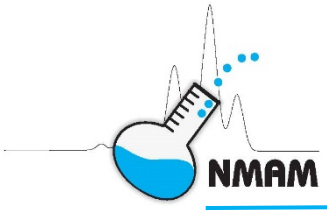

BACKUP DATA REPORT
NIOSH Method No. 6002

Title: Phosphine
Analyte: Phosphine
Author/developer: Developed under contract #210-76-0123
Date: March 17, 1978

Backup Data Report 6002
March 17, 1978

Substance: Phosphine
OSHA Standard: 0.3 ppm (0.4 mg/m^3)
Chemical Used: Phosphine in nitrogen, 306 and 350 µg/L, Matheson Gas Company

General Considerations

The method for phosphine has been tested in accordance with the various criteria for validation described in Reference 1 and in conformity with the statistical analysis described in Reference 2. The statistical criteria established for this program are related to the present suggested standard for air monitoring accuracy, i.e., the absolute total error (sampling and analysis) should be less than 25% in at last 95% of the samples analyzed at the level of the OSHA standard. In order to satisfy the statistical criteria, a measure of accuracy and precision was established, i.e., overall recovery must be 100 ± 10% and the pooled CV_T of an unbiased method must be less than or equal to 0.105. The fine points of the statistical basis for this program are discussed in Reference 2.

The protocol for the validation of a method for phosphine included the following experimental studies:

- Analysis of a total of eighteen analytical samples (six samples at each of the three test levels-0.5, 1, and 2X the OSHA standard) spiked with the appropriate amount of phosphine to represent a sample volume equal to sixteen liters;
- Analysis of a total of eighteen samples collected from dynamically generated test atmospheres (six samples at each of the three test levels-0.5, 1, and 2X the OSHA standard) for the same sample volume as above;
- Determination of the breakthrough capacity of mercuric cyanide coated silica gel tubes at high relative humidity at two test levels (1.07 and 2.39X the OSHA standard);
- Testing of the storage stability of collected samples;
- Assessment of the precision and accuracy of the method.

The details with respect to each of these items are discussed in the following appropriate sections. The method tested experimentally and documented in this report has passed all the requirements of this program.

Preliminary Experiments

The colorimetric analysis of phosphate by extraction of the phosphomolybdate complex into a mixture of iso-butanol and benzene and subsequent reduction using stannous chloride was chosen as the analytical method because of its increased sensitivity and lesser interferences over other colorimetric phosphate methods. The utility of the method over the range of 1-20 µg of phosphine was shown by preparation of a standard curve (using KH_2PO_4) over this range with a sensitivity of 0.0467 absorbance units per µg of PH_3 and a regression coefficient of 0.9993. The effect of mercuric cyanide on the method was checked by adding various amounts to a standard amount of phosphate. The results given below indicate that low levels of mercuric cyanide do not interfere with the analysis of phosphate.

Table 6002-1. Effect of added $Hg(CN)_2$

$Hg(CN)_2$ added (mg)	Phosphorus added (µg PH_3)	Phosphorus found (µg PH_3)
0	7.00	6.94
10.0	7.00	6.94
21.2	7.00	7.04

Experiments were performed to test the suitability of mercuric cyanide coated Chromosorb-P tubes for collection of phosphine. As received Chromosorb-P (Johns-Manville, acid washed) had a high and variable phosphate blank (2.01, 3.71 and 8.87 µg PH_3/200 mg). Repeated acid washing of this material (1 N H_2SO_4 at 50°C) reduced the phosphate blank to 0.63±0.1 µg PH_3 /200 mg (average of three determinations). This material was coated to a 2% loading of $Hg(CN)_2$ using a procedure similar to that described in NIOSH Method 6002 (Reference 3).

Spiked phosphine samples on the $Hg(CN)_2$ /Chromosorb-P sorbent were prepared by adding various amounts of the gas in nitrogen (350 µg/L) using a 50-cc syringe to 200 mg of the solid sorbent at a rate of 0.42 mL/min. The spiked samples were extracted for one hour at room temperature using 10 mL of 0.01 $KMnO_4$ in 0.4N H_2SO_4 solution and the extracts analyzed as described in NIOSH 6002 (Reference 3). The data obtained (shown below) indicate erratic recoveries.

Table 6002-2. Recovery of Phosphine from $Hg(CN)_2$ /Chromosorb-P

Volume Added (mL)	PH_3 added (µg)	PH_3 found (µg)	Recovery
20	7.00	6.94	0.991
20	7.00	6.78	0.968
20	7.00	6.03	0.861
20	7.00	5.70	0.814
40	14.00	9.38	0.670

Samples which were similarly spiked but stored for 8 days at room temperature before analysis similarly showed low and erratic recoveries. These data are given below.

Table 6002-3. Recovery of Phosphine from $Hg(CN)_2$ /Chromosorb-P after 8 days of storage

Volume Added (mL)	PH_3 added (µg)	PH_3 found (µg)	Recovery
19.3	6.75	5.59	0.828
19.3	6.75	5.29	0.784
19.3	6.75	5.00	0.741

These data suggested that the erratic results may be partly due to the poor spiking method and low capacity of the sorbent for phosphine. Experiments were thus performed to determine the capacity of the sorbent. These experiments were performed using a silver nitrate coated on silica gel (2% loading) indicator tube which gave a detectable stain in the presence of 0.4 µg of phosphine (sampling of a 0.7 µg/L PH_3 atmosphere for three minutes at 0.2 liter per minute) to determine when breakthrough occurred. For 200 mg of sorbent sampled at 0.2 liter per minute from an atmosphere of 0.7 mg/m^3 of phosphine in dry air, a detectable stain was observed after 32 ± 2 minutes of sampling (average of 3 tubes). The capacity of this sorbent is calculated to be less than 4.48 µg PH_3 under these conditions. These data confirm the previous expectation and accounts for the erratic results obtained in the spiking experiments.

Principle of the Method
The procedure for collection and analysis of air samples of phosphine is described in NIOSH Method 6002 (Reference 3). This method is based upon collection of phosphine on mercuric cyanide coated silica gel, extraction and oxidation of the phosphorus to phosphate using a hot acidic permanganate solution and colorimetric analysis of the phosphate using the stannous chloride reduction of a phosphomolybdate complex after extraction into a mixture of isobutanol and toluene. A sample volume of 16 liters is recommended.

