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FIELD TESTING OF SOLID-SORBENT SAMPLING–COLORIMETRIC ANALYSIS FOR HYDRAZINE IN AIR

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October 1980

Interim Report for Period 1 April 1978 - 30 November 1979

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USAF SCHOOL OF AEROSPACE MEDICINE
Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas 78235

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 technical report has been reviewed and is approved for publication.

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Hydrazine

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

A field sampling and analytical method for measuring hydrazine in air at and below the TLV concentration of 0.1 ppm was developed at USAFSAM. The method uses the Hach field water-analysis kit to analyze samples collected on acidified firebrick sorbent packed in a glass tube through which air is pulled by a miniature personal sampling pump. This report presents the results of a collaborative field study done by 13 participating organizations to validate this method for field use. The study showed that relatively inexperienced analysts had satisfactory results when using this method. For example, hydrazine

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20. ABSTRACT (Continued)

concentrations of 0.05 (one-half the TLV) to 0.33 ppm, collected over times ranging from 8 to 17 minutes, were measured with an accuracy of better than 80% (recovery ranged between 80% and 105% for the 8 concentrations analyzed). Field use of the method is recommended.

FIELD TESTING OF SOLID-SORBENT SAMPLING--COLORIMETRIC ANALYSIS FOR HYDRAZINE IN AIR

The United States Air Force School of Aerospace Medicine (USAFSAM) developed a simple and expedient method for field sampling and analysis of hydrazine in air (1). For sampling, air contaminated by hydrazine vapors is drawn through a glass tube containing an acid-impregnated solid sorbent. The solid sorbent efficiently traps the hydrazine as a salt stable to air oxidation. Analysis is done colorimetrically using a Hach colorimeter or spectrophotometer, Hach chemical reagents, and a minor modification of the Hach hydrazine-in-water method. The analytical approach was chosen mainly because the specific equipment and reagents were available and widely used by Air Force personnel doing water analysis. Overall, the sampling and analytical method is similar to that described in NIOSH method S-237 (2) but is more versatile and easier to implement. The NIOSH method uses bulkier and harder-to-handle liquid-filled impingers for sampling, with colorimetric analysis that relies on the reaction between hydrazine and p-dimethylaminobenzaldehyde (PDAB). The Hach reagent also contains PDAB and relies on the same reaction. NIOSH has validated their method only as low as 0.5 ppm, whereas the USAFSAM method described here has been shown useful to less than 0.01 ppm.

Since miniature personal sampling pumps and Hach kits (TA 906) are found on many Air Force bases, validation of the method would mean that the main problem in having a useful hydrazine method readily available in the Air Force would be developing a commercial source for the sampling tubes. To aid in validation, 13 Air Force activities, including USAFSAM, were selected to participate in a collaborative testing program. Program participants are listed in Table 1. The objective of this collaborative test was to validate only the analytical part of the method since we had no realistic way to provide all participants with access to a standard hydrazine-in-air source to field validate both sampling and analysis. Moreover, since interlaboratory variability for similar sampling is known (for example, NIOSH validation of the charcoal sampling method (3)), determination of interlaboratory variability in the extraction/analysis portion of the procedure should provide us with a good indication of overall sampling/analysis accuracy.

Most participants in this study already had limited skill in Hach analysis, and all were afforded the opportunity to learn the hydrazine procedures by

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1. Suggs, H. J., et al. A field procedure for determining low concentrations of hydrazine. SAM-TR-79-28, Dec 1979.

