only a small percentage of the sample.

Correspondence from G. D. Lake, AFPCL, Vandenberg AFB, California and the Olin Chemical Co. stated that they were using a Fractometer with a column of 15 percent triethanolamine on potassium hydroxide (KOH) washed Chromosorb W. The author prepared a similar column which proved to be adequate and did separate unsymmetrical dimethylhydrazine (UDMH) from hydrazine, MMH, water mixture (Fig. 3). This column had the disadvantages of long retention for the hydrazine, rapid column fatigue and incomplete separation of water and MMH.

The attenuations for the triethanolamine column using about a μl sample were 32X, 16X, 16X, and 8X for UDMH, water, MMH, and hydrazine, respectively (Fig. 3).

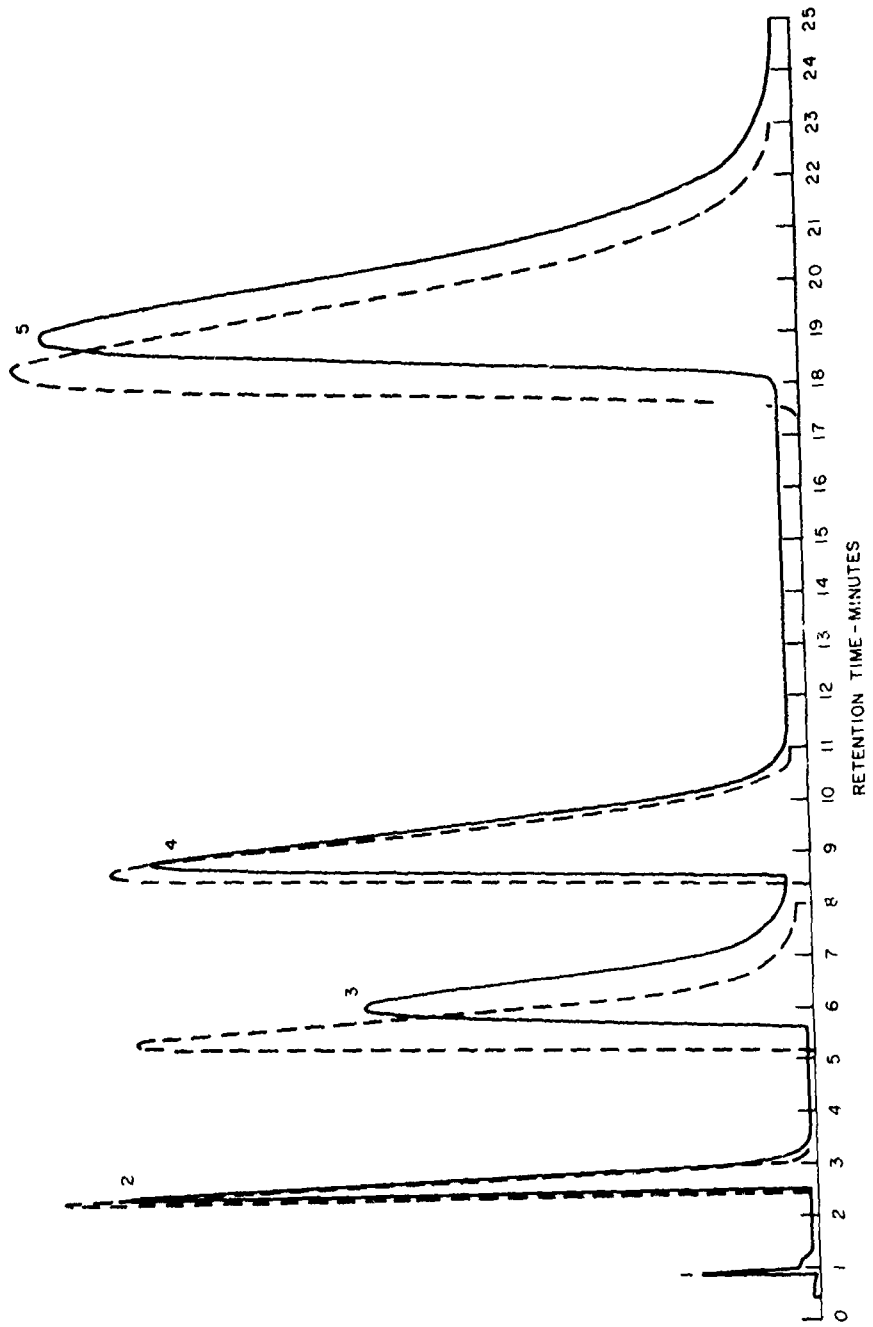


FIG. 3. Resolution of a Typical Mixture of Hydrazines and Water by 15 Percent Triethanolamine on KOH Washed Chromosorb W.
Identification of Peaks: 1. Air, 2. UDMH, 3. Water, 4. MMH, 5. Hydrazine.
-- Individual component run.
— Mixed component run (16.6% UDMH, 24.6% Water, 31.9% MMH, 26.9% hydrazine).

The Bell Aero Systems, Inc., in correspondence, stated they were using dual columns of 15 percent tetrahydroxyethylenediamine (THEED), 15 percent Carbowax 400 on Chromosorb W (60 to 80 mesh) with a program temperature control. They stated that this column required about 30 minutes elution time. Since no chromatogram was shown, the degree of separation could not be determined.

In the proposed Military Specification for MHF-3 (Ref. 11) a 30 percent Quadrol, N, N, N', N' - tetrakis (2 hydroxypropyl) ethylenediamine on firebrick was the suggested column. Work on similar columns by E. M. Bens of the Research Department indicated poor separations and long retention times of hydrazines when compared to the Dowfax 9N9 column.