Analytical Method
A detailed description of the procedure for analysis is given in NIOSH Method 6002. The reliability of the colorimetric method of analysis for phosphate (for acidic silica gel extracts) was established by checking the effects of the following:·

a. Stability of the absorbance with time.
b. Effect of mercuric cyanide.
c. Linearity of the calibration curve over the working range.

The results are discussed below.

The absorbance readings obtained in the analyses of three levels of phosphine (corresponding to those that would be obtained from collection at 0.5, 1, and 2X the OSHA standard) obtained from spiked mercuric cyanide coated silica gel tubes as a function of time are shown in Table 6002-3. These data indicate that the absorbances decrease as a function of time at rates which depend on the initial phosphorus concentration. The rate of decrease is slow, being about 1% per minute. Thus, in all absorbance measurements, readings were made 30 seconds after the addition of the stannous chloride reducing agent.

The lack of effect of mercuric cyanide on the analysis of standard amounts of phosphate was shown in the previous section.

A calibration curve was constructed according to the prescribed procedure using standards prepared from KH_2PO_4. The linear calibration curve fitted to the data by the method of least squares linear regression had a correlation coefficient of 0.9995 over the working range of 1.58-15.8 µg PH_3. The sensitivity of the method as given by the slope of the calibration curve is 0.0524 absorbance units per µg PH_3. The observed absorbances cover the range of 0.088-0.829 absorbance units.

All of the work described in this backup data report was done using isobutanol/benzene mixture in the extraction step of the colorimetric analysis. However, due to the OSHA standard limiting employee exposure to 1 ppm of benzene, the recommended analysis involves substitution of toluene for benzene in the extraction step.

Table 6002-3. Stability of the reduced Phosphomolybdate complex

Added Phosphorus (µg PH_3)	Absorbance (time)	% loss
4.1	0.200 (30 sec)	0
4.1	0.199 (60 sec)	0.5
4.1	0.198 (90 sec)	1.0
4.1	0.197 (120 sec)	1.5
7.6	0.363 (30 sec)	0
7.6	0.360 (60 sec)	0.8
7.6	0.357 (90 sec)	1.7
7.6	0.353 (120 sec)	2.8
13.4	0.699 (30 sec)	0
13.4	0.689 (60 sec)	1.4
13.4	0.683 (90 sec)	2.3
13.4	0.677 (120 sec)	3.1

The suitability of isobutanol/toluene solvent system for extraction of the phosphomolybdate complex was shown by preparation of a standard curve over the range of 0.693-13.86 µg PH_3 (added as KH_2PO_4) which had a sensitivity of 0.0501 absorbance units per µg PH_3 and a correlation coefficient of 0.9993.

The lack of effect of any silica extracted from the silica gel on the analysis using the isobutanol/toluene mixture was also confirmed by preparing a standard curve using an acidic permanganate which had been used to extract blank mercuric cyanide coated silica gel (10 mL extract of 300 mg silica gel). The standard curve was prepared to cover the range 0.693-13.86 µg PH_3 (added as KH_2PO_4) and had a sensitivity of 0.0508 absorbance units per µg PH_3 and a correlation coefficient of 0.9987. The good correlation coefficients and the agreement between the sensitivity of the method using benzene and that using toluene indicate that toluene is an acceptable substitute for benzene in the analytical method. Toluene is thus recommended in the sampling and analytical method but all the values given in this report were obtained using isobutanol/benzene in the extraction step.

Detection Limit

The detection limit for the determination of phosphorus using the phosphomolybdate/isobutanol-benzene/stannous chloride method was taken to be twice the standard deviations obtained for the absorbance of a set of six determinations of blank mercuric cyanide coated silica gel samples (300 mg). The data are given below:

Table 6002-4. Absorbance data for blank $Hg(CN)_2/SiO_2$

Sample	Absorbance
1	0.010
2	0.008
3	0.011
4	0.014
5	0.005
6	0.019

Avg=0.011; std dev=0.005

The detection limit corresponds to 0.010 absorbance units or 0.19 µg of PH_3.

Analysis

The reliability of the analytical method was based upon the analysis of 18 analytical samples. These samples were prepared by spiking 300 mg of mercuric cyanide coated silica gel with 11.0, 22.0 and 41.78 mL of phosphine gas in nitrogen (350 µg/L) representing the equivalent of a 16 liter sample at 0.5, 1 and 2X the OSHA standard. The procedure and apparatus used to prepare the spiked samples are described in Attachment A. The data for the full set of analytical samples are shown in Table 6002-5.

Table 6002-5. Analysis of spiked Phosphine samples

Level	µg added	µg found	Recovery
0.5S	3.85	3.74	0.971
	3.85	3.85	1.000
	3.85	3.72	0.966
	3.85	3.75	0.974
	3.85	4.01	1.042
	3.85	4.12	1.070
1S	7.70	7.37	0.957
	7.70	7.45	0.979
	7.70	7.64	0.992
	7.70	7.85	1.019
	7.70	7.59	0.986
	7.70	7.00	0.909
2S	14.62	14.47	0.990
	14.62	13.75	0.940
	14.62	14.52	0.993
	14.62	14.69	1.005
	14.62	14.58	0.997
	14.62	14.52	0.993

$\overline{CV}_1 = 0.0359$; $\overline{CV}_{A+\overline{DE}} = 0.0388$

Sampling and Analysis

Test atmospheres of phosphine were generated using the basic system described in Attachments B and C. A steady stream of phosphine in nitrogen (306 µg/L-see section on Independent Method for Verifying Generator Concentration) was delivered from a gas cylinder via a rotameter at a flow rate of 309 mL/min or 94.6 µg/minute of phosphine to a dry stream of air flowing at 0.1129 m^3/min.

The three sample lines were maintained at measured dilution ratios of 0.233:0.501:1.000 to produce test levels 0.5, 1 and 2X the OSHA standard. The delivery rate of the phosphine gas mixture was determined by calibration using a soap-bubble flow meter. The data are presented in the section on Independent Method of Verifying Generator Concentration.

Twenty-four samples were collected simultaneously at 0.2 liter per minute for 80 minutes (16 liters) in tubes containing a front section of 300 mg and a backup section containing 150 mg of treated silica gel. Eighteen samples, six each at the three test levels, were analyzed after one day as described in NIOSH Method 6002. The six remaining were stored and analyzed after seven days.

The data obtained for the eighteen samples analyzed after one day are shown in Table 6002-6. The average recovery was 100.3%.

