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A FIELD PROCEDURE FOR DETERMINING LOW CONCENTRATIONS OF HYDRAZI--ETC(U)
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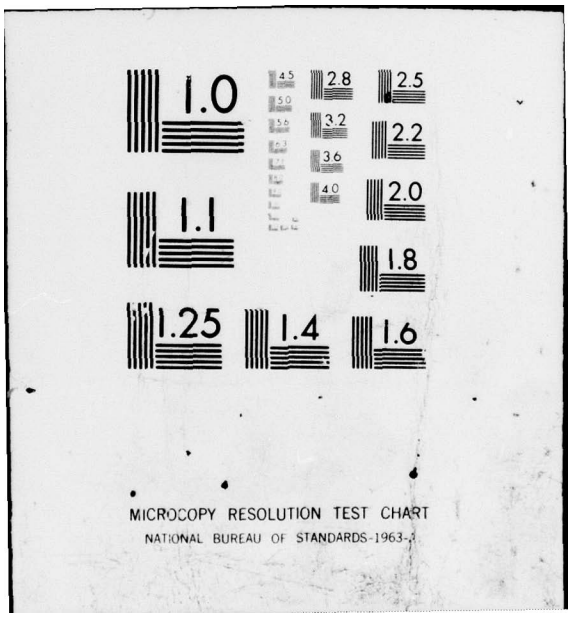
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Report SAM-TR-79-28

A FIELD PROCEDURE FOR DETERMINING LOW CONCENTRATIONS OF HYDRAZINE.

LEVEL II

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USAF SCHOOL OF AEROSPACE MEDICINE
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NOTICES

This interim report was submitted by personnel of the Crew Environments Branch, Crew Technology Division, USAF School of Aerospace Medicine, Aerospace Medical Division, AFSC, Brooks Air Force Base, Texas, under job order 7930-11-36.

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This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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

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

When the TLV for hydrazine exposure was lowered to 0.1 ppm, the only field approach for sampling and analysis that could be used with minimum difficulty involved bubbler sampling, with analysis by the paradimethylaminobenzaldehyde (PDAB) colorimeter method. This method presents problems to the wearer of the sampling system and has been validated only to 0.5 ppm by NIOSH. We have modified and extended the PDAB technique to analyze samples collected on a solid sorbent (acid-treated firebrick) rather than collected with a bubbler, and have shown the usefulness of the technique at exposure concentrations to 0.01 ppm

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20. ABSTRACT (Continued)

and less during long-term sampling. Along with a change in sampling technique, field analysis was simplified by using a commercially available test kit and procedure for hydrazine in water. The method has been studied in the laboratory, and field analysis has been validated in a collaborative test involving analysis of preexposed sampling tubes by a number of participating bioenvironmental engineers and environmental health technicians.

A FIELD PROCEDURE FOR DETERMINING LOW CONCENTRATIONS OF HYDRAZINE

INTRODUCTION

In 1977 the American Conference of Governmental and Industrial Hygienists (ACGIH) reduced the order of magnitude of the threshold limit value (TLV) for hydrazine from 1 to 0.1 ppm (6). Industrial hygienists had virtually no proven way to determine personal time-weighted-average (TWA) exposures at the new lower limit. The method recommended (3), NIOSH method S237, involves bubbler sampling, with analysis based on a colored complex formed with p-dimethylaminobenzaldehyde (PDAB). Bubbler sampling, however, is not desirable for personal-exposure monitoring because it restricts wearer movement. Furthermore, the NIOSH method, having been validated only as low as 0.5 ppm (5), does not meet the 0.1-ppm requirement.

To develop a suitable field procedure for Air Force use in determining TWA exposure to hydrazine, we have investigated the use of solid-sorbent sampling tubes (acid-treated firebrick contained in glass tubing) to collect samples for analysis by the PDAB method. Others (2,8) have studied similar sampling systems which they have used in conjunction with gas chromatographic analyses. To make our method truly a field method, we adapted the Hach Chemical Company water-testing laboratory kit and procedure for hydrazine in water to analyze for airborne hydrazine collected with the sorbent tubes. This procedure is particularly advantageous in the Air Force because the kit is available and used routinely at many bases to perform various waste-water analyses in the field. Since battery-operated personal-sampling pumps are also generally available at Air Force bases, only the procedures and a source for the sampling tubes are required to make this an operationally useful method.