In developing a workable column for the analysis of hydrazine, MMH, and water mixtures, several columns were prepared and tested. The first was a column prepared as described in Ref. 4 with 10 percent Dowfax 9N9 and 1 percent sodium hydroxide on Chromosorb W. This column did not separate water from MMH. A second column was prepared with 10 percent Dowfax 9N9 and 1 percent sodium hydroxide on Teflon 6 (Ref. 12). This column partially separated water from MMH, but not sufficiently for good analysis. A third column was prepared as described in the column preparation section with 10 percent Dowfax 9N9 on Teflon 6 without sodium hydroxide. This column separated the three components sufficiently for good analysis with only a slight increase in hydrazine tailing. An interesting feature of this analysis was the shifting of retention times of the components depending on whether each one is injected separately or in mixtures. This anomaly is shown in Fig. 4 and 5.

The peaks were eluted in the order of air, ammonia, water, MMH, and hydrazine. The retention times were approximately 2, 3, and 4-1/2 minutes for water, MMH, and hydrazine, respectively (Table 2 and Fig. 4 and 5).

The chromatogram shows the presence of air and ammonia which could be present as an impurity in the sample or as a result of decomposition of the hydrazine upon injection into the Fractometer. This decomposition was particularly evident at a high injector temperature used in some of the early work. The injector temperature in the analysis in this study was near the temperature (110°C) of the column. The amount of ammonia is small (less than 1 percent) and was found to have no significant effect on the relative response ratios.

TABLE 2. Retention Times of Hydrazines - Water Mixtures.
(110°C at 40 ml/min)

Mixture	Component	Retention time, ^a min
1	Water (10%)	2.0
	MMH (90%)	3.2
2	Water (3%)	2.0
	N ₂ H ₄ (97%)	4.4
3	Water (25%)	2.2
	MMH (40%)	3.4
	N ₂ H ₄ (35%)	5.0
4	Water (1.6%)	4.0
	MMH (84.1%)	3.1
	N ₂ H ₄ (14.3%)	. 6

^aRetention times measured from injection.