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

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

TABLE 1. PARTICIPANTS IN COLLABORATIVE FIELD TESTING OF HYDRAZINE SOLID-SORBENT SAMPLING--COLORIMETRIC ANALYSIS

1. USAFSAM/VNL
   Brooks AFB TX 78235
2. USAFSAM/EDE
   Brooks AFB TX 78235
3. USAF OEHL
   Brooks AFB TX 78235
4. USAF Hospital/SGPM
   Davis-Monthan AFB AZ 85707
5. USAF Hospital/SGB
   Hill AFB UT 84406
6. USAF Hospital/SGPM
   Luke AFB AZ 85309
7. USAF Hospital/SGPM
   McConnell AFB KS 67221
8. USAF Hospital/SGPM
   Minot AFB ND 58701
9. USAF Hospital/SGPM
   Nellis AFB NV 89110
10. USAF Medical Center/SGPM
    Scott AFB IL 62225
11. USAF Hospital/SGB
    Tinker AFB OK 73145
12. USAF Hospital/SGPM
    Vandenberg AFB CA 93437
13. USAF Medical Center/SGPB
    Wright-Patterson AFB OH 45433

analyzing three practice samples a few weeks before receiving the first set of test samples. Two approaches were used for testing. Approach one used samples prepared by dynamically exposing the sampling-tube sorbent to hydrazine produced by a calibration gas generator-dilution system that simulated actual field exposures. Approach two used samples prepared by pipetting known quantities of hydrazine onto the solid sorbent contained in the sampling tube. In both instances, the tube contents were extracted and analyzed by the test participants. Unexposed tubes served as blanks for both approaches. Reagents were provided by our laboratory to standardize the potential source of error from reagent procurement and preparation. A specific date was set for analysis so that all tubes could be analyzed at the same postexposure time. Sample air volumes were provided for each dynamically loaded sample so that results could be calculated in both µg/l and ppm. A data/questionnaire sheet was included with the samples to simplify response and gather comments on subjective aspects of the procedure.

METHODS AND MATERIALS

Sampling Tubes

The sorbent sampling tube (Fig. 1) was a 6-mm-ID x 15-cm-long glass tube packed with 300 mg of 10% by weight sulfuric acid on 30/60-mesh firebrick (GasChrom R). Stainless-steel 60-mesh screen plugs held the sorbent in place, and Parafilm was used to cap the ends of a tube until ready for sampling. Tubes were resealed with Parafilm after exposure to hydrazine unless analyzed immediately.

Sets of six tubes were exposed simultaneously, with one sample per set analyzed by the PDAB method to verify the loading concentration of the set. The tubes were dynamically exposed to various airborne concentrations of hydrazine, using the hydrazine generator-dilution system illustrated in Figure 2.

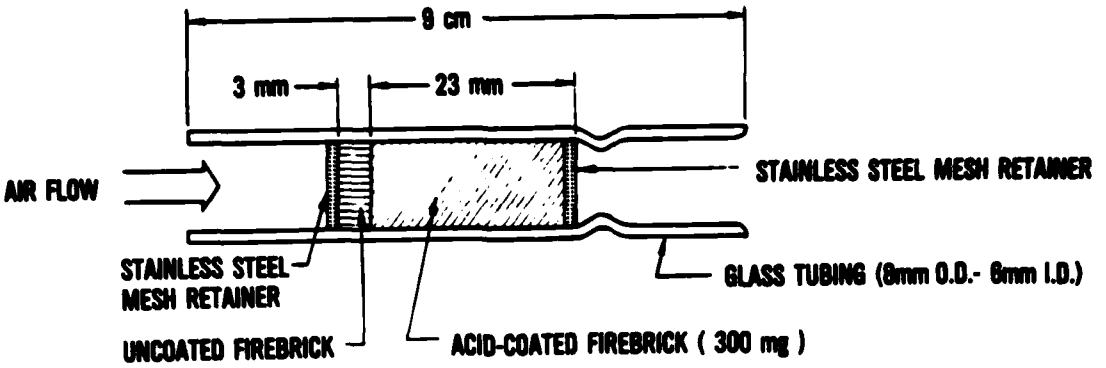

Figure 1. Drawing of solid-sorbent sampling tube for measuring hydrazine in air.