Table 6002-6. Phosphine Generated Samples Analysis (n=6)

Test Level	µg found	Liters found	mg/m^3 found	mg/m^3 taken	Recovery
0.5S	3.53	18.08	0.1952	0.1950	1.001
	3.14	15.36	0.2044	0.1950	1.048
	2.64	14.08	0.1875	0.1950	0.962
	3.88	20.88	0.1858	0.1950	0.953
	3.27	18.48	0.1769	0.1950	0.907
	3.64	16.64	0.2188	0.1950	1.122
1S	6.49	16.08	0.404	0.420	0.962
	5.50	14.08	0.391	0.420	0.931
	5.94	15.04	0.395	0.420	0.940
	8.03	20.48	0.392	0.420	0.933
	5.89	15.28	0.385	0.420	0.917
	7.21	16.48	0.438	0.420	1.043
2S	12.95	16.08	0.805	0.838	0.961
	16.55	17.44	0.949	0.838	1.132
	12.51	15.76	0.794	0.838	0.947
	12.73	15.60	0.813	0.838	0.970
	17.41	17.92	0.972	0.838	1.160
	16.64	18.00	0.924	0.838	1.103

Storage Stability

Studies were done to assess the stability of phosphine samples upon storage for seven days at ambient conditions. For these studies six samples collected at the OSHA standard level were stored for seven days and analyzed. These results were compared with the data for six samples collected simultaneously and analyzed after one day. The data for these samples are shown in Table 6002-7. The results indicate that the samples are stable over a seven-day period. The average recovery was 95.5% for the one-day-old samples vs. 101.7% for the seven-day-old samples.

Table 6002-7. Storage stability of collected samples (1S level)

Days Stored	mg found	Liters found	mg/m^3 found	mg/m^3 taken*	Recovery
1	6.49	16.08	0.404	0.420	0.962
1	5.50	14.08	0.391	0.420	0.931
1	5.94	15.04	0.395	0.420	0.940
1	8.03	20.48	0.392	0.420	0.933
1	5.89	15.28	0.385	0.420	0.917
1	7.21	16.48	0.438	0.420	1.043
7	6.43	15.28	0.421	0.420	1.002
7	6.70	15.68	0.427	0.420	1.017
7	7.32	15.60	0.469	0.420	1.117
7	5.83	15.28	0.382	0.420	0.910
7	7.13	15.20	0.469	0.420	1.117
7	8.03	20.32	0.395	0.420	0.940

Breakthrough Tests

Breakthrough tests were done in an atmosphere where the relative humidity was 90%. Breakthrough is defined as the time at which the effluent concentration from the collection tube (containing 300 mg of mercuric chloride-treated silica gel) is 5% of the concentration in the test gas mixture. The criterion for acceptance is that the volume of air that has passed through the tube at the time of breakthrough must be greater than 1.5 times the volume of air that would be passed through the tube during collection of a field sample, when the substance of interest in the test atmosphere is at the 2X OSHA standard level.

A description of the equipment used is included in Attachment B under the section on Breakthrough Studies.

These tests were conducted at two test levels (1.1X and 2.4X the OSHA standard) by taking samples after various sampling times (1 to 4 hours) and analyzing both the front and backup sections of the tube. The sampling rate was 0.2 liter per minute. The results obtained for the experiments are presented in Table 6002-8. The data for the 2.4X the OSHA standard level are plotted in Figure 6002-1 and indicate a 5% breakthrough volume of 20.75 liters at this level. This indicates a maximum sampling volume of 16.5 liters at the 2S level. The capacity of the tube is 19.9 µg PH_3. Based on this data, a sampling volume of 16 liters is recommended for phosphine (80 minutes at 0.2 liter per minute).

Table 6002-8. Breakthrough data

Level mg/m^3	Volume sampled L	Front found µg	Backup found µg	Total found µg	%breakthrough
0.446	10.14	4.18	0.30	4.48	6.70
0.446	15.84	6.44	0.30	6.74	4.45
0.446	21.12	8.53	0.25	8.78	2.85
0.446	30.8	12.98	0.30	13.28	2.26
0.446	36.5	15.40	0.31	15.71	1.97
0.446	49.2	20.70	0.50	21.20	2.36
0.928	10.14	9.24	0.10	9.34	1.07
0.928	15.84	13.74	0.53	14.27	3.71
0.928	23.40	22.53	1.30	23.83	5.45
0.928	26.40	24.42	2.00	26.42	7.57
0.928	29.53	26.62	3.40	30.0	11.33
0.928	34.2	26.84	4.12	31.0	13.29

