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HYDRAZINE AND MONOMETHYLHYDRAZINE MEASUREMENT IN WATER AND AIR --ETC(U)

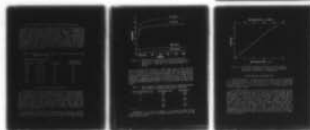
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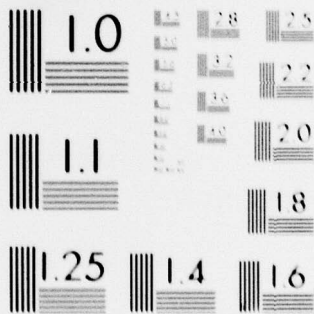
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**HYDRAZINE AND MONOMETHYLHYDRAZINE MEASUREMENT
IN WATER AND AIR USING THE SCAN METHOD.**

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Leonard J. Luskus Ph.D.

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Interim Report for Period 1 September 1978 - 31 December 1978

1 Sep - 31 Dec 78

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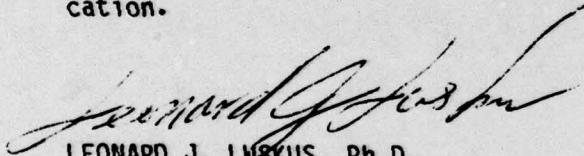
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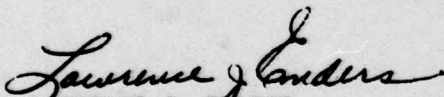
This technical report has been reviewed and is approved for publication.



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SAM-TR-79-18	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) HYDRAZINE AND MONOMETHYLHYDRAZINE MEASUREMENT IN WATER AND AIR USING THE SCAN METHOD		5. TYPE OF REPORT & PERIOD COVERED Interim Report 1 Sep 78 - 31 Dec 78
7. AUTHOR(s) Leonard J. Luskus, Ph.D. Michael L. Turpin, Airman First Class, USAF		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS USAF School of Aerospace Medicine (VNL) Aerospace Medical Division (AFSC) Brooks Air Force Base, Texas 78235		8. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS USAF School of Aerospace Medicine (VNL) Aerospace Medical Division (AFSC) Brooks Air Force Base, Texas 78235		10. PROGRAM ELEMENT PROJECT, TASK AREA & WORK UNIT NUMBERS 62202F 7930-11-36
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE November 1979
		13. NUMBER OF PAGES 12
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Hydrazine Monomethylhydrazine MMH SCAN		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The SCAN kit is a commercially available product used for analysis of hydrazine in boiler and waste water. The SCAN approach was tested and evaluated for its intended use and also for its adaptability for (1) measuring hydrazine in air and (2) measuring monomethylhydrazine (MMH) in both air and water. The technique involves aspiration of an aqueous sample (impinger or solid-sorbent extract) into an air-evacuated ampoule which contains a color-forming reagent. The intensity of the resulting color is read on a spectrophotometer. Test results indicated the SCAN method to be adequate for quick and easy field		

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20. ABSTRACT (Continued)

analysis of hydrazine in water to 0.01 mg/liter and in air to concentrations as low as 0.015 ppm, using a 15-liter air sample. MMH analysis required a color development time of 30 to 90 min which would interfere in certain field applications. MMH was measured at concentrations as low as 0.1 ppm, using 15-liter air sample.

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HYDRAZINE AND MONOMETHYLHYDRAZINE MEASUREMENT IN WATER AND AIR USING THE SCAN METHOD

INTRODUCTION

The SCAN kit¹ is a commercially available product used for analysis of hydrazine in boiler and waste water. SCAN (simplified colorimetric analysis) is an acronym for the technique involving aspiration of an aqueous sample into an air-evacuated (vacuum) ampoule containing a reagent (p-dimethylaminobenzaldehyde [PDAB]) that reacts with hydrazine to produce a yellow color. Hydrazine concentration is estimated by reading color intensity on a spectrophotometer, using the sampling ampoule as a cuvette.