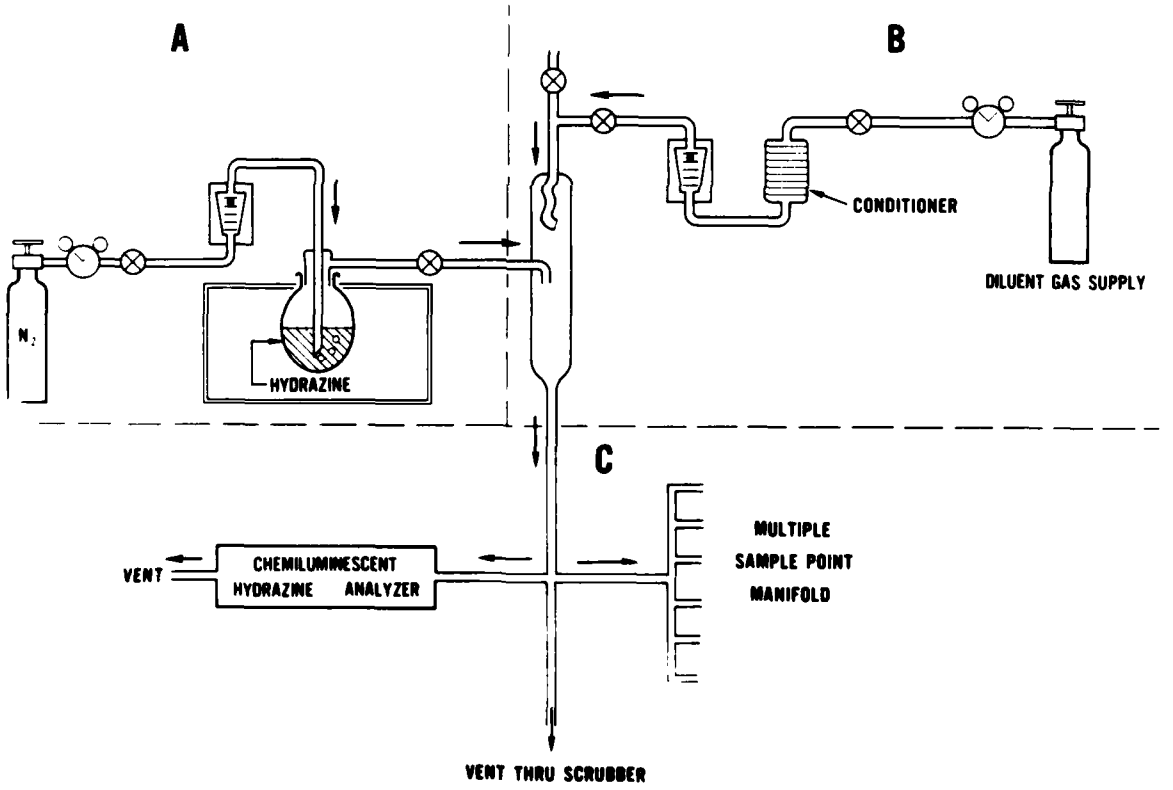

Figure 2. Schematic of hydrazine generator-dilution system used to expose solid-sorbent sampling tubes.

Apparatus

A spectrophotometer measuring sample transmittance at 458 nm or a colorimeter measuring transmittance through an appropriate blue filter was required for this investigation. Consistent with Air Force inventory, the Hach model DR/2 spectrophotometer and the Hach model DR-EL colorimeter with Hach No. 5543 color filter were used for the analyses. Calibration curves (Fig. 3) were supplied to study participants, as were standard hydrazine sulfate solutions for cases where the participant might want to personally prepare the curves. Matched colorimeter bottles of 2.54-cm (1-in) pathlength (Hach No. 13537) were used for all analyses reported herein.