The sampling procedure described here is similar to the one used for sampling organic contaminants with charcoal tubes. The same considerations are necessary in locating and affixing the sampling tube and pump on the individual, and the same need for accurate measurement of sample airflow. High-volume (1-3 lpm) sampling pumps are used for short-duration area sampling, and low-volume (0.05 to 0.20 lpm) pumps for long-duration personal (exposure) sampling.

Field analysis is relatively simple, with minimal handling of the sample, when using the Hach approach. The exposed solid sorbent is dumped directly from a sampling tube into a measured volume of dilute sulfuric acid in a colorimeter bottle. Commercially available Hach hydrazine reagent is added to the bottle. After a fixed color development time, the bottle is topped to a specified volume with glacial acetic acid, and a reading is made on the Hach colorimeter or spectrophotometer. The entire analysis can be completed within half an hour,

and running several samples concurrently would take little more time. As little as 0.5 µg of hydrazine per sample can be detected easily. When the sample contains more than 5 µg, the complex color is too intense to read; however, simple aliquoting techniques can be used to extend the useful upper limit to over 100 µg per sample. Aliquoting must be done before adding reagent.

This paper presents the results of a laboratory evaluation at the USAF School of Aerospace Medicine and a collaborative validation study of the method by bioenvironmental engineering groups at several participating bases. A field application of the technique by the USAF Occupational and Environmental Health Laboratory is summarized.

MATERIALS AND METHODS

Sampling Tubes

The solid-sorbent sampling tube is a 6-mm-ID x 15-cm glass tube packed with 300 mg of 20% by weight sulfuric acid on 30-60-mesh firebrick. The sorbent is held in place by glass-wool plugs. Tubes used in this study were sealed at each end by Parafilm. Sample-tube flow characteristics determined at 23°C and 60% relative humidity with an MSA model PAS 1000 sampling pump are illustrated in Figure 1.

Sampling tubes used in the laboratory to evaluate both sampling and analytical technique were exposed in two ways; statically, by doping with microliter quantities of aqueous hydrazine sulfate standards, and dynamically, by using the hydrazine generator/dilution system shown schematically in Figure 2. Dynamically generated hydrazine concentrations were established from flow rate and vapor-pressure data and verified by bubbler samples measured precisely by the PDAB method. A prototype chemiluminescent hydrazine analyzer (7) was used to monitor hydrazine generation and concentration stability in real time. Typically, dynamically generated concentrations could be maintained within 10% over 30-60-minute periods. Dilution air varied from 40% to 70%, relative humidity at approximately 23°C (73°F).

Reagents

The reagents used in this study were all analytical reagent grade or better and included:

a. Sulfuric acid, conc.
b. Glacial acetic acid
c. Firebrick, 30-60 mesh (purchased as Gaschrom-R from Applied Science Laboratories, State College PA)
d. p-Dimethylaminobenzaldehyde hydrazine reagent. (Hydraver II, purchased from Hach Chemical Co., Ames IA)
e. Hydrazine, anhydrous
f. Hydrazine sulfate