Because of the growing Air Force interest in and need for hydrazine-measurement techniques, at USAFSAM we included the SCAN method in our hydrazine-methods test and evaluation program. The specific objective of the USAFSAM testing effort was to look not only at the manufacturer's intended use of the SCAN method for boiler- and waste-water analysis, but also for its adaptability for (1) measuring hydrazine (Hz) in air and (2) measuring monomethylhydrazine (MMH) in both air and water. MMH was included in the test program because of its color-producing reaction with the hydrazine reagent and Air Force-NASA requirements for air monitoring of MMH rocket-fuel use and handling associated with space-shuttle and Minuteman III missile operations.

The test and evaluation presented here includes data on a new solid-sorbent method² used for collecting samples of hydrazine vapors from air. Water and impinger/bubbler sources of hydrazine were simulated using standard solutions of the hydrazines.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

The Test Kit

The components of a SCAN kit are illustrated schematically in Figure 1. The kit used for this study (catalog No. 5003) consists of 30 disposable sampling ampoules, a water blank, a calibration ampoule, and a sample cup. All ampoules are of glass, approximately 9.5-cm X 1-cm inside diameter (ID). Each sampling ampoule contains a measured

¹Chemetrics, Inc., Mill Run Drive, Warrenton VA 22186.

²Luskus, L. J., and H. J. Kilian. Solid-sorbent sampling and colorimetric analysis of hydrazine. USAFSAM, unpublished data.

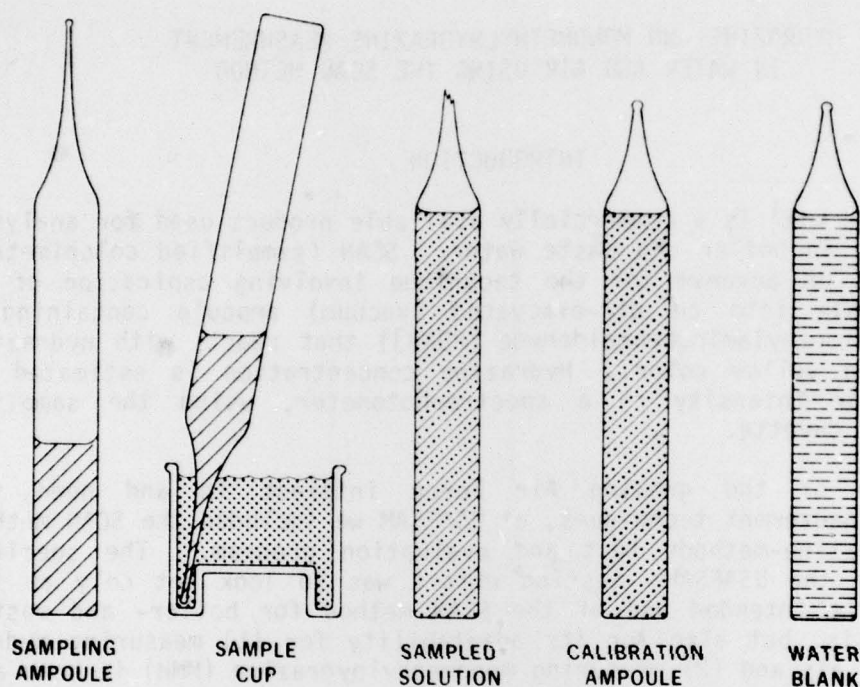


Figure 1. SCAN kit components shown schematically.

amount of reagent that has been sealed under vacuum. Breaking the ampoule tip under the surface of a liquid sample causes aspiration and mixing of a quantitative amount of the sample with the reagent. The sample cup (Fig. 1) is designed to facilitate clean and reproducible breaking of the ampoule tip. The intensity of color produced by the hydrazine-reagent reaction is measured on a spectrophotometer at a specified time after mixing (10 min recommended for hydrazine). Readings are made at 445 nm, using the sampling ampoule as the cuvette--no transfer or handling of solutions is necessary.