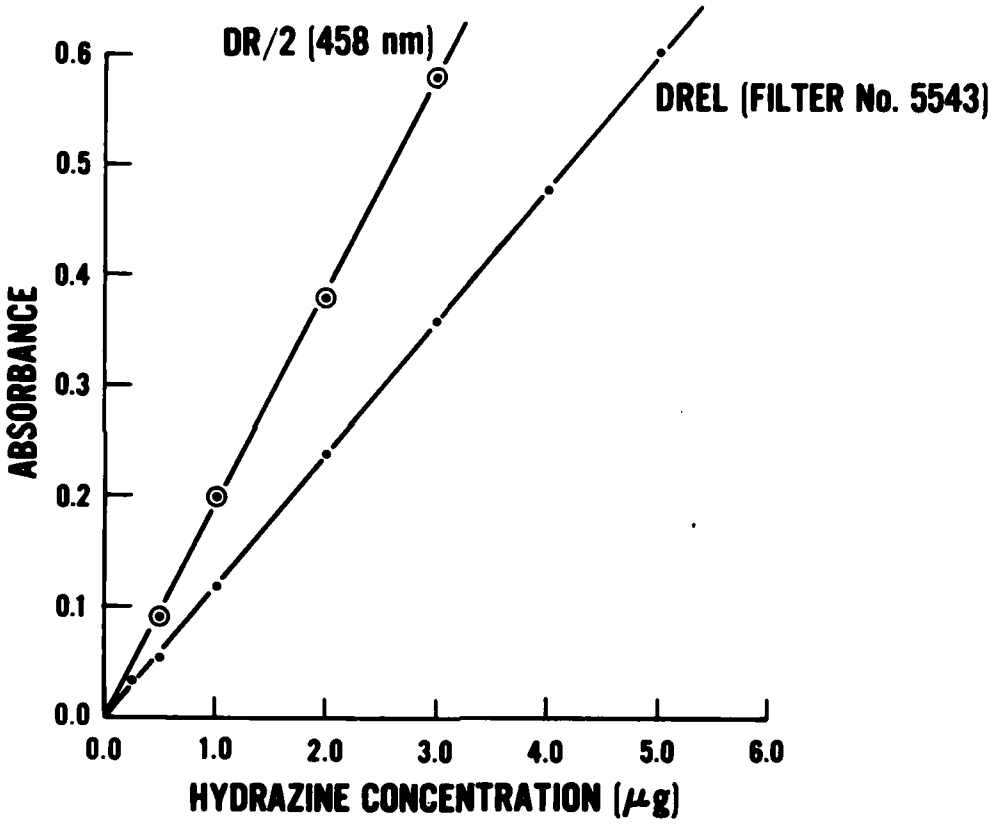

Figure 3. Hydrazine calibration curves for Hach DR/2 spectrophotometer and Hach DR-EL colorimeter.

Reagents

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

a. Sulfuric acid, conc.

b. Sulfuric acid, 0.1N

c. Acetic acid, glacial

d. Firebrick, 30/60 mesh, Gaschrom-R, Applied Science Laboratories, P. O. Box 440, State College PA 16801

e. p-Dimethylaminobenzaldehyde hydrazine reagent, Hydraver II, Part No. 1790, Hach Chemical Co., P. O. Box 907, Ames IA 50010

f. Hydrazine, "Baker Grade," Part No. 7-N360, J. T. Baker Chemical Co., Phillipsburg NJ 08865

g. Hydrazine sulfate, Part No. 4-2177, J. T. Baker Chemical Co., Phillipsburg NJ 08865

Analytical Procedure

The following procedure was used by laboratory and test participants.

1. Measure into each of two colorimeter bottles, one labeled blank and the other labeled unknown, 10 ml of 0.1N H_2SO_4.

2. Add 1 ml Hydraver II reagent (mark on dropper is equivalent to 1 ml) to each bottle.

3. With wirehook, remove stainless-steel plug from the sampling tube and pour contents, including plug, into the properly labeled colorimeter bottle.

4. Set timer for 8 minutes; swirl each bottle intermittently.

5. Bring each bottle to 25-ml total volume with glacial acetic acid. (The graduated line on the colorimeter bottle is a 25 ml calibration mark. If no line is present, the bottle must be calibrated and marked.)

