BACKUP DATA REPORT
NIOSH Method No. 6016

Title: Ammonia by IC

Analyte: Ammonia

Author/developer: Developed under contract 210-76-0123

Date: 1977

Substance: Ammonia
OSHA Standard: 50 ppm (35 mg/m^3)
Chemical Used for Validation: Ammonia (Matheson Gas Products)

General

The procedure for collection and analysis of air samples containing ammonia is described in NIOSH Method 6016. This method consists of collection of ammonia on sulfuric acid-treated silica gel, desorption with 0.1N sulfuric acid, and analysis of the resulting solution by an ammonia electrode.

This method has been tested for validity for a 30-liter air sample using the criteria for validation outlined in Reference 1. Using these criteria, the absolute total error (sampling and analysis) is less than 25% at the OSHA standard level 95% of the time.

The protocol used for testing this method was to:

- Analyze 18 samples (6 each at 0.5X, 1X, and 2X the OSHA standard) spiked with the appropriate amounts of ammonia to represent 30-liter air samples.

- Analyze 18 samples collected from dynamically generated test atmospheres (6 samples collected at each of 0.5X, 1X, and 2X the OSHA standard).

- Determine the breakthrough capacity of sulfuric acid-treated silica gel at high relative humidity.

- Test the storage stability of six collected samples.

- Assess the precision and accuracy of the method.

Details of these procedures are discussed below.

Analysis

A description of the method of analysis is given in NIOSH Method 6016. The results of the desorption efficiency tests are in Table 6. Silica gel, 20/40 mesh, available through SKC, Inc. was used in the validation study.   The silica gel was treated with sulfuric acid before use.

Methyl amine and ethyl amine have been shown to cause significant interference in the analytical method. When methyl and ethyl amine are present in the same molar quantity as ammonia, the electrode response was found to be 36 and 31 times greater than that of ammonia, respectively.

Sampling and Analysis

Before generation of test atmospheres of ammonia, the generation dilution system was calibrated using a test atmosphere of methyl chloride. The system is described in Attachment A. A total hydrocarbon analyzer was used to measure the dilution ratios. After calibration of the dilution system, generation of test atmospheres of ammonia was conducted. A compressed gas cylinder containing pure ammonia was used. The gas was diluted with the appropriate amount of house air to obtain samples at 2X the OSHA standard level. Dilutions to 1X and 0.5X the OSHA standard levels were made as described in Attachment A. The samples were collected as described in Method 6016 using sampling tubes containing sulfuric acid-treated silica gel connected in series with a 37-mm, 0.8 micrometer cellulose ester membrane prefilter to remove particulate ammonium salts. Six

samples were collected from each chamber for 150 minutes to obtain 30-liter air samples. The results of the analyses of these samples are presented in Table 7. In addition, the backup sections of the sampling tubes at the 2X level were analyzed and found to contain less than the limit of detection, which was 0.5 mg/m^3.

An additional six samples were collected at 1X the OSHA standard level. The extra samples were used for the storage stability study.

Storage Stability

A study was done to assess whether ammonia would be successfully stored for one week after collection. A second set of six samples at 1X the OSHA standard level (33.8 mg/m^3, as determined by the independent method) was collected at the same time as the samples that were used for validation. The samples were collected for 150 minutes at an average flow rate of 0.2 liter/minute. These sample tubes were capped and stored on the laboratory bench for one week before analysis. The results of the analyses are given below in Table 1.

Table 1. Storage Stability Test

Samples Analyzed Immediately (mg/m^3)	Samples Analyzed After One Week (mg/m^3)
33.1	34.5
32.2	35.3
33.0	33.3
32.1	33.4
32.4	33.9
32.2	32.4
Mean=32.5	Mean =33.6
Std dev=0.4	Std dev = 0.8
CV=0.012	CV=0.024

The criterion for acceptance was that the mean of the six samples stored at room temperature for seven days should be within ± 10% of the mean of the set analyzed at the beginning of the storage period. The two means compare within 3%; thus, the storage stability was adequate.