Avg recovery 0.446 level=0.962; avg recovery 0.928 level=0.976

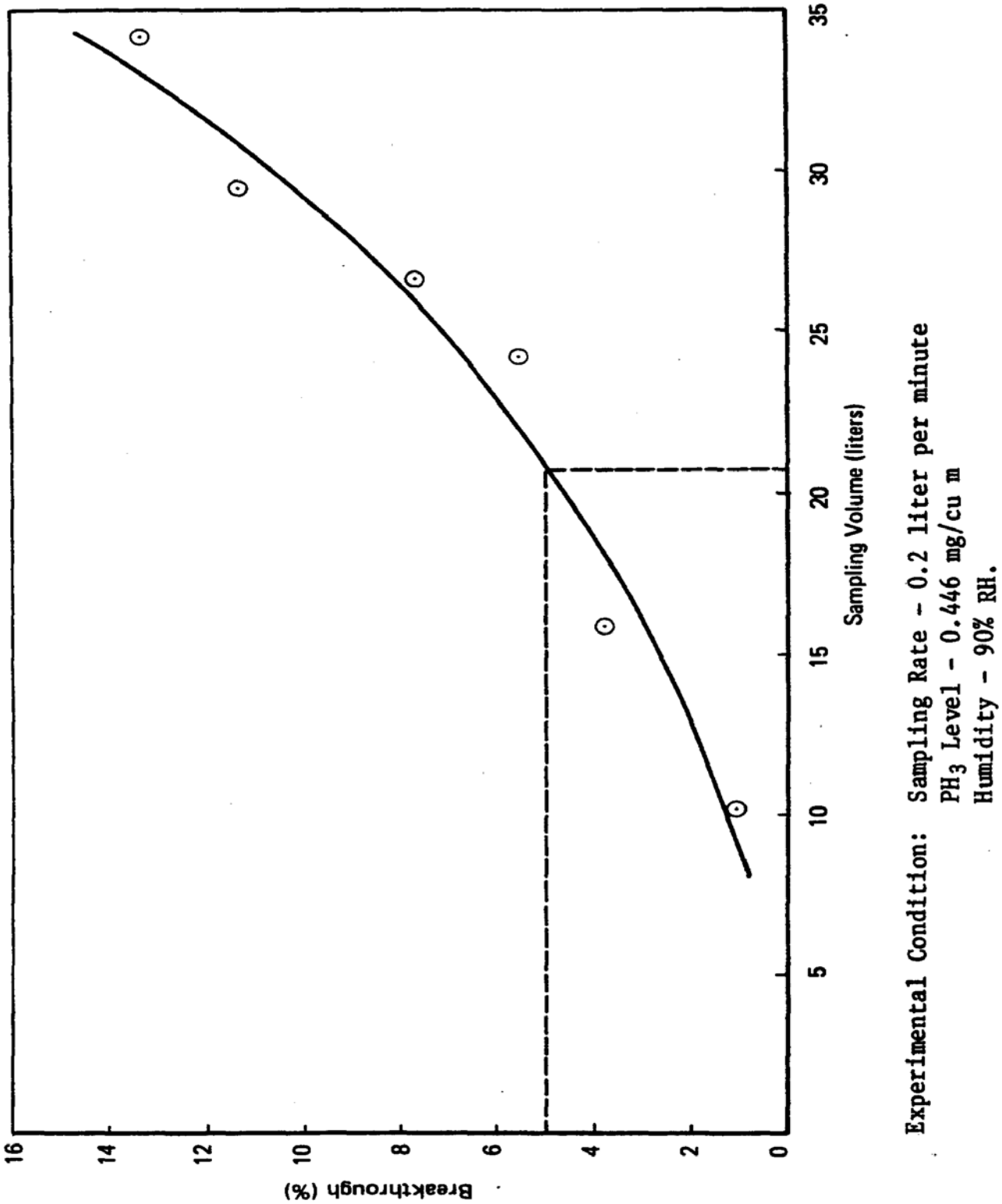

Figure 6002-1. Breakthrough curve for phosphine collected on $Hg(N)_2/SiO_2$ tubes

Independent Method of Verifying Generator Concentration

Attempts to determine the generated phosphine concentration by collection in a series of impingers filled with 10 mL of 0.01 N $KMnO_4$ in 0.2 N H_2HSO_4 at 0.2 liter per minute indicated a collection efficiency of only about 50% (see data below). This low collection efficiency precluded the use of this method as an independent method.

Table 6002-9. Collection efficiency of impingers

Volume collected (L)	PH_3 found front (µg)	PH_3 found back (µg)	%Collection efficiency*
21.24	4.20	2.20	47.6
27.12	4.05	2.00	50.4
26.64	4.40	1.95	55.7

*The collection efficiency has been determined using the equation µg found (2nd impinger)/µg found (1st impinger)=1-(collection efficiency). This equation assumes that the collection efficiency is independent of the phosphine level for the two impingers.

The generator concentration of phosphine was established by experimentally determining the concentration of the stock phosphine in nitrogen mixture and the delivery rate of the mixture (in mL/min) into a measured dilution air flow (in m^3/min). The concentration of the 25 line was calculated using these values (in mg/m^3). The concentration of the 0.58 and 18 lines can be calculated by measuring the dilution ratios of these lines relative to the 25 line (main).

The concentration of the stock phosphine gas in nitrogen was determined by injection of a 20-cc or 40-cc sample of the gas into an evacuated gas sampling bottle containing 10 mL of an acidic permanganate solution (0.01 N $KMnO_4$ in 0.2 N H_2SO_4). The gas sampling bottle was shaken mechanically for 30 minutes. The phosphate content of the acidic solution was determined colorimetrically using the same procedure described in NI0SH Method 6002. No difference in phosphine level was observed for samples shaken for 30 minutes or 2 hours. The data obtained for the two stock samples of PH_3 in N_2 used in this study are given in Table 6002-10.

Table 6002-10. Phosphine concentrations in stock samples

Sample*	Volume Analyzed	µg PH_3 found	Level (µg/L)	Avg (µg/L)	Std dev	CV
1	20.04	6.59	329			
1	40.08	14.87	371			
1	20.24	7.27	359			
1	40.48	14.45	357			
1	20.22	6.83	338			
1	20.22	7.00	346	350	15.31	0.0437
2	20.04	5.69	284			
2	20.24	6.47	320			
2	20.34	6.27	308			
2	20.24	6.60	326			
2	20.34	6.21	305			
2	20.22	5.89	291	306	16.18	0.053

*Sample 1 used in analytical set and other experiments; sample 2 used in generated set.

The delivery rate of the stock phosphine gas into the generation system was determined by calibration of the flow using a soap-bubble meter. The data obtained for the delivery rate in mL/min at 21.5°C and 761.8 mm Hg are shown below:

Flow mL/min.
310
309
309
310
307
310

Average: 309 mL/min or 94.6 µg PH_3/min; Std Dev=1.17; CV= 0.0038

The corrected main line flow was found to be 0.1129 m^3/min at the respective atmospheric temperature and pressure conditions given above. The dilution ratios used to produce the test levels at 0.5, 1 and 2X the OSHA standard were 0.233; 0.501; 1.000. Based on these data, the "taken" generator concentration at the 0.5, 1 and 28 lines are, respectively; 0.195; 0.420; 0.838 mg/m^3.

Confirmation of the Absence of Particulate Phosphate in the Generation of Phosphine at High Humidity Atmospheres

Experiments were made to determine if any particulate phosphoric compounds were formed in the breakthrough experiments where phosphine was generated in a high-humidity atmosphere. In these experiments, samples of the phosphine were collected on six treated silica gel tubes (both front and backup sections) and the results compared to three samples which were passed through 1.0 µm polytetrafluoroethylene filters (PTFE) prior to collection in the tubes. The results are presented in Table 6002-11 and indicate that little particulate phosphorus is present and little adsorption of PH_3 occurs on the filter.