6. Place Parafilm over mouth of bottle and invert 5-6 times.

7. Set timer for 4 minutes, a time for bubbles to disappear. Tapping on table intermittently facilitates bubble removal.

8. Read %T on Hach spectrophotometer at 458 nm or on Hach colorimeter using No. 5543 color filter. (Use the blank to set 100%T and read samples against this setting.)

9. Convert %T to OD (absorbance) using table provided, and read µg of hydrazine off calibration curve.

Test Protocol

The first step in the collaborative test program was to send all participants a package containing the items listed as "provided" in Table 2. Three exposed tubes labeled with their hydrazine concentration were included in this package to give the participants practice, familiarity with the method, and confidence in their ability to handle the unknown test samples.

TABLE 2. EQUIPMENT AND MATERIAL NEEDED FOR COLLABORATIVE FIELD TEST

Provided	Not provided
Instructions/information	Hach colorimeter
Analytical procedure	Hach spectrophotometer
Data sheet/questionnaire	Hach color filter No. 5543
Calibration curves	Timer
Conversion table (%T to absorbance)	
Sampling tubes (exposed and unexposed)	
Parafilm	
Wire hook	
Sulfuric acid (0.1N)	
Hydraver II reagent	

The second phase of testing involved sending each participant (1) two unexposed sampling tubes to serve as blanks, (2) five exposed tubes of known hydrazine concentration (1, 2.5, 4.5, 6, and 8 µg) to verify the accuracy of the provided calibration curve, and (3) three sets of sampling tubes of three hydrazine concentrations (9 tubes) unknown to the participants.

Sampling tube analyses by the participants were scheduled for the same day to remove any postexposure effects.

Test data sheets (Fig. 4) were completed at end of analyses and forwarded to USAFSAM/Crew Environments Branch with the test results.

Air volumes used in exposing sampling tubes were provided to the participants to permit calculation of airborne hydrazine concentrations (µg/l and ppm).

RESULTS AND DISCUSSION

Background

Three sets of samples were sent to participating bases, although the original intent was to send only one set. The first set of samples resulted in only five responses because of mailing problems, so a second set of samples was prepared and provided for testing. This second set resulted in 10 responses, which more nearly satisfied the original requirement for participation by a good-size cross-section of our field laboratories. After compiling results of the first two testing efforts, we decided to try a third time. The first two sample sets produced what appeared to be some error contributed to by problems in the dynamic loading of the sampling tubes. That is, the analytical results may have included error in generation of hydrazine concentrations in air as well as error intrinsic to the analysis and to personal factors. Thus, a third set of samples was prepared by loading tubes with standardized aqueous sulfuric acid solutions of hydrazine sulfate, and the results of the analyses were compared with those obtained from the dynamically loaded sets.

Sample Set 1

Results of the field analyses of the first set of sampling tubes are summarized in Table 3. "True values" are an average of 10 measurements of

COLLABORATIVE TEST
HYDRAZINE IN AIR FIELD ANALYSIS
(FOR TEST SAMPLES ONLY - DO NOT USE FOR PRACTICE TUBE RESULTS)

Participant Code Nr. _____ Date Samples Received _____

Date Analysis Required _____ Date Analysis Done _____

Time analysis started (start from opening first test sample tube) _____

Time analysis completed (time last reading recorded _____

Lapsed time _____

Time for break in analysis, eg lunch etc _____

Net Analysis time _____

Hach Instrument used: [ ] DR/EL 1: confirm filter used _____

[ ] DR/EL 2: confirm wave length used _____

Tube Nr	Air Volume (liters)	% Transmission	O.D	ug Hydrazine	ug/liter	ppm

Analyst: Education level (highest level completed) _____

AFSC _____ Total years environmental health work _____

Use Hach kit routinely Yes [ ] No [ ]