The SCAN method uses a calibration ampoule to compensate for differences in response between various spectrophotometers an analyst might use. After 100%T is set with the water blank, the percent transmittance (%T) of the calibration ampoule is determined. Using Table 1, this calibration reading is converted into a "calibration factor" which, according to the manufacturer, must be determined only once--a recheck is necessary only after maintenance is performed on an instrument.

Sample readings made on the spectrophotometer are converted to concentration values ($\mu\text{g/ml}$ of hydrazine), using Table 2. These uncorrected values are multiplied by the calibration factor (Table 1) to obtain correct Hz concentration. For example:

1. Calibration ampoule reads 46%T.
2. Calibration factor (Table 1) is 1.21.
3. Sample ampoule reads 32.5%.
4. Uncorrected concentration (Table 2) is 0.320 $\mu\text{g/ml}$.
5. Corrected result is $0.320 \times 1.21 = 0.387 \mu\text{g/ml}$.

TABLE 1. INSTRUMENT CALIBRATION FOR HYDRAZINE AT 445 nm
(USING STANDARD CALIBRATION AMPOULE)

<u>Calibration ampoule reading (%T)</u>	<u>Calibration factor^a</u>
35	0.91
36	0.92
37	0.94
38	0.97
39	1.00
40	1.03
41	1.05
42	1.08
43	1.11
44	1.14
45	1.17
46	1.21
47	1.24
48	1.28
49	1.32
50	1.36
51	1.40
52	1.43
53	1.48
54	1.53
55	1.57

^aMultiply uncorrected concentration (Table 2) by calibration factor.

Standard Preparation

Standard solutions were prepared by weighing out the appropriate amount of reagent-grade Hz and MMH sulfate salts and dissolving them in 0.1 N sulfuric acid. Concentrations are expressed in micrograms throughout this report, either total sample analyzed or per milliliter of analyzed solution. When making measurements in air, using the total sample volume is generally more convenient since this volume is independent of the volume of liquid used in the workup and analysis. Hydrazine concentration can be converted from $\mu\text{g/sample}$ to parts per million by volume (ppm) in air (760 mmHg, 25°C) by using equation 1:

$$\text{ppm} = \frac{\mu\text{g's sampled}}{\text{liters of air}} \times \frac{24450}{\text{molecular weight}} \quad (1)$$

Representative ppm values corresponding to total $\mu\text{g's}$ measured for 15-min and 8-hr sampling times at flow rates of 1 liter/min are presented in Table 3.

TABLE 2. CONVERSION OF %T TO HYDRAZINE CONCENTRATION AT 445 nm (FOR SPECTRONIC 20 AND MINI 20)

Sample ampoule (%T)	Hydrazine ($\mu\text{g/ml}$)									
	0	1	2	3	4	5	6	7	8	9
10	.704	.673	.645	.619	.595	.572	.551	.532	.513	.495
20	.479	.463	.448	.433	.419	.406	.393	.381	.369	.358
30	.347	.336	.326	.315	.306	.297	.288	.279	.270	.261
40	.253	.245	.237	.230	.222	.215	.209	.201	.194	.187
50	.181	.174	.168	.162	.156	.150	.144	.138	.133	.126
60	.121	.116	.112	.109	.106	.103	.098	.095	.090	.087
70	.083	.079	.075	.072	.069	.065	.061	.058	.054	.050
80	.047	.044	.041	.038	.034	.031	.029	.025	.022	.019
90	.016	.013	.010	.007	.004	.001	--	--	--	--

TABLE 3. CONVERSION OF μg HYDRAZINE AND MMH TO ppm (760 mmHg, 25°C)

μg	Hydrazine (ppm)		MMH (ppm)	
	15-liter sample	480-liter sample	15-liter sample	480-liter sample
1	0.05	0.0016	0.035	0.0011
10	0.51	0.016	0.35	0.011
50	2.5	0.079	1.8	0.055

Solid-Sorbent Sampling Tubes

Sampling tubes were prepared by filling 10-cm X 6-mm-ID glass tubing with 300 mg of 20% by weight H_2SO_4 on firebrick (GasChrom R. - 30/60 mesh).² The firebrick was held in place with glass-wool plugs. Tube ends were capped with Parafilm until the tubes were needed for sampling. These sampling tubes were exposed to the hydrazines by directly pipetting known microliter amounts of standard solutions onto the solid sorbent. The tubes were allowed to sit at least 24 hours after exposure and before analysis.