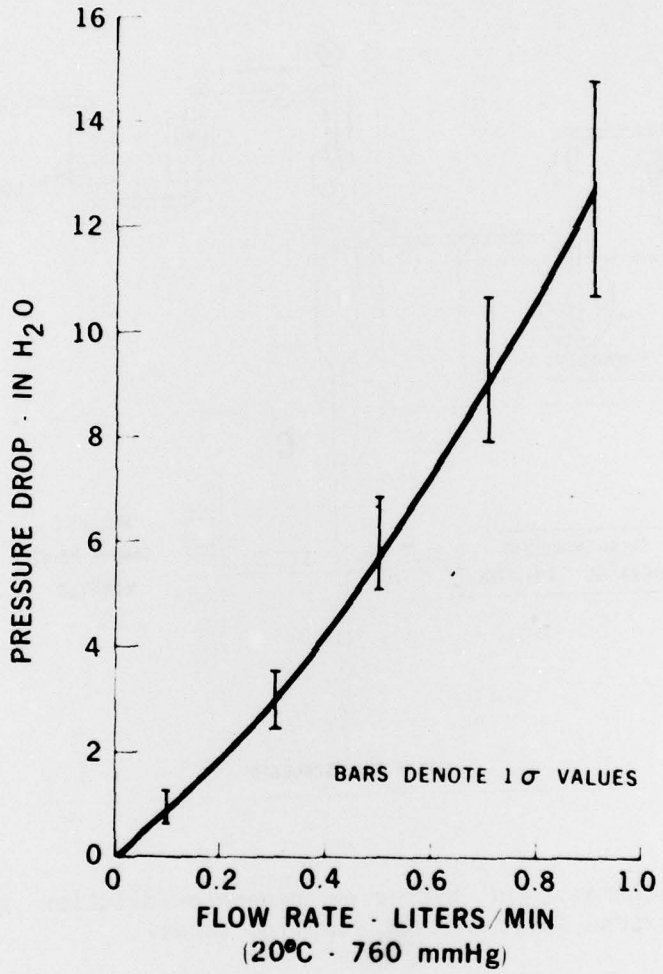

Figure 1. Pressure drop for typical solid-sorbent hydrazine-sampling tube. Data collected at 23°C (corrected to a standard 20°C) and 60% relative humidity.