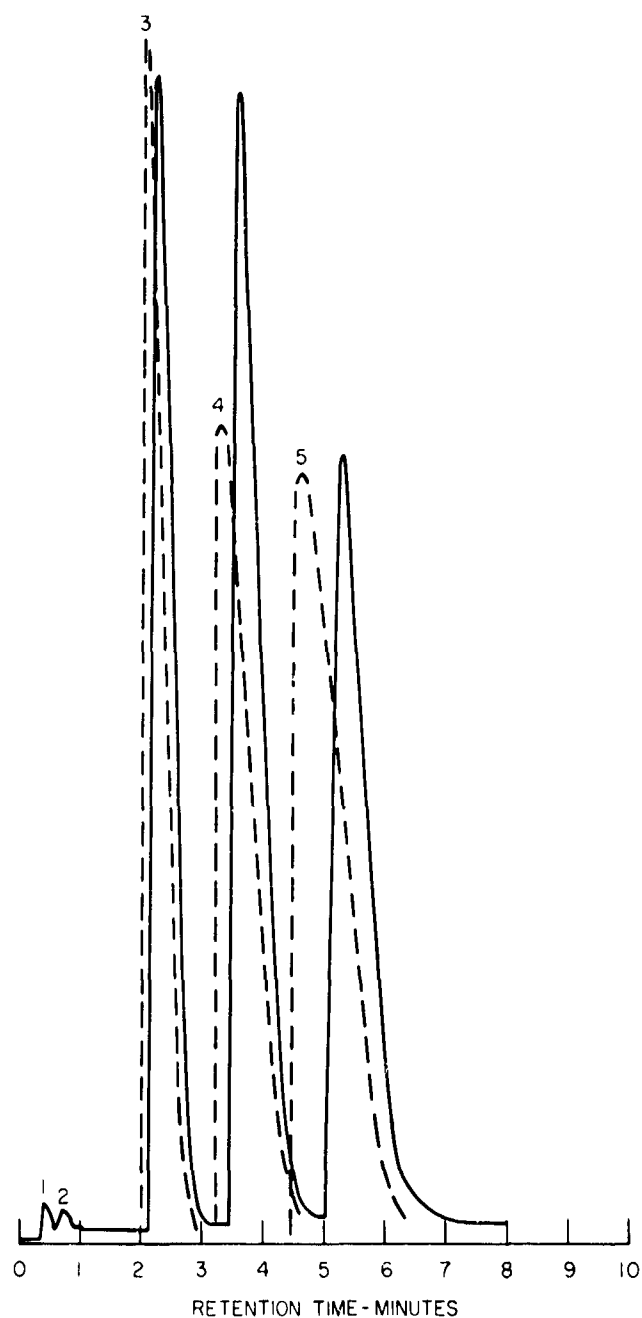


FIG. 4. Resolution of a Typical Mixture of Hydrazines and Water by 10 Percent Dowfax 9N9 on Teflon 6.

Identification of Peaks: 1. Air, 2. Ammonia, 3. Water, 4. MMH, 5. Hydrazine
-- Individual component run
— Mixed component run (25% water, 40% MMH, 35% hydrazine).