Analytical Procedure

Samples for this study were prepared in two ways. Microliter quantities of standard acidic solutions of Hz and MMH were pipetted (1) directly into a final volume of 12 ml of 0.1 N H_2SO_4 or (2) directly onto the solid sorbent contained in a sampling tube--the solid sorbent then was extracted over a 10-min period with 12 ml of 0.1 N H_2SO_4 . The two methods of preparing samples simulated, respectively, impinger and solid-sorbent sampling of hydrazine contaminants in air. Actual collection of hydrazines from air by the impinger and solid-sorbent methods was not included in this study because earlier work on the PDAB analysis² had established the valid usefulness of the simulation. Once the Hz/MMH sample was prepared, the resulting 12 ml of solution was analyzed as follows:

1. After a 10-min warmup of a Spectronic 20 spectrophotometer, a calibration factor was determined at 445 nm by reading %T of the calibration ampoule and then using Table 1. The distilled water blank was used to set 100%T.

2. The entire 12-ml sample was added to the plastic sample cup.

3. A sampling ampoule was inserted under the liquid to the bottom of the cup and the tip was broken (see Fig. 1). The volume of sample not drawn into the ampoule would normally be saved in case the Hz/MMH concentration produced too intense a color to read. The retained sample could be aliquoted/diluted for further analysis.

4. For color development, 10 min were allowed for Hz and 60 min for MMH.

5. A reading was made at 445 nm--using the water blank to set 100%T (0 absorbance). For Hz, Table 2 was used to convert the %T reading to concentration ($\mu\text{g/ml}$); this was then multiplied by the calibration factor to get the final corrected concentration, again in $\mu\text{g/ml}$. To obtain total sample trapped on the sorbent or by the impinger, it was only necessary to multiply by the sample volume (12 ml).

Calibration factors and concentration (%T) data were not available for MMH since the SCAN method was developed only for Hz; otherwise, the analytical procedure was the same.

RESULTS AND DISCUSSION

Testing of the SCAN method started with a check on quality control of kit components and solutions. Specific potential problem areas investigated included variation of ampoule path lengths, reproducibility of calibration ampoule readings, variation of volumes sampled, and color stability.

Variation of Ampoule Optical Path Length

The reproducibility of optical path length for 10 sample ampoules (randomly selected from a total of 160) was determined by analyzing a solution of known hydrazine concentration. A mean absorbance of 0.337 (47%T) with a coefficient of variation of 1.58% indicated insignificant path-length differences between ampoules. A check on the difference in path length as a function of positioning in the spectrophotometer of the same ampoules (10 ampoules--6 positions) gave the same absorbance and coefficient of variation. The ampoules appear remarkably well quality controlled dimensionally.

Calibration Ampoule Reproducibility

The color intensity of the calibration ampoules showed no change when held over a 3-month period. Repeated readings of six calibration ampoules, including readings at each of six positions, gave an absorbance value of $0.339 \pm .010$ ($45.8 \pm .5$ %T) at 445 nm on our Spectronic 20 instrument.