Table 6002-11. Comparison of filtered and unfiltered phosphine samples

Sample Type	Volume sampled (L)	Total µg PH_3 found*	Level (mg/m^3)
Unfiltered	10.14	9.34	0.921
Unfiltered	15.84	14.27	0.901
Unfiltered	23.40	24.13	1.031
Unfiltered	26.40	26.42	1.001
Unfiltered	29.53	30.00	1.016
Unfiltered	34.20	31.00	0.906
Filter through PTFE filter	24.24	24.55	1.013
Filter through PTFE filter	23.64	20.94	0.886
Filter through PTFE filter	22.80	20.85	0.914

*Sum of front and backup sections.

Precision and Accuracy

The precision of the method was determined by using the statistical procedures described in Reference 2 and the data in Tables 6002-5 and 6002-6.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation at 0.5, 1, and 2X the OSHA standard for generated samples. The data (Table 6002-6) gave a chi squared value of 2.39, indicating that the hypothesis of equal variance is satisfied at p (probability) less than 0.01. Thus, $\overline{CV}_T$ is calculated based on the pooled data.

The precision of the method is expressed in terms of the coefficients of variation for the analytical method, the sampling and analytical method, and the overall method which includes a pump error of 0.05. These values are shown below.

$\overline{CV}_1$=0.0359 $\overline{CV}_2$=0.0744 $\overline{CV}_T$=0.0908

The accuracy of the method was determined by comparison of the average value found by analysis of six samples at each of the three test levels with the Taken generator concentration discussed in the appropriate section. The data summarized below show good agreement (Found and Taken) with an average of 100.2%.

Table 6002-12. Accuracy of method

Test level	mg/m^3 taken	mg/m^3 found	Agreement (found/taken)
0.5S (generated set)	0.1950	0.1948	0.999
1S (generated set)	0.420	0.401	0.955
2S (generated set)	0.838	0.877	1.047
1S (storage stability)	0.420	0.427	1.017
1S (breakthrough)	0.446	0.429	0.962
2S (breakthrough)	0.928	0.957	1.031

Avg agreement=1.002

The difference between the Taken and Found concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Further confidence in the accuracy of the tested method is established by the results of the desorption efficiency test and the storage stability test, described in the appropriate sections.

References

1. NIOSH [1976]. Statement of Work: Article 1. NIOSH contract no. 210-76-0123. U.S. Department of Health, Education and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health.

2. NIOSH [1977]. Documentation of NIOSH Validation Tests. Cincinnati, OH: U.S. Department of Health, Education and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health. DHEW (NIOSH) Publication No. 77-185.

3. NIOSH [1976]. Phosphine: NIOSH Method No. S332 (validation date 3/17/78). NIOSH Contract No. 210-76-0123. U.S. Department of Health, Education and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health.

ATTACHMENT A
PROCEDURE AND APPARATUS USED TO PREPARE SPIKED PHOSPHINE SAMPLES

The apparatus shown in Figure 6002-A-1 was used to prepare spiked samples of phosphine for the determination of the analytical method recovery. Spiking was performed according to the following procedure. Standard phosphine in nitrogen gas mixture was flushed through the sampling loop for 3 minutes at a rate of 50 mL/min with the exit valve open to the atmosphere. The valve was closed and the system pressurized at 20 psi with the phosphine gas mixture. The four-way valve was turned to the open position to adjust the pressure in the loop to atmospheric. The four-way valve was rotated to introduce a nitrogen flow of 2.9 mL min through the loop. The exit valve was adjusted to let the gas flow through the sorbent tube at that rate. This process was continued for 20 minutes. Sampling loops of approximately 10 and 40 mL were used. The exact volume of gas spiked was determined using the procedure described below. In order to spike with approximately 20 mL of gas, the 10 mL sampling loop was used and the process done twice.

The exact volume of phosphine spiked onto the sorbent tube was determined using the following procedure. A mercury manometer (made out of 1 mm I.D. tubing) was attached to the end of the exit valve. A fitting with a rubber septum was attached to the other side of the exit valve. The four way valve was turned to the closed position and the pressure in the sealed system was adjusted to atmospheric. Air was introduced into the system (1 mL or 5 mL increments) using a gas tight syringe through the rubber septum and the pressure in the system recorded after each incremental addition. The volume of this system (spiking volume+ manometer volume) was determined using the equation

V (in mL) =intercept + slope

Where the slope and intercept values are calculated from a plot of the equation:

$$\frac{1}{p} = (\text{slope})\Delta V + \text{intercept}$$

Where: p=total pressure (in mm Hg)
ΔV= incremental volume added (mL)

The manometer volume was determined using a similar procedure and this volume subtracted from the total to arrive at the spiking volume. The values for the volume spiked using the apparatus with the small and the large loops connected, respectively, were (average of three measurements) 10.99 ± 0.10 and 41.78 ± 0.30 mL.