Breakthrough Tests

A breakthrough test was performed at an average relative humidity of 85%. Details of the method of generating atmospheres containing high relative humidities are given in Attachment B. The test atmosphere was generated from a gas cylinder of pure ammonia.

Breakthrough is defined as that time when 5% of the influent concentration appears in the effluent of the front section of sorbent.

Since the concentration of ammonia in the air samples could not be monitored directly, it was necessary to measure the amount of ammonia collected on the front and backup sections of sulfuric acid-treated silica gel tubes and calculate the breakthrough time. The test for breakthrough was conducted as follows:

Breakthrough was measured by sampling through 12 sampling tubes containing 200 mg of sulfuric acid-treated silica gel in the front section and 100 mg in the backup section. Single tubes were removed after 150 minutes and every 15 minutes thereafter, and backup sections were analyzed. The data is summarized in Table 2.

The concentration in the generator was 68.6 mg/m^3 and was determined by averaging the data collected in the following two methods.

The first method consisted of collection of a 2-liter sample in a midget bubbler containing 10 ml of 0.1 N HCl at a flow rate of 0.5 liter per minute. The samples were collected at a point before the primary dilution system. The concentration of ammonia was determined by titrating the unconsumed HCl with 0.05 N sodium hydroxide to a pH 7 endpoint. The second method consisted of collecting samples of ammonia in a midget bubbler containing 10 ml of 0.01 N HCl from the 1X sampling chamber. The samples were collected for 15 minutes at an average flow rate of 0.962 liter/min. The concentration of ammonia was determined by titrating the unconsumed HCl with 0.05 N sodium hydroxide to a pH 7 endpoint.

Table 2. Breakthrough Test

Sample Volume (L)	µg found (front)	µg found (backup)	mg/m^3
30.3	1838	ND*	60.7
33.2	2044	ND	61.6
36.7	5564	ND	60.8
39.9	5846	ND	63.0
43.4	2869	ND	66.1
45.4	2981	ND	65.7
48.0	3150	ND	65.6
52.1	3525	ND	67.7
54.4	3600	ND	66.2
55.9	3694	ND	66.1
61.8	3975	ND	64.3
63.4	3862	ND	60.9

*N.D. = Not Detected at a detection limit of 15 micrograms.

From the above data, breakthrough did not occur.

Independent Method
Two independent methods of measuring the concentration of test atmospheres of ammonia were used. Method 1 consisted of collection of a 2-liter sample in a midget bubbler containing 10 mL of 0.1 N HCl at a flow rate of 0.5 liter/minute. The samples were collected at a point before the primary dilution system. One set of three samples each was taken both prior to and after collection of the 24 samples used for validation. The concentration of ammonia was determined by titrating the unconsumed HCl with 0.05 N NaOH to a pH 7 endpoint. Test chamber concentrations (Table 3) were calculated with the known dilution airflow, subsequent serial dilution air ratios, and measured ammonia concentration.

Table 3. Concentration Determined by Independent Method I

Level	Measurements made before collection of validation samples (mg/m³)	Measurements made after collection of validation samples (mg/m³)
2X	69.3	70.4
2X	70.0	71.3
2X	71.4	71.1
1X	34.6	35.2
1X	35.0	35.6
1X	35.7	35.5
0.5X	17.31	17.60
0.5X	17.50	17.82
0.5x	17.84	17.76

Method 2 consisted of collection of samples in midget bubblers containing 10 mL of 0.01 N sulfuric acid. Samples were collected from the 1X sampling chamber at 15-minute intervals at an average flow rate of 0.542 liter/minute. An 8-mL aliquot of the 10 mL sample was mixed with 1 mL 10 N NaOH and 6 mL deionized water. The ammonia concentration was measured with an ammonia electrode. The 2X and 0.5X sampling chamber concentrations were calculated with the known dilution air ratios and measured 1X sample chamber concentration. Table 4 summarizes the data collected.