Sampled Volume

The volume of aqueous sample drawn into the analysis ampoule was 5.9 ± 0.2 ml (coefficient of variation of 3.4%). This was based on weighing 20 ampoules before and after aspiration. Minimum safe volume needed for analysis when using the cup supplied with the SCAN kit, is about 15 ml. We used 12 ml and had a failure rate of about 5%--where breaking the sampling ampoule resulted in aspiration of an indeterminate amount of air along with sample. Since air sampling at the American Conference of Governmental and Industrial Hygienists (ACGIH) threshold-limit-value (TLV) concentrations (0.1 ppm Hz and 0.2 ppm MMH) requires as much sensitivity as can be obtained, it may be useful to redesign the cup for use with less sample (about 8 ml). A simple technique we found applicable was to use glass beads to decrease the wasted residual volume needed to keep the tip of the ampoule covered with liquid during aspiration.

Color Stability

Hydrazine: Color intensity reached maximum within 10 min of adding the color reagent to aqueous samples containing 0.01 to 0.7 $\mu\text{g/ml}$ of hydrazine. The color was stable for at least 30 min, allowing some freedom in setting up timed multisampling procedures.

MMH: Color intensity did not reach maximum until about 180 min after the color reagent was added, although 90% of final intensity was reached within 60 min for MMH concentrations in the range of 0-4 $\mu\text{g/ml}$ (Table 4). Higher MMH concentrations would require longer development time, as would be expected if, for example, an insufficient amount of color reagent was available for reaction.

TABLE 4. COLOR INTENSITY OF THE MMH-SCAN REACTION AS A FUNCTION OF TIME

MMH concentration		Absorbance								
($\mu\text{g}/\text{sample}$)	($\mu\text{g}/\text{ml}$)	min:	10	20	30	60	90	120	180	240
50	4.17		.432	.558	.597	.632	.638	.638	.645	.647
40	3.33		.350	.467	.495	.518	.518	.521	.528	.529
7.5	0.42		.072	.085	.094	.098	.098	.100	.103	.104
2.5	0.21		.029	.032	.038	.038	.037	.037	.041	.042

Hydrazine Analysis of Standard Solutions

Samples of hydrazine in 0.1 N sulfuric acid were analyzed by the SCAN method, with results presented in Table 5. Hydrazine concentration is given in μg 's, which represents the total amount of hydrazine collected from air, using 12 ml of acid in an impinger. The microgram value is obtained simply by multiplying corrected Table 2 $\mu\text{g}/\text{ml}$ of analyzed solution values by the impinger volume in milliliters. Accuracy and precision of the method were evaluated using triplicate samples--a larger number of samples would have been desirable, but we were limited to ampoules on hand. Accuracy was found acceptable, especially when considering that concentrations of 1.20-0.30 μg correspond to air concentrations of 0.06-0.015 ppm for a 15-liter air sample, and to much lower concentrations for larger air samples. Precision of the method was very good, as can be seen from the coefficients of variation, also listed in Table 5.

TABLE 5. ANALYSES OF STANDARD HYDRAZINE SOLUTIONS BY THE SCAN COLORIMETRIC METHOD

Hydrazine concentration (μg)			Coefficient of Variation (%)
True value	SCAN	% Recovery	
6.00	6.28 \pm .06	105	1.0
4.50	4.69 \pm .05	104	0.2
3.00	3.04 \pm 0	101	0
1.80	1.65 \pm .03	92	1.8
1.20	1.05 \pm .03	88	2.9
0.60	0.49 \pm .02	82	3.5
0.30	0.26 \pm .03	87	11.5

Hydrazine Analysis of Exposed Solid-Sorbent Sampling Tubes

Results of analysis of hydrazine-exposed solid-sorbent (acidified firebrick) sampling tubes are summarized in Table 6. Compared with impinger/bubbler techniques with collection efficiencies of 60-90%, the sampling tubes are basically 100% efficient; however, an extraction step is required that could affect recovery. The percent-recovery values listed in Table 6 indicate that extraction is not a serious problem and that the accuracy of the SCAN method is relatively good for what is essentially a field rather than a laboratory technique. Precision of the measurements made is on the order of that expected for typical colorimetric analyses using a Spectronic 20 spectrophotometer. Accuracy and precision compare favorably with results from the solution analysis discussed in the last section.