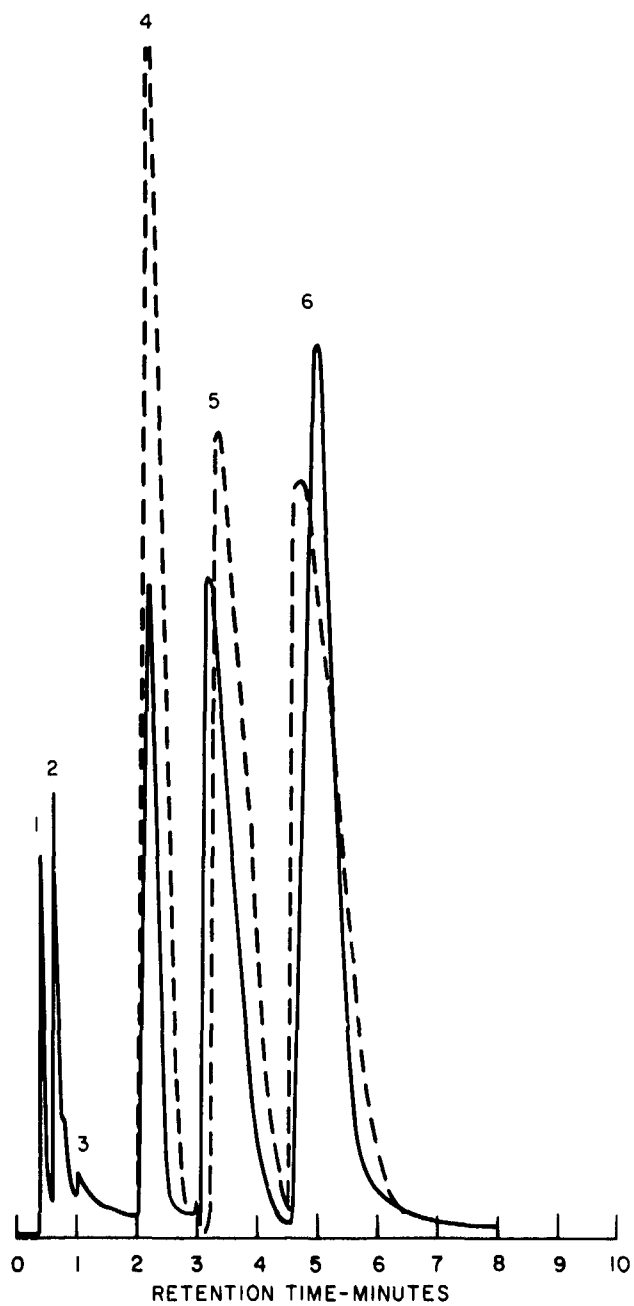


FIG. 5. Resolution of MHF-3 Fuel by 10 Percent Dowfax 9N9 on Teflon 6.

Identification of Peaks: 1. Air, 2. Ammonia, 3. Impurities, 4. Water, 5. MMH, 6. Hydrazine.

-- Individual component run

— Mixed component run MHF-3 (MAX 2% water, $86 \pm 2\%$ MMH, $14 \pm 2\%$ hydrazine)

The chromatograms of hydrazine and MMH, both individually and in mixtures at low attenuation, show an impurity peak which occurs between the MMH and hydrazine peaks. The impurity was not identified and the amount was too small to be determined at the attenuations used during the analysis. Two of the chromatograms obtained during the analysis of the mixtures are shown in Fig. 4 and 5.

A chromatogram of a typical mixture of hydrazines and water was prepared with a composition of 25.0 percent water, 40.4 percent MMH, and 34.6 percent hydrazine (Fig. 4). The attenuation setting for this mixture was at 32X for all peaks. The chromatographic analysis showed a composition of 24.3 percent water, 40.8 percent MMH, and 34.9 percent hydrazine. The reciprocal response ratios used were obtained from a prepared mixture of 20.8 percent water, 48.7 percent MMH, and 30.5 percent hydrazine. The ratios were 1:1.29 and 1:1.22 for water to MMH and water to hydrazine, respectively (Table 1).

The reproducibility of this procedure is shown in Table 3. The reciprocal response ratios used were obtained from a prepared known sample. These ratios were then used to calculate the percent composition of this same known sample in subsequent runs.

TABLE 3. Reproducibility of Analysis

Component	Reciprocal ^a response ratio	True ^b value in %	Sample determinations, % composition			Av. %	Difference, %
			1	2	3		
H ₂ O	1	25.00	24.98	24.90	24.95	24.94	-0.06
MMH	1.24	40.36	40.38	40.39	40.23	40.33	-0.03
N ₂ H ₄	1.18	34.64	34.63	34.70	34.82	34.72	+0.08

^aReciprocal response ratios determined from the prepared mixture sample 20 Table 1.

^bTrue values of the prepared mixture, sample 20, Table 1.

An MHF-3 fuel mixture prepared by the Liquid Propellants Branch was analyzed. The nominal composition of MHF-3 is 86 ± 2 percent MMH, 14 ± 2 percent hydrazine and 2 percent maximum water. The attenuations were 4X, 64X, 16X for water, MMH and hydrazine, respectively. The air and ammonia peaks were at 4X (Fig. 4). The analysis of the chromatogram (Fig. 4) showed a composition of 1.5 percent water, 84.2 percent MMH, 14.3 percent hydrazine. The relative response ratios used were obtained from a prepared mixture of 0.8 percent water, 85.4 percent MMH, 13.8 percent hydrazine with ratios of 1:1.35 and 1:1.19 for water to MMH and water to hydrazine, respectively (Table 1). These analyses were duplicated to within ± 0.5 percent.

BAF fuel mixtures of hydrazine, MMH and water were supplied by the Liquid Propellants Branch and Bell Aero Systems, Inc. This is a proprietary fuel; therefore, the composition and analysis are not available for publication. The analyses were duplicated to within ± 0.5 percent.

A number of chromatographic analyses were made on prepared samples. The statistical data indicated that 99 percent of all values collected will fall within ± 0.71 percent of the average value of three data points at the 95 percent confidence level. If the mean of three data points is used, the mean will be within ± 0.41 percent of the true value of each of the components as calculated by weight.