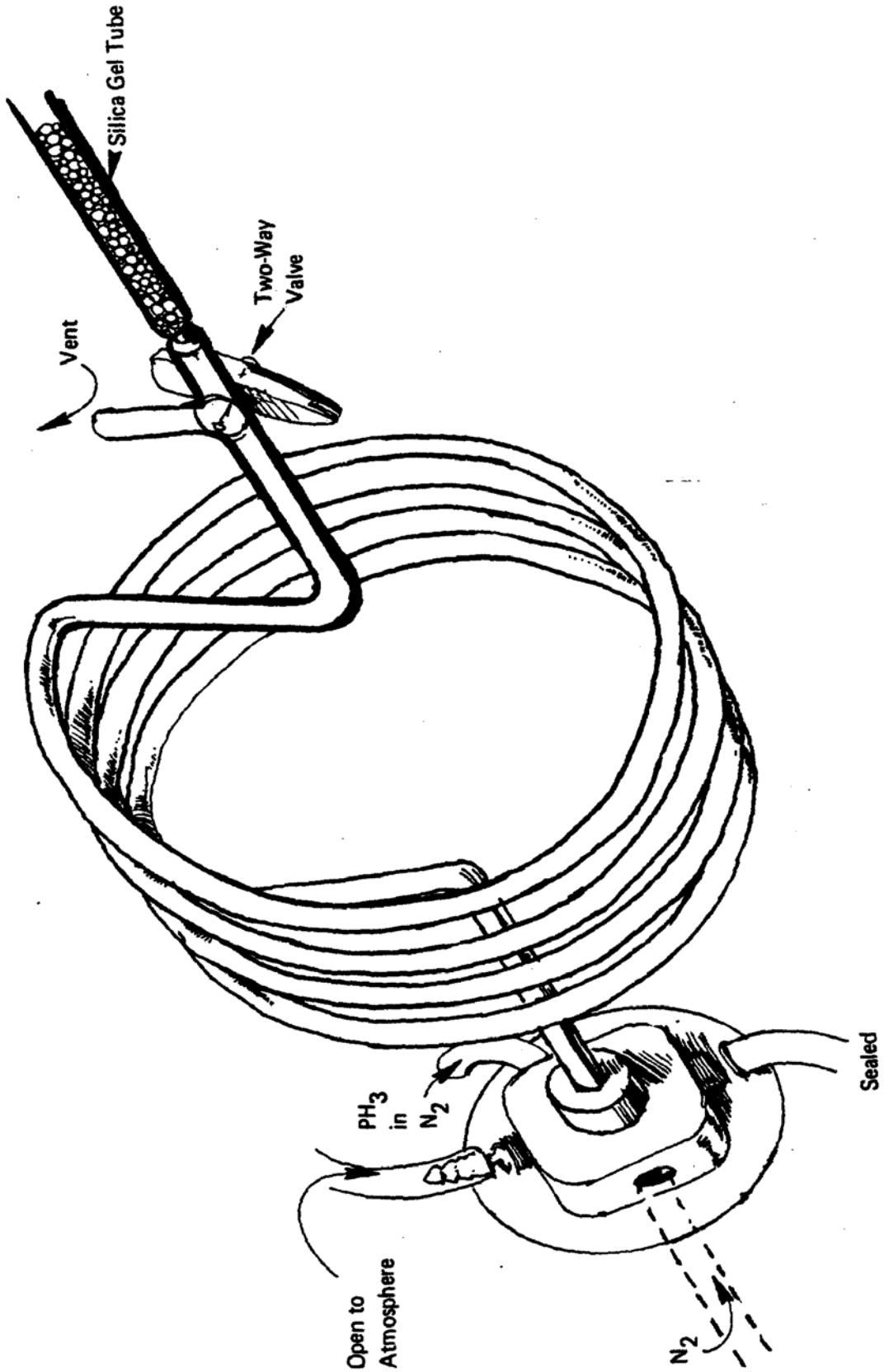

Figure 6002-A-1. Apparatus used to prepare spiked phosphine samples

ATTACHMENT B
VAPOR DILUTION/SAMPLING SYSTEM

The vapor generation/dilution system used for the validation studies of several vapors and gases, such as this analyte, is shown schematically in Figure 6002-B-1. The system basically consists of a main line air stream to which are added predetermined amounts of various liquids, gases or aerosols to generate the desired vapor concentrations. From the main line, three dilution arms branch off in which the desired multiples 0.5, 1.0 and 2.0 times the OSHA Standard concentration level are established. Six sampling devices are connected in parallel to each of the three dilution lines and are connected via critical flow orifices (CFOs) to the three corresponding vacuum lines.

Air flow rates through the system are established by means of CFOs and flow restrictors. The primary air system derived from the house air compressor is maintained at 20.0 psig. The appropriate orifice diameters are chosen to maintain an air flow of approximately 0.1 m^3/min in the Main Line and an addition of 0.05 m^3/min to each of the dilution lines. The main line is maintained at 8 cm H_2O pressure by means of a needle valve. Appropriate flow restrictor diameters are chosen for the 0.5S, 1S and 2S dilution lines so as to give the desired final concentrations of vapor in air.

The system was designed to generate either 4X or 2X the OSHA Standard concentration in the Main Line. When a 4X level is generated, 0.05 m^3/min of dilution air is added to each dilution line. Orifices are selected so that the 0.5S, 1S and 2S lines have flows equal to approximately 0.007, 0.017 and 0.050 m^3/min respectively of the Main Line concentration added to the dilution air, thus giving the desired final concentrations. Where a Main Line concentration of 2X the OSHA Standard is generated, no dilution air is added to the 25 dilution line-0.017 m^3/min is simply allowed to flow through this line and 0.050 m^3/min of dilution air is added to the 0.050 m^3/min and 0.017 m^3/min of Main Line mixture admitted to the 15 and 0.5S dilution lines, respectively.

All materials which the vapor may contact before collection are 316 or 304 stainless steel. A glass heater is included where the liquids are added to the main line. Shutoff ball valves are placed in the dilution lines to allow their independent operation and the calibration of air flows. The Main Line has a 2.54-cm (1 in) O.D., and the dilution lines are 1.90-cm (0.75 in) O.D. Diameters were chosen to give turbulent flow with an approximate minimum Reynolds number of 3000.

Air Supply
Air from the house compressor is treated by passing it sequentially through a cotton filter, a silica gel bed, a charcoal bed and a high efficiency glass fiber filter for removal of water, hydrocarbons and particulate. This air is then connected to a manifold containing six takeoff ball valves. The pressure (20 psig) at the manifold is maintained with a Nullmatic Moore 40H50 regulator and monitored with an Ashcroft 0-60 psig test gauge. The air supply is used for each of the dilution system connections as well as for the flame ionization detector monitor flame and "zero" air.

Sample Collection Manifold
Sample flow through the sampling devices connected to the dilution lines is established by connecting each device by means of a short piece of flexible tubing to a CFO which is connected to a. 1.27 cm (1/2 in) O.D. vacuum manifold. Each dilution line has a separate manifold which derives its vacuum from a Model 0322 Gast vacuum pump. The orifices are jewel orifices pressed into a threaded Teflon rod. One end of the rod is screwed into a tee on the manifold, and the other has a hose tabulation fitting connected to it. The orifice is protected from plugging by means of a piece of 100 mesh stainless steel screen.