TABLE 6. ANALYSES OF EXPOSED HYDRAZINE SAMPLING TUBES BY THE SCAN COLORIMETRIC METHOD

<u>Hydrazine concentration (μg)</u>			<u>Coefficient of Variation (%)</u>
<u>True value</u>	<u>SCAN</u>	<u>% Recovery</u>	
6.00	5.79 \pm .22	97	3.8
4.50	4.49 \pm .24	100	5.3
3.00	2.75 \pm .10	92	3.8
1.80	1.50 \pm .02	83	1.3
1.20	1.03 \pm .02	86	2.2
0.60	0.72 \pm .03	120	3.5
0.30	0.29 \pm .01	97	3.5

MMH Analysis of Standard Solution

MMH analyses by the SCAN technique required much longer color development than the 10 min used for hydrazine analysis. Figure 2 summarizes data collected on color development (absorbance as a function of time) for different MMH concentrations in 0.1 N sulfuric acid solutions and shows the need for at least a 60-min development period. To get more than 90% of maximum color intensity, longer development times were required at higher concentrations than at lower. The overall slow color-forming reaction time and the longer development times needed with increases in MMH concentration indicated too dilute a concentration of PDAB in the SCAN reagent mix.

The plot of absorbance versus concentration in Figure 3 resulted from analyses done at 445 nm, using a 60-min color-development period. A longer development period would have decreased the extent of the

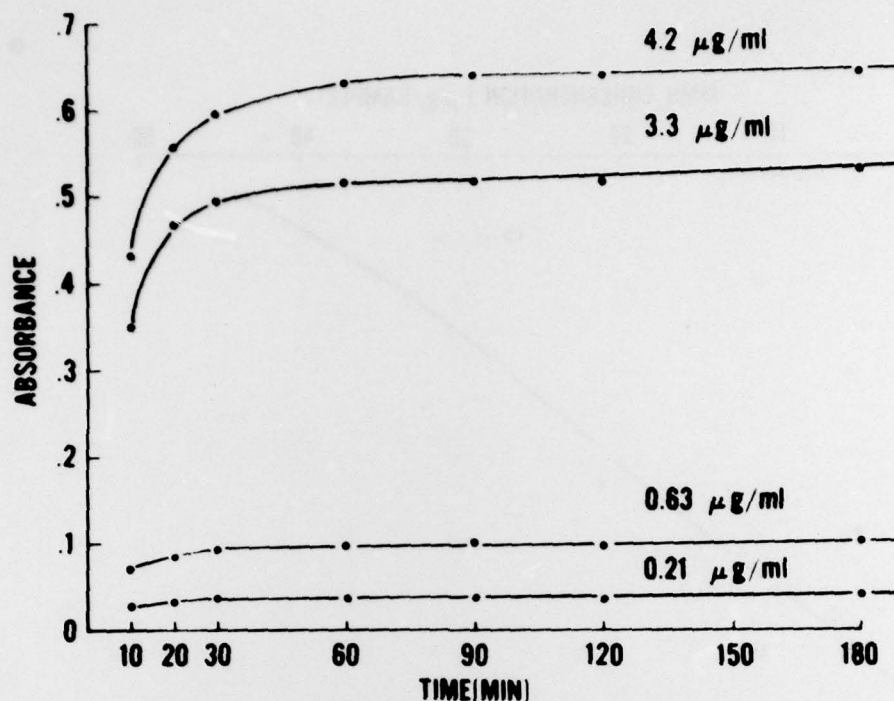


Figure 2. Absorbance as a function of time for various concentrations of MMH analyzed using SCAN (Hydrazine) method and a Spectronics 20 Spectrophotometer at 445 nm.

observed nonlinearity of the plot. Measurements made to obtain the Figure 3 plot were very precise (average coefficient of variation was 3.7%). Sensitivity of the method was adequate for many applications, with MMH concentrations of 3 µg in 15 liters of air (0.1 ppm) easily detectable. Analyses were actually done both at 445 nm and at the literature-recommended wavelength³ of 480 nm, but because of the insignificant differences observed (Table 7), 445 nm was used throughout the study.