Table 4. Concentration Determined by Independent Method II

Time interval (minutes)	2X (mg/m³)	1X (mg/m³)	0.5X (mg/m³)
0-15	64.8	32.4	16.2
15-30	64.8	32.4	16.2
30-45	65.8	32.9	16.5
45-60	65.8	32.9	16.5
60-75	58.9	29.4	14.7
75-90	57.8	28.9	14.4
90-105	64.8	32.4	16.2
105-120	69.4	34.7	17.4
120-135	68.5	34.2	17.1

The concentration of ammonia in the test atmospheres was determined by averaging the data collected by the two independent methods (Table 5).

Table 5. Taken Concentration

	2X (mg/m³)	1X (mg/m³)	0.5X (mg/m³)
Method 1 avg	70.6	35.3	17.6
Method 2 avg	64.5	32.2	16.1
Average of the 2 methods	67.6	33.8	16.9

Precision and Accuracy
The statistical procedures and a definition of the terms used are described in Reference 2.

Bartlett's test for homogeneity of variances was applied to the coefficients of variation of 0.5X, 1X, and 2X the OSHA standard for generated samples. The data (Table 7) gave a chi squared value of 7.76. Thus, Bartlett's test is passed and it is feasible to pool the coefficients of variation to calculate $\overline{CV_T}$.

The precision of the analytical method was assessed using the data in Table 6. The pooled Coefficient of Variation ($\overline{CV_1}$) for three sets samples was found to be 0.038.

Table 6. Desorption Efficiency Data

Level	μg found	μg taken	DE μg found/μg taken	n	mean	Std dev	CV_1
0.5X	525	525	1.000	6	1.074	0.051	0.047
0.5X	600	525	1.143				
0.5X	562	525	1.070				
0.5X	544	525	1.036				
0.5X	579	525	1.103				
0.5X	572	525	1.090				
1X	1134	1050	1.080	6	1.053	0.046	0.044
1X	1048	1050	0.998				
1X	1172	1050	1.116				
1X	1134	1050	1.080				
1X	1088	1050	1.036				
1X	1059	1050	1.009				
2X	2280	2100	1.086	6	1.069	0.017	0.016
2X	2269	2100	1.080				
2X	2194	2100	1.045				
2X	2250	2100	1.071				
2X	2269	2100	1.080				
2X	2212	2100	1.053				

$$\overline{CV}_1 = 0.038; \ \overline{CV}_{A+\overline{DE}} = 0.041$$

Precision and accuracy of the total sampling and analytical method was evaluated using the data in Table 7 and the results obtained from breakthrough tests and storage stability tests. The pooled Coefficient of Variation (CV_2) for the three sets of samples collected from test atmospheres is 0.034. To obtain a measure of the accuracy of the method, the mean value of the concentration found by analysis at each level was compared with the value for the concentration taken.

The average recovery (concentration found divided by concentration taken) for all three levels was 97.6%. The value for the taken concentration was obtained as described under the Independent Method Section. The difference between the taken and found concentrations is considered to result from experimental uncertainties in the value for the taken concentration and does not represent a bias in the method. Further confidence in the accuracy of the tested method is established by the results of the breakthrough test and the storage stability test, described above.

The total Coefficient of Variation (CV_T) is 0.062.

Table 7. Precision and Accuracy data

Test level	μg found	Corrected μg found*	Liters	mg/m^3 found**	mg/m^3 taken	recovery	N	mean	Std dev	CV$_2$
0.5X	506	475	29.2	16.27	16.9	93.6	6	15.82	0.43	0.027
0.5X	488	458	29.2	15.68	16.9					
0.5X	510	479	30.7	15.60	16.9					
0.5X	495	464	28.4	16.34	16.9					
0.5X	497	467	30.7	15.21	16.9					
0.5X	487	457	28.9	15.81	16.9					
1X	1050	986	29.8	33.1	33.8	96.2	6	32.5	0.4	0.012
1X	1059	994	30.9	32.2	33.8					
1X	1041	977	29.6	33.0	33.8					
1X	1050	986	30.7	32.1	33.8					
1X	1059	994	30.7	32.4	33.8					
1X	1050	986	30.6	32.2	33.8					
2X	2212	2077	30.3	68.5	67.6	103.0	6	69.6	3.5	0.050
2X	2156	2024	29.6	68.4	67.6					
2X	2269	2130	29.8	71.5	67.6					
2X	2119	1990	30.9	64.4	67.6					
2X	2381	2236	29.8	75.0	67.6					
2X	2113	2113	30.4	69.5	67.6					

CV$_2$=0.050

$\overline{CV}_2$=0.034

*An average desorption efficiency (D.E.) of 1.065 was used to calculate corrected μg.