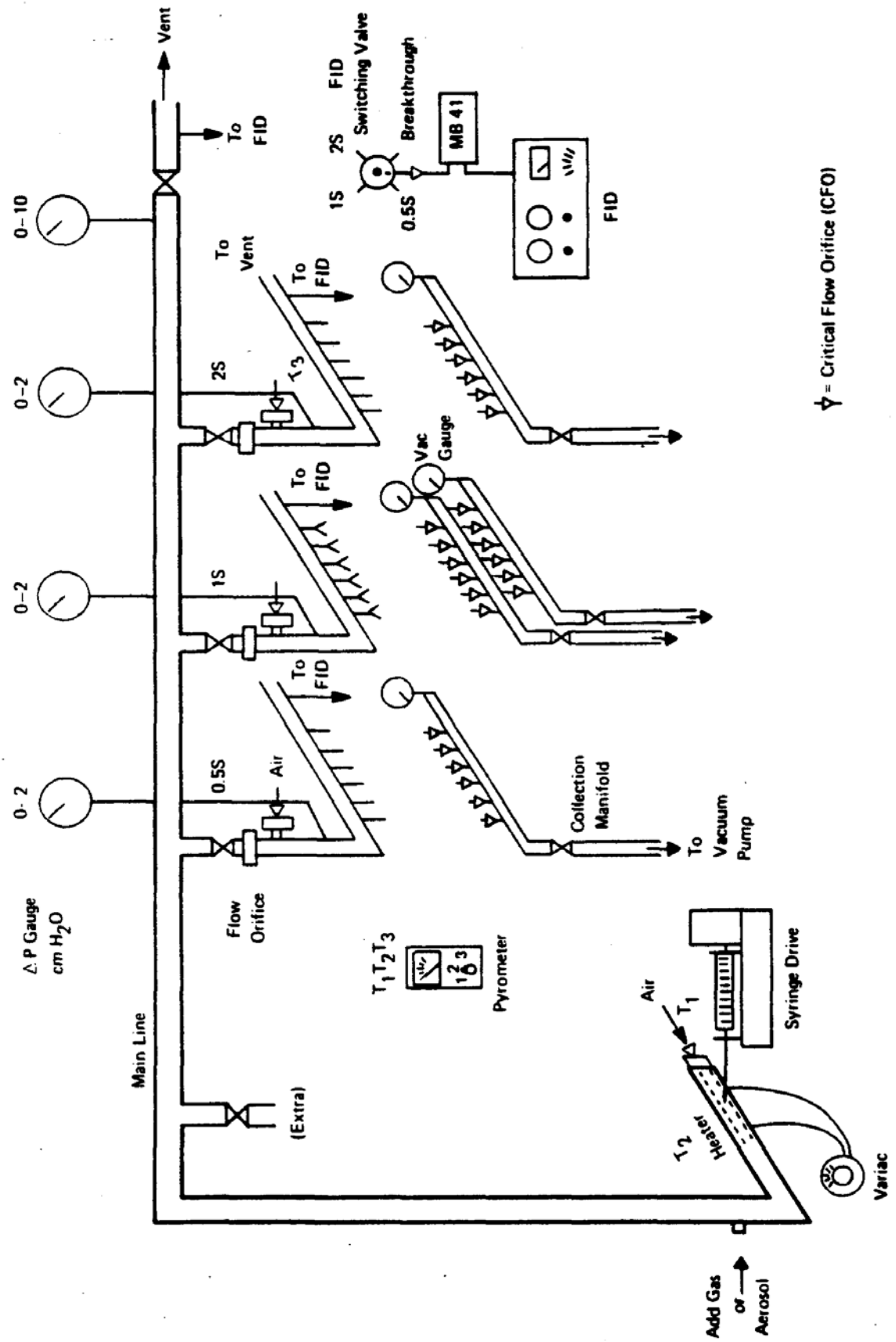

Figure 6002-B-1. Vapor Generation/dilution/sampling system

Vent System
All excess vapor-laden air is collected via a 3.81-cm (1.5 in) PVC manifolding system where it is passed through a 0.3 x 0.3 x 0.6-M charcoal bed. Flow is established by means of a pressure blower on the exit side of the charcoal bed, and it is vented to the laboratory hood exhaust.

Air Flows Calibration

Main Line-The air flow delivered by the Main Line CFO was determined by measurement with a Singer Dry Test Meter. The meter had previously been calibrated with a spirometer primary standard. Using the 0.310-cm diameter orifice at 20 psig air pressure, the flow was found to be 0.1086 m^3/min corrected to 25°C and 760 nm Hg.

Dilution Lines-The air flow through each of the dilution line CFOs and restrictor orifices was similarly measured with the Dry Test Meter to assure that they met design parameters, but these values did not provide the primary basis for determination of vapor concentration.

Collection CFOs-Since the flow rate through the sample collection CFOs was lower (0.2 and 1.0 liter per minute) than appropriate for use with the Dry Test Meter, the flow rate of each of these orifices was measured using an SKC soap bubble meter which was independently calibrated by gravimetrically measuring water capacity.

All volume measurements have been referenced to normal temperature and pressure of 25°C and 760 mm Hg.

Dilution Ratios
The concentration of vapor in the dilution lines is determined from the concentration calculated in the Main Line and the dilution ratio determined between the dilution lines and the main line. These dilution ratios were measured by adding a controlled amount of propane gas to the Main Line and then measuring the relative concentration in each of the lines using a Beckman Model 402 heated hydrocarbon analyzer. The procedure was repeated several times and is regularly checked during the program.

In the case where 4X or 2X concentration level conditions were generated, the dilution ratios reported below were observed.

Table 6002-B-1. Dilution ratios

Case generated	Main Line	Relative Conc (2S)	Relative Conc (1S)	Relative Conc (0.5S)
4X	1.000	0.510	0.256	0.131
2X	1.000	1.000	0.499	0.227

Each of these sets of values represents a different set of air flow and orifice selection conditions as previously discussed. Point to point comparison of the six sample ports on each manifold showed less than a 1% variation in concentration among them.

Monitors
To provide a ready check on operating conditions, several gauges or monitors have been included in the system. Dwyer Magnehelic gauges monitor the pressure on the Main Line and each of the dilution lines. A 0-10 cm H_2O gauge is used on the Main Line (Setpoint 8 cm) and 0-2 cm H_2O gauges are used for the dilution lines. The purpose of these latter gauges is to provide a check against possible back pressure developing in these lines which would affect the dilution ratios.

The flame ionization detector (FID) is used to determine the time at which the Main Line concentration has reached equilibrium and to monitor the concentration level during breakthrough studies and sample collection.

Breakthrough Studies

A. Low Relative Humidity (Dry Air)

For the measurement of sorbent tube capacity for a given vapor (breakthrough) six sorbent tubes containing only the 100 mg "front half" section of sorbent are connected in parallel to the 25 dilution line and to a 0.635-cm (1/4-in) O.D. stainless steel six-port manifold. Flow through the manifold is controlled by a CFO and is established using a Metal Bellows Corp. Model MB41 pump. Flow through the orifice was measured as 1.14 liters per minute providing a 0.19-liter per minute flow to each of the tubes. (A separate set of orifice allows a similar determination at a flow rate of 1.0 liter per minute through each tube.) Equal flow through each of the tubes is insured by carefully selecting and/or adjusting packing in the tubes to have an equal pressure drop when precalibrated at a 0.2-liter per minute flow rate.