TABLE 7. COLOR INTENSITY OF MMH-SCAN REACTION AT HYDRAZINE (445nm) AND LITERATURE-RECOMMENDED MMH (480nm) WAVELENGTHS

MMH concentration (µg)	Wavelength (nm)	Absorbance
50	445	.594
	480	.590
25	445	.315
	480	.310
5	445	.071
	480	.065

³Reynolds, B. A., and A. A. Thomas. A colorimetric method for the determination of hydrazine and monomethylhydrazine in blood. Am Ind Hyg Assoc J 26:527 (1965).

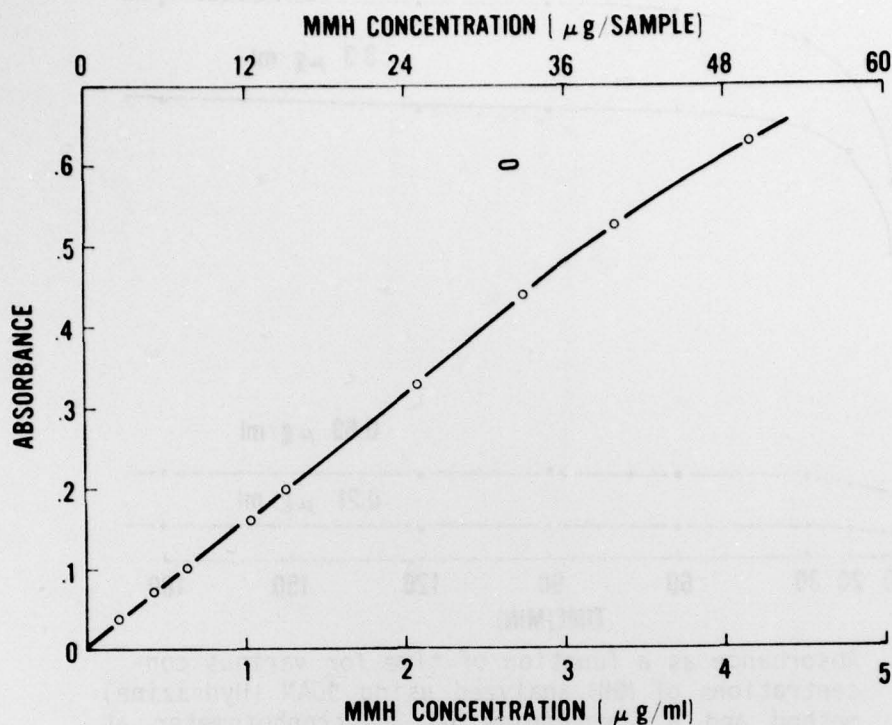


Figure 3. Relationship between absorbance and MMH concentration using SCAN method, a Spectronic 20 spectrophotometer, and 60-min color development.

CONCLUSIONS AND RECOMMENDATIONS

The SCAN method is a viably accurate and easy to use field method for analyzing extremely low concentrations of hydrazine in water and air. Concentrations in air, for example, can be measured to 0.015 ppm (present ACGIH TLV for an 8-hr-day exposure is 0.1 ppm), using a .5-liter air sample volume.

For field use where a 30- to 60-min color development period (which permits some inaccuracies) does not interfere with the purpose of the measurement, the SCAN technique is also adequate for measuring MMH in water and air. Under the conditions prevailing in this study, MMH can be measured at a concentration as low as 0.1 ppm (present ACGIH TLV is 0.2 ppm) using a 15-liter air-sample volume. However, it would be better if the reagent contents of the SCAN sampling ampoule were modified to reduce color development time and possibly increase sensitivity. Sensitivity of the hydrazine tube, as used for MMH, can be increased by a factor of about 2 simply by reducing the volume of impinger/bubbler-collected solution or solid-sorbent extract and using a more efficiently designed sample cup that permits aspiration of a larger fraction of sample.