It has been observed empirically that the ratio of the MMH to hydrazine can vary up to 5 percent and the analysis will remain within 1 percent of the true values.

The accuracy of the chromatographic analysis ultimately depends on the accuracy of the acidimetric analysis of the hydrazine and MMH used in the preparation of the synthetic mixtures.

The 10 percent Dowfax 9N9 on Teflon 6 material was used with other instruments to determine the reproducibility of the column under different conditions. A Fractometer, using a disc integrator and a column similar to the one used in the previous analyses, was used to analyze prepared mixtures. Also an Aerograph Autoprep Model A-700 using a Royson integrator and a 6-foot coiled aluminum column 1/4-inch OD was used to analyze prepared mixtures. The results were comparable to those obtained previously and showed no greater variation than was observed in the original analysis.

A column was used for approximately 200 analyses without apparent fatigue, showing excellent stability. The column should not be used for other compounds while being used for hydrazine analysis because of the highly reactive characteristics of hydrazines.

CONCLUSIONS

Statistical analysis of the data obtained from gas chromatographic analysis with the Dowfax 9N9 indicates that mixtures of hydrazine, MMH, and water can be determined to within ± 0.5 percent of the true value of each component.

The 10 percent Dowfax 9N9 on Teflon 6 column has the advantage of short retention times (individual runs required approximately 7 minutes) minimal tailing, excellent resolution and column stability. It has the disadvantage of being unable to separate UDMH and water.

Appendix A

PROCEDURE FOR ACIDIMETRIC ANALYSIS OF HYDRAZINES

The acidimetric procedure (Ref. 8) for analysis of hydrazines was used to determine the percent purity of the individual hydrazine and MMH samples. This method does not analyze for mixed hydrazines except in conjunction with other methods. This method has a precision of about ± 0.1 percent, if there are no interferences from ammonia and other basic compounds.

APPARATUS AND REAGENTS

1. 0.5N hydrochloric acid (HCl) standardized with 0.5N sodium hydroxide (NaOH) standardized with potassium acid phthalate
2. Methyl red indicator in 95 percent ethanol
3. 10 ml buret
4. 1 ml tuberculin syringe with no. 27 needle
5. Distilled water, carbon dioxide (CO₂) free by boiling or bubbling with helium
6. Analytical balance
7. 250 ml beaker

PROCEDURE

1. To a 250 ml beaker containing 50 ml of distilled water, CO₂ free, titrate approximately 3 ml of 0.5N HCl. Record accurately the amount of HCl as this is used in the calculations.
2. Using a 1 ml tuberculin syringe, with the tip of the needle in the solution, measure a 0.20 to 0.25 gram sample weighed to the nearest 0.1 milligram by difference into the beaker of HCl solution. Allow the solutions to stand approximately 30 minutes. Since the solutions are acidic, the hydrazines are not reactive with oxygen or CO₂.
3. Add 10 drops of methyl red indicator and titrate to the red end point with 0.5N HCl. After 10 minutes again titrate to the red end point.

4. Calculation:

$$\begin{aligned} & \% \text{ free hydrazine + basic material} \\ & = \frac{\text{ml (HCl)} \times \text{N (HCl)} \times \text{mol wt (hydrazine)}}{10 \times \text{sample weight in grams}} \end{aligned}$$

molecular weights:

hydrazine 32.05

MMH 46.08

UDMH 60.12

Appendix B

GAS CHROMATIC PROCEDURE FOR ANALYSIS OF MIXED
HYDRAZINE (HYDRAZINE AND MMH) AND WATER

This gas chromatographic procedure was developed for the analysis of some of the MHF and BAF series fuels which are mixtures of hydrazine, MMH and water. This procedure determines the percentage of each component in the mixture to an accuracy of ± 0.5 percent.

APPARATUS

1. Perkin-Elmer Model 154-C Vapor Fractometer with dual chamber thermistor thermal conductivity cell
2. Leeds and Northrup (5 mv full scale) recorder
3. Instron integrator, two-counter model
4. Hamilton microsyringe, 10 μ l
5. Helium, tank fitted with regulating pressure gage
6. Column (6-foot x 1/4-inch OD) packed with 10 percent Dowfax 9N9 on Teflon 6.