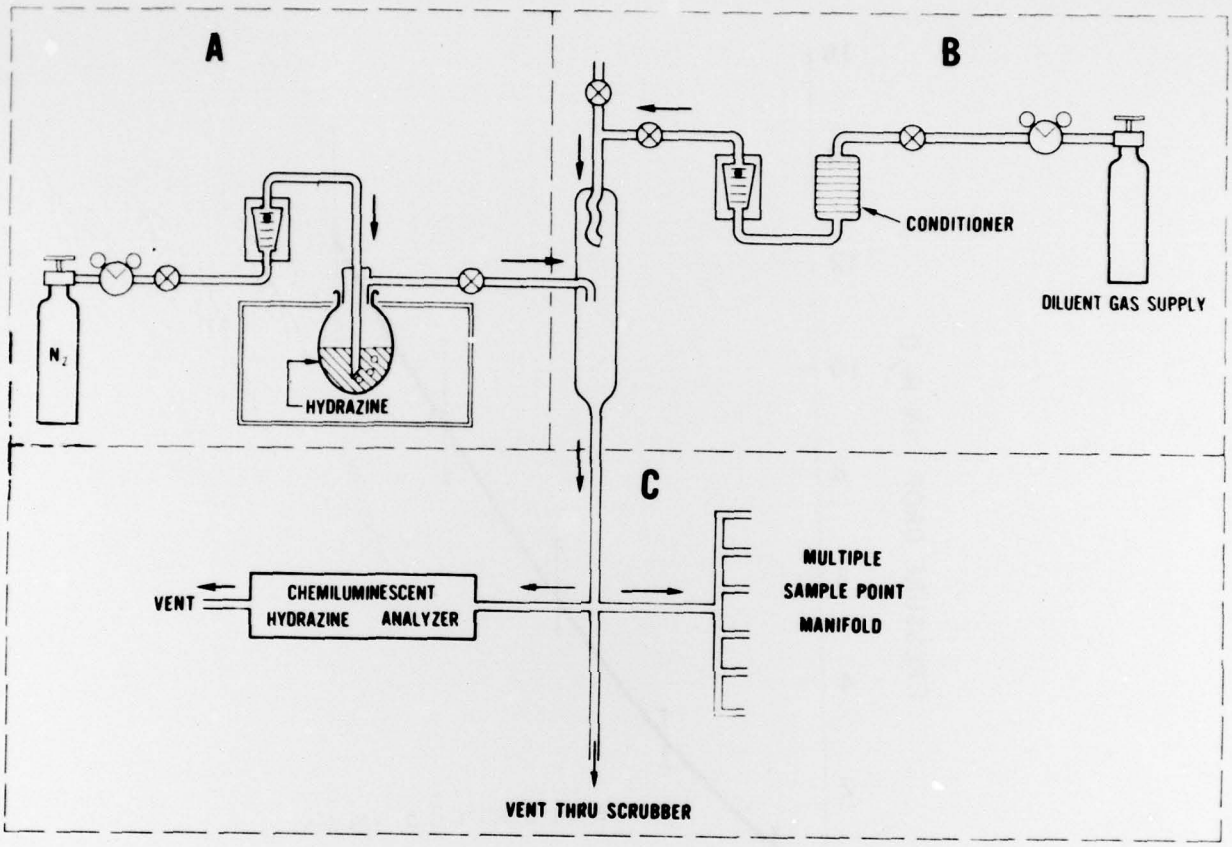

Figure 2. Schematic of hydrazine generator/dilution system used to expose solid-sorbent sampling tubes.

Instrumentation

A Hach model DR-EL colorimeter, with Hach No. 5543 blue filter, and a Hach model DR-2 spectrophotometer at a 455-nm setting, were used in these investigations. Matched 25-ml colorimeter bottles provided with the Hach kits were used as the cuvettes for all analyses.

Analytical Procedure

The field analytical procedure, as used in the laboratory and field testing program, is reproduced below in outline form to stress its simplicity:

a. An estimated 10-ml aliquot of 0.1N sulfuric acid was measured into a 25-ml colorimeter bottle. (A blank was prepared in the same manner at the same time.)
b. The solid sorbent was poured directly into the bottle.
c. Hydraver II reagent (1 ml) was added using the reagent bottle dropper.
d. Contents were swirled intermittently during 8 minutes allotted for color development.
e. The bottle was filled to the 25-ml mark with glacial acetic acid and contents were mixed.
f. Four minutes were allowed for solution bubbles to disappear.
g. The solution was read on a colorimeter using a Hach No. 5543 (Corning 5-60) color filter or on a spectrophotometer at 455 nm.
h. Concentrations (in µg) of hydrazine were obtained from a calibration curve such as the one shown in Figure 3, which was made using a Hach colorimeter. Calibration curves were obtained using standard hydrazine sulfate solutions.

RESULTS AND DISCUSSION

Laboratory Evaluation

Results from a preliminary test and evaluation of the solid-sorbent/PDAB method are presented in Table 1. Overall recovery when dosing with microliter pipettes was very good over the range of 1- to 9.95-µg sample size, with recovery values all better than 95%, even after 20 days had elapsed between tube exposure and analysis in aging tests. Two lots of tubes were subjected to 8 hours of 1-lpm pure air flow, after loading with 1.01 and 9.95 µg of hydrazine, to investigate the oxidation stability of hydrazine trapped on the solid sorbent. Data again showed 95% or better recovery and indicated the usefulness of the sampling tubes to measure long-term exposures where most exposure results from a short-term high concentration occurring early or late in the sampling period.

Results obtained for dynamically exposed sampling tubes are presented in Table 2. Collection efficiency appears to be independent of concentration and sample flow rate within the ranges of the variables tested. A chemiluminescent hydrazine analyzer (sensitive to 0.015 ppm) and backup tubes were used to determine if and how much hydrazine was not retained on the primary sampling tube. Neither method detected any breakthrough of hydrazine. Recovery of hydrazine from the solid sorbent