Number of different kinds of analysis done (eg DO, Iron, Cl^-, etc) _____

Average number samples/analyses per month _____

Subjective evaluation of laboratory proficiency _____

Method - Evaluation by Analyst	Easy				Difficult
Is the procedure easy to understand	[ ]	[ ]	[ ]	[ ]	[ ]
Are tubes easy to open, empty	[ ]	[ ]	[ ]	[ ]	[ ]
Is extraction easy to do	[ ]	[ ]	[ ]	[ ]	[ ]
Is measurement easy to make	[ ]	[ ]	[ ]	[ ]	[ ]
Are calculations easy	[ ]	[ ]	[ ]	[ ]	[ ]

Please describe any difficulty you encountered in the procedure:

How did you calculate results - long hand [ ]

slide rule [ ]

calculator [ ]

Any other comments:

Figure 4. Collaborative study questionnaire/data sheet.

hydrazine concentrations made in our laboratory before, during, and after exposure of the sampling tubes; analyses of the 10 tubes were done within 8 hours of exposure.

TABLE 3. TESTING OF HYDRAZINE SAMPLING TUBES: FIRST SAMPLE SET

Participant	Hydrazine found--µg/sampling tube		
True value	1.00 ± .05	3.20 ± .05	4.15 ± .07
A	0.82 ± .08	3.20 ± .05	4.12 ± .13
B	0.97 ± .03	3.15 ± .06	5.40 ± .09
C	0.68 ± .03	2.80 ± .05	3.70 ± .07
D	0.96 ± .05	2.93 ± .16	3.75 ± .10
E	0.58 ± .03	2.88 ± .13	3.87 ± .06
Means of 5 groups	0.80 ± .17	2.99 ± .18	4.17 ± .68
CVm	0.21	0.06	0.16
Volume of air sampled at 1 l/min	14 l	8.26 l	17 l
Hydrazine concentration calculated	0.05 ppm 0.918 µg	0.27 ppm 2.92 µg	0.17 ppm 3.79 µg

Precision and accuracy for this study were good. Precision for the individual sets of measurements showed a coefficient of variation (CVs) of better than 10% for all reported results. Precision of the five-group means (CVm) was better than 21%. Accuracy of the lowest concentration measured (1.00 µg collected at 1 l/min from an air source approximately 0.05 ppm in hydrazine) was lower than expected; however, some of this error can be explained by the time between sampling-tube exposure and analysis. For example, Suggs et al. (1) showed recovery of hydrazine at this concentration to be about 95% after 20 days of exposed tube storage. While the potential loss of hydrazine from this source is minimal, it is accountable and would increase the accuracy estimation by 25% (recovery of 0.80 µg from 0.95 µg rather than from 1.00 µg).

Sample Set 2

Results from the second set of dynamically exposed sampling tubes are summarized in Table 4. Hydrazine air concentrations used for exposing the tubes ranged between 0.076 and 0.33 ppm. Accuracy and precision of the measurements were in agreement with those found in set 1.

Sample Set 3

The third set of samples differed from the preceding sets in the manner of sampling-tube loading. The exposed tubes were prepared by doping with standard hydrazine sulfate solutions using microliter pipets. The USAFSAM laboratory determined true values by analyzing samples prepared at the same time and held for the same length of times as the field samples. (True values had been determined at time of loading for the first two sets.) Values obtained by analyses were within 3% of calculated standards. Results of this sample set are presented in Table 5. If results from two of the participants (I and K) are omitted as outliers, the demonstrated precision is better than in the case of

the dynamically loaded sampling-tube sets. Accuracy is somewhat better. Dynamic loading of the sampling tubes seems to have contributed some uncertainty to the true value, but not enough to affect the overall conclusion that the analytical method is very rugged and reproducible in the hands of even relatively unskilled analysts.