PROCEDURE

1. The Fractometer is adjusted to a column temperature of 110°C, in accordance with the Perkin-Elmer Instruction Manual.
2. The helium flow rate is adjusted to 40 ml per minute by controlling the Fractometer pressure valve.
3. The integrator and recorder are turned on and then calibrated with the Fractometer in accordance with the Integrator Instruction Manual so that the integrator count rate is linearly proportional to the recorder scale reading. The recorder should operate at a chart speed of 1/2 inch per minute.
4. When the column temperature is stabilized at 110°C, a hydrazine sample of approximately 10 μ l is injected. Usually one or two injections are sufficient to condition the column as shown by reproducibility of the analysis.

5. When conditions are stable, the column conditioned and the attenuation set to the desired position, dependent upon the estimated sample concentration, the instrument is then ready for analysis of samples.

6. Inject approximately $5 \mu\text{l}$ sample of the unknown hydrazine mixture. The peaks are counted and recorded as they appear. The analysis requires approximately 7 minutes and an additional 10 minutes is allowed before the next analysis to insure complete return of recorder to baseline. From three to five determinations of each sample are usually sufficient for accurate analysis.

7. The composition of the unknown mixture is estimated and the reciprocal response ratios from a mixture of similar composition is obtained from Table 1 and used to calculate the percent composition. This value is further refined for greater accuracy by the following steps.

a. From the calculated percent composition a similar mixture is prepared using hydrazines of known composition as determined by the acidimetric analysis (Appendix A) or equivalent method.

b. This prepared sample is then analyzed as described in step 6. From the analysis the reciprocal response ratios are determined as described in the calculation section.

c. The average relative response ratios obtained are then used to calculate the percentage composition of the unknown sample.

REFERENCES

1. Kuwada, D. M. "Determination of Water in Hydrazine by Gas Chromatography," J OF G C. March 1963, pp. 11-13.
2. Cain, E. C., and M. Stevens. "Determination of Water in Hydrazines," Gas Chromatology. Academic Press, 1961. pp. 343-350.
3. Cordes, H. F., and C. W. Tait. "Determination of Water in Several Hydrazines," ANAL CHEM, Vol. 29 (1957), p. 485.
4. O'Donnell, J. F., and C. K. Mann. "Gas Chromatographic Separation of Amines and Amides," ANAL CHEM, Vol. 36 (1964), p. 2097.
5. Hagstrom, R. A., and others. "Gas Chromatographic Methods for Liquid Propellant Analysis," Olin Mathieson Chemical Corp., New Haven, Conn., 15 March 1965. (AFRPL-TR-65-69, Olin QPR 10381-1).
6. Military Specification MIL-P-26536B. "Propellant, Hydrazine," 13 March 1964.
7. Military Specification MIL-P-27404. "Propellant, Monomethylhydrazine," 3 April 1962.
8. Penneman, R. A., and L. F. Audrieth. "Quantitative Determination of Hydrazine," ANAL CHEM, Vol. 20 (1964), p. 1058.
9. Smith, B. D., and W. W. Bowden. "Accurate Multicomponent Analysis by Gas Chromatography," ANAL CHEM, Vol. 36 (1964), p. 87.
10. Messner, A. E., and others. "Correlation of Thermal Conductivity Cell Response with Molecular Weight and Structure," ANAL CHEM, Vol. 31 (1959), p. 230.
11. Military Specification MIL-P- (WP) Series (FSC 9135). "Propellant, Mixed Hydrazine Fuel, MHF-3" (Proposed).
12. Kirkland, J. J., "Fluorine Containing Polymers as Solid Supports in Gas Chromatography," ANAL CHEM, Vol. 35 (1963), p. 2003.