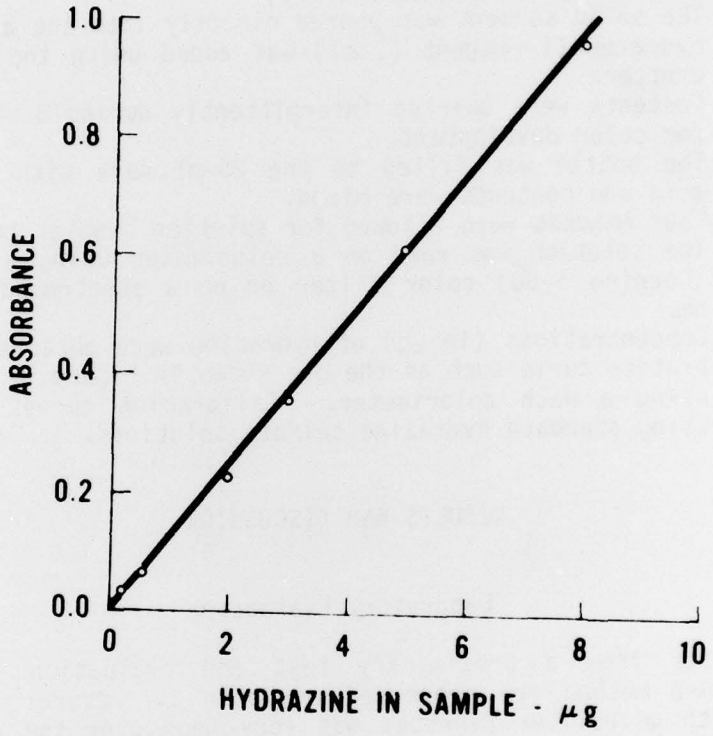

Figure 3. Calibration curve for hydrazine measured by PDAB on a Hach colorimeter.

TABLE 1. ANALYSIS OF STATICALLY LOADED HYDRAZINE SAMPLING TUBES

Calc. standard	Anal. standard	Hydrazine concentration (µg) P-1[a]	P-7[b]	P-20[c]	P-0[d]
1.00	1.01±.03	1.01±.03	.96±.06	.96±.04	.95±.04
4.00	3.97±.08	3.93±.05	3.88±.10	3.85±.05	
10.00	9.95±.12	9.88±.13	9.75±.12	9.70±.10	9.75±.39

[a]Sample tubes analyzed immediately after hydrazine exposure.
[b]Sample tubes analyzed 7 days after hydrazine exposure.
[c]Sample tubes analyzed 20 days after hydrazine exposure.
[d]Sample tubes analyzed after hydrazine exposure followed by 8 hours of exposure to a 1-lpm air flow.

TABLE 2. RESULTS OF DYNAMICALLY EXPOSING HYDRAZINE SAMPLING TUBES

Hydrazine concentration (ppm in air)	Sampling rate (lpm)	Time (min)	Hydrazine concentration (µg) Exposed	Recovered	% Recovery
0	1.0	60	0	0	
0.28	0.2	30	2.23	2.09	93.7
0.31	0.3	20	2.42	2.60	107.4
0.46	0.1	40	2.42	2.40	99.2
0.59	1.0	4	3.10	2.90	93.5
0.71	0.2	60	11.25	10.56	93.9
10.29	0.5	20	135.40	137.00	101.2

did not differ significantly from that recorded for the static exposures presented in Table 1. The small differences that were observed can be explained by the difficulty in controlling the generation of airborne concentrations of hydrazine and in verifying the hydrazine concentration delivered to the sampling tubes. All data resulted from replicate sets containing at least six samples.

Field Test and Evaluation

A USAF Occupational and Environmental Health Laboratory (OEHL) study of hydrazine exposures at various maintenance tasks involved with the F-16 hydrazine-fueled emergency power unit (1) afforded an opportunity to field test and evaluate the method. A summary of the samples collected during this study is presented in Table 3. Many of the samples were collected in duplicate and showed the method itself to be very reproducible; thus, the variability in exposures for each of the three tasks is considered to be true exposure variability.