Once a steady state vapor concentration is established, the 2S concentration level is used to set the 100% point on the hydrocarbon analyzer. Then the valve is switched, and the flow from the breakthrough manifold is passed through the hydrocarbon analyzer and monitored either until 5% of the 25 level is observed or for a period of four hours-whichever occurs first.

B. High Relative Humidity

For the generation of a high relative humidity atmosphere, at least 80% R.H., water vapor is delivered into the generator Main Line via one of the side arms as shown in Figure 6002-B-2. A peristaltic pump, Cole Parmer Masterflex, Model No. 7013, is used to deliver water into a heated copper coil (1/8 in x 10 feet) contained in a tube furnace; the furnace temperature is maintained above 110°C and monitored by a thermocouple and optical pyrometer. Water is delivered at the rate of 1.9 g per minute to blend with the analyte-containing dry air stream flowing at a rate of 1.100 m^3/min to produce an atmosphere of at least 80% R.H. at 25°C and 760 mm Hg.

All other aspects of the breakthrough test procedure are as described above.

Procedure

The overall procedure for a given sample is as follows:

1. Line air flow and dilution ratios are verified.
2. Sample delivery rate is determined by appropriate calibration.
3. Sample is fed into Main Line until vapor concentration equilibrium is established.
4. The breakthrough experiment is performed and subsequent sample collection volumes adjusted if necessary.
5. The four sets of six samples from the three concentration levels are collected simultaneously.

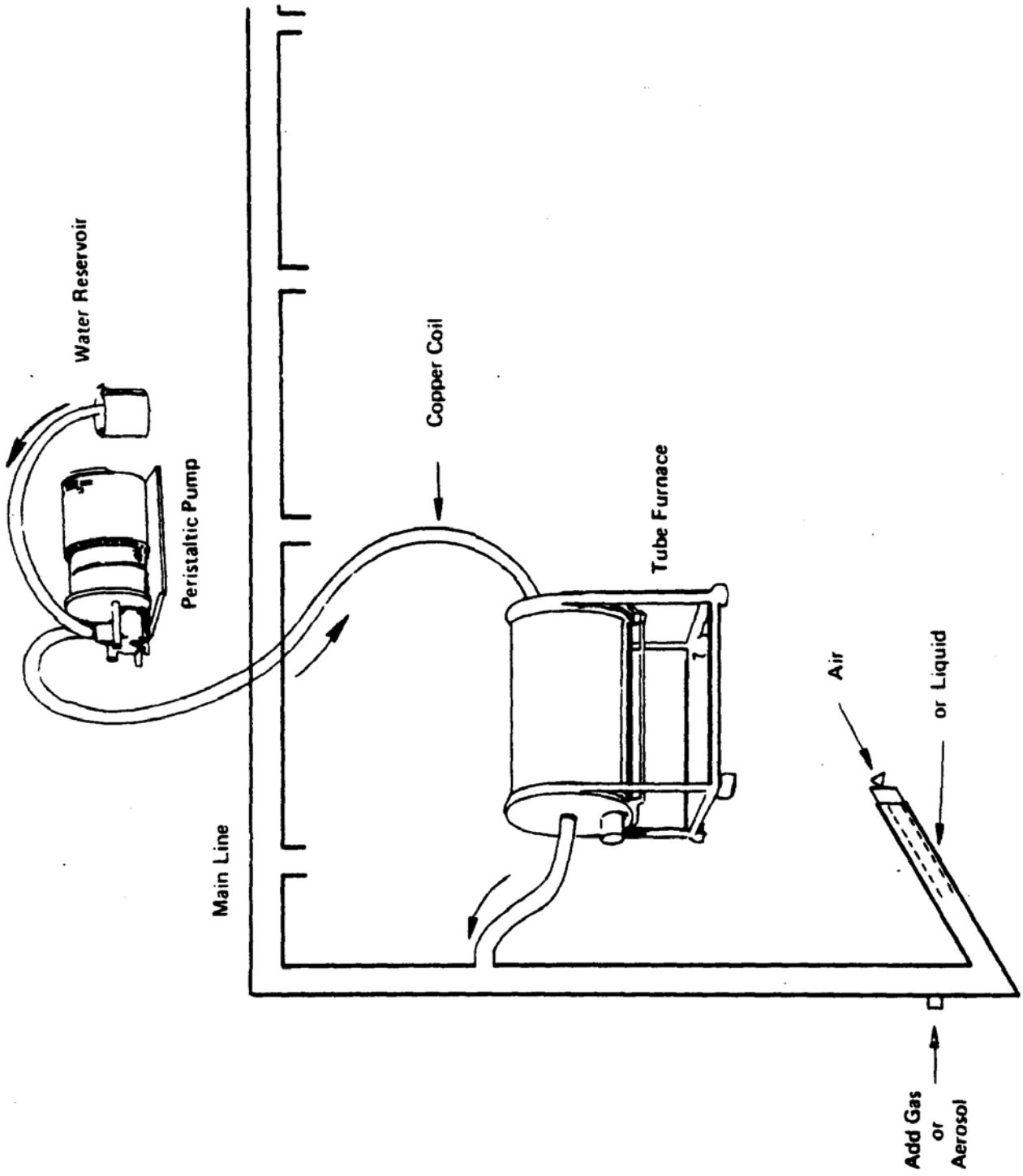

Figure 6002-B-2. Generation of high humidity atmospheres

ATTACHMENT C
GAS GENERATION

Controlled Gas Injection

When gaseous substances are to be tested, the desired concentration of vapor is generated by a controlled flow injection. When a cylinder of gas is used, the gas is fed into the dilution/sampling system through a calibrated gas rotameter. The delivery rate is calibrated by either a dry gas meter or bubble meter depending on the flow rate used.

Calculation of Main Line Concentration

The calibrated gas delivery rate in mL/min is converted by ideal gas law calculations to units of mg/min. The Main Line concentration is then determined by dividing the delivery rate in mg/min by the Main Line flow rate in m^3/min. This gives the concentration generated in units of mg/m^3.

If a gas mixture is used for generation, the exact content of the cylinder is determined by chemical analysis. A correction factor is then applied to the calibrated delivery rate and the Main Line concentration calculated as above.