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R&D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1 ORIGINATING ACTIVITY (Corporate author) U. S. NAVAL ORDNANCE TEST STATION CHINA LAKE, CALIFORNIA		2a REPORT SECURITY CLASSIFICATION CONFIDENTIAL
		2b GROUP 4 DOWNGRADED AT 3-YEAR INTERVALS DECLASSIFIED AFTER 12 YEARS
3 REPORT TITLE GAS CHROMATOGRAPHIC ANALYSIS OF HYDRAZINE, MONOMETHYLHYDRAZINE AND WATER IN MIXED HYDRAZINE FUELS (U)		
4 DESCRIPTIVE NOTES (Type of report and inclusive dates) TECHNICAL REPORT		
5 AUTHOR(S) (Last name, first name, initial) JONES, RICHARD M.		
6 REPORT DATE AUGUST 1965	7a TOTAL NO OF PAGES 25	7b NO OF REFS 12
8a CONTRACT OR GRANT NO b PROJECT NO. BUWEPS TA RMMP-24-080/216-1/F009-060-02 c d	9a ORIGINATOR'S REPORT NUMBER(S) NAVWEPS REPORT 8788, NOTS TP 3882	
		9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
10 AVAILABILITY/LIMITATION NOTICES QUALIFIED REQUESTERS MAY OBTAIN COPIES OF THIS REPORT DIRECT FROM DDC		
11 SUPPLEMENTARY NOTES CONTAINS APPENDIXES A AND B	12 SPONSORING MILITARY ACTIVITY BUREAU OF NAVAL WEAPONS (DEPT. OF NAVY)	
13 ABSTRACT A gas chromatographic procedure is described for the analysis of a mixture of hydrazine, monomethylhydrazine (MMH) and water. Analyses were obtained by the use of a Perkin-Elmer Vapor Fractometer Model 154-C with a Leeds and Northrup recorder and an Instron integrator. A column packed with 10 percent Dowfax 9N9 on Teflon 6 was used. The elution of the peaks required about 7 minutes and the peaks appeared in the order of water, MMH, and hydrazine. The composition analyses were duplicated within ± 0.5 percent of the amount of the individual components present in a synthetic mixture. The synthetic mixture was prepared from materials which had been analyzed by the acidimetric method. (U)		

DD FORM 1473 0101-807-6800
1 JAN 64

UNCLASSIFIED
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Hydrazine						
Monomethylhydrazine						
Water						
Chromatographic						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.

ABSTRACT CARD

U. S. Naval Ordnance Test Station
Gas Chromatographic Analysis of Hydrazine, Monomethylhydrazine and Water in Mixed Hydrazine Fuels (U) by Richard M. Jones. China Lake, Calif., NOTS, August 1965. 20 pp. (NAVWEPS Report 8788, NOTS TP 3882), CONFIDENTIAL.
 ABSTRACT. A gas chromatographic procedure is described for the analysis of a mixture of hydrazine, monomethylhydrazine (MMH) and water.
 Analyses were obtained by the use of a Perkin-Elmer Vapor Fractometer Model 154-C with a Leeds and Northrup recorder and an Instron integrator. A column packed with 10 percent Dowfax 9N9

Card UNCLASSIFIED ○ 1 card, 4 copies (Over)

U. S. Naval Ordnance Test Station
Gas Chromatographic Analysis of Hydrazine, Monomethylhydrazine and Water in Mixed Hydrazine Fuels (U) by Richard M. Jones. China Lake, Calif., NOTS, August 1965. 20 pp. (NAVWEPS Report 8788, NOTS TP 3882), CONFIDENTIAL.
 ABSTRACT. A gas chromatographic procedure is described for the analysis of a mixture of hydrazine, monomethylhydrazine (MMH) and water.
 Analyses were obtained by the use of a Perkin-Elmer Vapor Fractometer Model 154-C with a Leeds and Northrup recorder and an Instron integrator. A column packed with 10 percent Dowfax 9N9

Card UNCLASSIFIED ○ 1 card, 4 copies (Over)

U. S. Naval Ordnance Test Station
Gas Chromatographic Analysis of Hydrazine, Monomethylhydrazine and Water in Mixed Hydrazine Fuels (U) by Richard M. Jones. China Lake, Calif., NOTS, August 1965. 22 pp. (NAVWEPS Report 8788, NOTS TP 3882), CONFIDENTIAL.
 ABSTRACT. A gas chromatographic procedure is described for the analysis of a mixture of hydrazine, monomethylhydrazine (MMH) and water.
 Analyses were obtained by the use of a Perkin-Elmer Vapor Fractometer Model 154-C with a Leeds and Northrup recorder and an Instron integrator. A column packed with 10 percent Dowfax 9N9

Card UNCLASSIFIED ○ 1 card, 4 copies (Over)