TABLE 3. FIELD TEST AND EVALUATION OF HYDRAZINE SAMPLING TUBES

Variables	Personal exposure			Other measurements
	Task A	Task B	Task C	
Number of samples	12	12	22	12
Time duration (minutes) - minimum	13	8	19	1.0
- maximum	33	9	108	55
Flow rate (liters/minute) - minimum	1.2	1.0	1.2	1.1
- maximum	1.9	2.0	2.1	2.1
Concentration (µg/liter) - minimum	0.01	<0.01	0.01	0.03
- maximum	0.17	0.14	0.71	633+
- mean	0.045	0.038	0.161	NA
- SD	0.054	0.055	0.147	NA

Collaborative Study

Since laboratory studies of the solid-sorbent sampling tubes with Hach kit analysis and the OEHL field use of the method showed great promise, a collaborative validation test of the method for field use was undertaken. Thirteen participant bases and activities were selected, and predosed sample tubes were provided for analysis by each participant. Participants were selected on the basis of having the Hach kit on hand and having an individual operator familiar with other Hach analyses. Detailed procedures were provided and instructions given that there should be absolutely no deviation from the procedures as written. Three "practice" tubes were provided to permit familiarization with the procedure prior to running the test samples. Finally three tubes, each at a different dose level, were provided to each participant, with instructions to analyze the samples on a specified date. This procedure allowed the variability of only the analytical method to be determined. Sampling variability was assumed similar to that reported for charcoal tubes in a study by NIOSH (4).

Because of various problems encountered with lost samples, the collaborative study results are not complete. Preliminary data received from five of the participating bases are summarized in Table 4. These results show relatively good agreement with laboratory studies, with an

TABLE 4. COLLABORATIVE TEST OF HYDRAZINE SAMPLING TUBES

Participant	Hydrazine found - µg/sample tube		
True value	1.00	3.20	4.15
A	0.82	3.20	4.12
B	0.97	3.15	5.40
C	0.68	2.80	3.70
D	0.96	2.93	3.75
E	0.58	2.88	3.87
Mean of 5 groups	0.80	2.99	4.17
SD of means	0.17	0.18	0.68

expected but acceptable small decrease in precision and accuracy. The use of a laboratory-prepared calibration, rather than having each participating base prepare standards for calibration, did not contribute to the observed variability. In terms of airborne concentrations, the 1.00-, 3.20-, and 4.15-µg values were derived by trapping hydrazine from appropriate volumes of air containing 0.05, 0.27, and 0.17 ppm respectively.

CONCLUSIONS

Returns from the collaborative study are not sufficient to determine a coefficient of variability for this procedure. The limited results, however, appear reasonable for a field test where participants had no experience with the method. Even limited experience would be expected to improve the precision of the method.

When the trade-off between sampling times and flow rates required to collect a minimum of 1 µg is considered, the procedure is useful for determining concentrations well below 0.1 ppm for all but very short sampling times. The sample could be aliquoted in the field, and half the sample could be analyzed on the spot to provide immediate decision-making data, with the remainder sent for verification analysis to a central laboratory for more precise analysis under laboratory conditions.

REFERENCES

1. Christiansen, W. D. An evaluation of occupational exposure to hydrazine (H-70) during routine maintenance tasks associated with the F-16 emergency power unit. USAF Technical Report OEHL-78-23, Brooks AFB, Texas, Mar 1978.

2. Dee, L. Personal Communication, USAF Rocket Propulsion Laboratory, Edwards AFB, Calif., 1978.

3. NIOSH manual of sampling data sheets. USDHEW (NIOSH) Publication No. 77-159. Cincinnati, Ohio, Mar 1977.

4. Reckner, L. R., and J. Sachdev. Collaborative testing of activated charcoal sampling tubes for seven organic solvents. USDHEW (NIOSH) Publication No. 75-184, Cincinnatti, Ohio, June 1975.

5. Taylor, D. G., R. E. Kupel, and J. M. Bryant. Documentation of the NIOSH validation tests. USDHEW (NIOSH) Publication No. 77-185. Cincinnati, Ohio, Apr 1977.

6. Threshold limit values for chemical substances in workroom air adopted by ACGIH for 1977. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1977.

7. Volltrauer, H. N., and L. J. Luskus. Breadboard chemiluminescent analyzer for measurement of hydrazines. SAM-TR-77-36, Dec 1977.

8. Wood, G. O., and R. G. Anderson. Development of air-monitoring techniques using solid sorbents. Progress report April 1-September 30, 1976. Report LA-6738-PR, Los Alamos Scientific Laboratory of the University of California, Los Alamos, N. Mex., Mar 1977.