TABLE 4. TESTING OF HYDRAZINE SAMPLING TUBES: SECOND SAMPLE SET

Participant	Hydrazine found--µg/sampling tube		
True value	1.26 ± .12	3.97 ± .29	7.35 ± .44
A	1.05 ± .44	3.90 ± .46	----
B	.93 ± .06	4.15 ± .78	8.27 ± .12
C	1.33 ± .46	2.93 ± .47	7.60 ± 1.35
D	1.44 ± .60	4.98 ± .56	7.35 ± .98
E	.77 ± .55	3.85 ± .61	7.78 ± 1.37
F	1.00 ± .53	3.93 ± 1.04	8.23 ± .58
G	.77 ± .15	3.80 ± 2.63	----
H	.75 ± .27	4.40 ± 1.54	7.67 ± 1.16
I	1.30 ± .46	4.37 ± .39	7.98 ± .93
J	1.17 ± .15	3.43 ± .06	6.87 ± .75
Mean of 10 groups	1.05 ± .25	3.97 ± .56	7.71 ± .46
CVm	.24	.14	.06
Volume of air sampled at 1 l/min	12 l	9 l	17 l
Hydrazine concentration calculated	0.076 ppm	0.33 ppm	0.33 ppm
	0.91 µg	3.91 µg	7.36 µg

TABLE 5. TESTING OF HYDRAZINE SAMPLING TUBES: THIRD SAMPLE SET

Participant	Hydrazine found--µg/sampling tube	
True value	1.03 ± .05	4.15 ± .05
A	.99 ± .03	4.50 ± .10
B	.87 ± .12	4.17 ± .12
C	----	----
D	1.00 ± .12	4.20 ± .13
E	.73 ± .03	4.05 ± .10
F	.96 ± .04	3.95 ± 0
G	.99 ± .17	4.55 ± 0
H	.82 ± .19	3.37 ± .25
I	1.02 ± .50	7.02 ± 1.4
J	.83 ± .03	3.84 ± .35
K	1.38 ± .11	5.74 ± .20
Mean of 10 groups	.95 ± .17	4.54 ± 1.07
CVm	.18	.22
Mean of 8 groups *	.89 ± .10	4.08 ± .38
CVm	.11	.09

* Excluding participant I and K values.

Comments

Responses to the questionnaires returned with the analytical results were incomplete and hard to quantify in any statistically valid manner. Nevertheless, some of the information obtained was useful and is discussed in this section.

Total elapsed time for analyses of nine samples ranged between 1 and 4 hours, with a net time of 1 to 3 hours. Of the 17 reported times, 8 showed a break of at least 1 hour during time of analysis. The most important observation in this instance is not the actual time for analysis, which included setup of apparatus and running of practice samples, but the interruption of analyses at undetermined points without adversely affecting the analytical results.

The instruments used during the collaborative study were three DR/2 spectrophotometers (4 sets of analyses) and nine DR-EL colorimeters (16 sets of analyses). Data do not indicate the superiority of one instrument over the other with regard to accuracy or precision. The colorimeter did suffer a disadvantage in that it was necessary for at least two of the participants to measure blank and exposed tubes relative to water and subtract the difference to get a final reading. The portable instruments used did not always permit enough light to reach the detector when the colored blank was used to set 100%T. Subjectively, users of both instruments preferred the spectrophotometer because it was more versatile and easier to use.

Education and experience levels of the analysts are indicated by their AFSC designations as 90750 and 90770 environmental health technicians and their on-the-job experience ranging between 2 and 14 years. They were asked to evaluate the five potential problem areas with a rating of 1 through 5: easy to difficult. In assessing ease in understanding the procedure, ease in opening and using tubes, ease of extraction, ease of measurement, and ease of calculation, the participants gave mainly a rating of 1 with a scattering of 2's in all categories.

Calculations of ppm and mg/m^3 were a problem to only one participant. One set of data was rejected because the participant had set the wrong wavelength on the spectrophotometer. The anomalous data resulting in rejection were explained by the wrong wavelength that was recorded on the questionnaire.

CONCLUSIONS AND RECOMMENDATIONS

The data from this collaborative study show that the firebrick solid-sorbent hydrazine-measurement technique can yield satisfactory results when used by relatively unskilled analysts with little prior experience. We therefore recommend that the technique be made operational in the field.


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