U. S. Naval Ordnance Test Station
Gas Chromatographic Analysis of Hydrazine, Monomethylhydrazine and Water in Mixed Hydrazine Fuels (U) by Richard M. Jones. China Lake, Calif., NOTS, August 1965. 22 pp. (NAVWEPS Report 8788, NOTS TP 3882), CONFIDENTIAL.
 ABSTRACT. A gas chromatographic procedure is described for the analysis of a mixture of hydrazine, monomethylhydrazine (MMH) and water.
 Analyses were obtained by the use of a Perkin-Elmer Vapor Fractometer Model 154-C with a Leeds and Northrup recorder and an Instron integrator. A column packed with 10 percent Dowfax 9N9

Card UNCLASSIFIED ○ 1 card, 4 copies (Over)

NAVWEPS Report 8788

on Teflon 6 was used. The elution of the peaks required about 7 minutes and the peaks appeared in the order of water, MMH, and hydrazine. The composition analyses were duplicated within ± 0.5 percent of the amount of the individual components present in a synthetic mixture. The synthetic mixture was prepared from materials which had been analyzed by the acidimetric method.

NAVWEPS Report 8788

on Teflon 6 was used. The elution of the peaks required about 7 minutes and the peaks appeared in the order of water, MMH, and hydrazine. The composition analyses were duplicated within ± 0.5 percent of the amount of the individual components present in a synthetic mixture. The synthetic mixture was prepared from materials which had been analyzed by the acidimetric method.

NAVWEPS Report 8788

on Teflon 6 was used. The elution of the peaks required about 7 minutes and the peaks appeared in the order of water, MMH, and hydrazine. The composition analyses were duplicated within ± 0.5 percent of the amount of the individual components present in a synthetic mixture. The synthetic mixture was prepared from materials which had been analyzed by the acidimetric method.

NAVWEPS Report 8788

on Teflon 6 was used. The elution of the peaks required about 7 minutes and the peaks appeared in the order of water, MMH, and hydrazine. The composition analyses were duplicated within ± 0.5 percent of the amount of the individual components present in a synthetic mixture. The synthetic mixture was prepared from materials which had been analyzed by the acidimetric method.

SUPPLEMENTARY

INFORMATION



DEPARTMENT OF THE NAVY
U. S. NAVAL ORDNANCE TEST STATION
CHINA LAKE, CALIFORNIA 93557

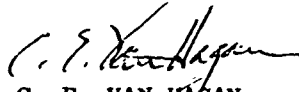
IN REPLY REFER TO
751/CEV:ga
12 April 1966

From: Commander, U. S. Naval Ordnance Test Station
To: Distribution List of NavWeps Report 8788, NOTS TP 3882

Subj: NavWeps Report 8788 (NOTS TP 3882) Gas Chromatographic Analysis
of Hydrazine, Monomethylhydrazine and Water in Mixed Hydrazine
Fuels, dated August 1965; transmittal of errata sheet for

Encl: (1) Errata sheet dated 3 March 1966 for subject report

1. It is requested that the corrections described on the enclosed errata sheet be incorporated in NavWeps Report 8788, NOTS TP 3882.


C. E. VAN HAGAN

ERRATA

Page 16, paragraph 1 under Procedure, line 2: delete "3" and
replace it with "10"

Page 16, paragraph 2 under Procedure, line 2: delete "0.20 to 0.25"
and replace it with "0.10 to 0.15"

Page 16, paragraph 2 under Procedure, line 4: delete "Allow the
solutions to stand approximately 30 minutes."

Page 16, paragraph 3 under Procedure, lines 1 and 2: delete "red end
point with 0.5N HCl. After 10 minutes again titrate to the red
end point." and replace it with "first change in the red color to
a lighter red or clear with 0.5N NaOH."

Page 17, paragraph 4 under Calculations, formula change: delete
$$\frac{\text{ml (HCl)} \times \text{N (HCl)} \times \text{mol wt (hydrazine)}}{10 \times \text{sample weight in grams}}$$

and replace it with

$$\frac{(\text{ml HCl} \times \text{N HCl}) - (\text{ml NaOH} \times \text{N NaOH}) \times \text{mol wt (hydrazine)}}{10 \times \text{sample weight in grams}}$$