**All values have passed the Grubbs' outlier test at the 1% confidence level as described in Reference No. 2.

References

1. NIOSH [1976]. Contract 210-76-0123. Cincinnati, OH: 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: Department of Health, Education and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW, NIOSH Publication No. 77-185.

Attachment A: Generation of Test Atmospheres

The system for generating and collecting samples of vapor, inorganic/organic particulate, dusts, and fumes consists basically of a sample generator, a mixing and dilution section, and three sampling chambers.

Samples are generated at a concentration 2X the OSHA standard, serial dilutions are made to 1X and 0.5X the standard, and samples are collected simultaneously at the three concentrations. A schematic of the generation system and associated components is presented in Figure A1.

The generation system is large enough to be used for polydispersed aerosols as well as for gases and vapors. The primary dilution chamber is 48 inches by 4 inches and may handle air flows up to 400 liters/minute. The large volume dilution chamber is important for several reasons. Even at high airflow rates, the velocity of particles is low to allow complete solvent evaporation in the generation of aerosols. The air velocity is also low enough to avoid impaction on the walls while great enough to prevent particle diffusion to the walls. For these same reasons, the sample rationing system is only 1 inch in diameter and handles a flow of only 52 liters/minute. Gravitational settling is avoided by maintaining a sufficient air velocity.

The sampling cones for the three chambers are 6-inch I.D. at the base (point of sample collection) and narrow to 1-inch I.D. at the point of attachment to the sample rationing system. A constant total air flow of 26 liters/ minute through each cone causes a gradual reduction in aerosol velocity toward the point of sample collection. The air velocity at the collection point is 2.4 cm/second.

All portions of the generation system that come in contact with the test atmosphere are constructed of stainless steel or Teflon to avoid any contamination problems. Sections of the generation system at which dilution air is added are constructed such that the incoming air forms a "high-velocity sheath" around the air/analyte mixture that is to be diluted. This sheath serves two functions. The dilution air sheath becomes increasingly less coherent and stable as it moves downstream of its point of entrance and hence is turbulently mixed with air/analyte test atmosphere. At the point of entrance of the dilution air stream, a Venturi effect accelerates the air/analyte mixture to a high velocity. The dilution air sheath also prevents interaction of the accelerated air/analyte stream with the walls of the chamber, thus eliminating a large source of aerosol loss by impaction.

The system being used to generate the initial concentrations of vapor, gas, or particulate is interfaced with the dilution apparatus at the primary dilution chamber. The output of the generator is diluted with the appropriate amount of air to obtain a concentration 2X the OSHA standard. Of the total amount of material generated at the 2X level, a flow of 52 liters/minute enters the rationing system. Under control of a vacuum exhaust orifice, material at the 2X level enters the first sampling chamber at a rate of 26 liters/minute. Downstream of the entrance to the first sampling chamber, dilution air is added (via a critical orifice) at a rate of 26 liters/minute. Thus the flow of material at the 2X level that did not enter the first sampling chamber (26 liters/minute) is diluted with air at a flow rate of 26 liters/minute to a final concentration of 1X the OSHA standard level. Analyte at the 1X level then enters the second sampling chamber at a rate of 26 liters/minute. The remaining flow, 26 liters/minute is diluted again with air at 26 liters/minute to achieve 0.5X the OSHA standard level. The analyte/air mixture at the 0.5X level is drawn into the third sampling chamber at 26 liters/minute. The remaining material in the rationing system not drawn into the sampling chambers is removed at a rate of 26 liters/minute by the fourth critical orifice in the vacuum exhaust system. This removal of test atmosphere volumes and addition of measured volumes of air thus achieves serial dilutions to 1X and 0.5X the OSHA standard level.
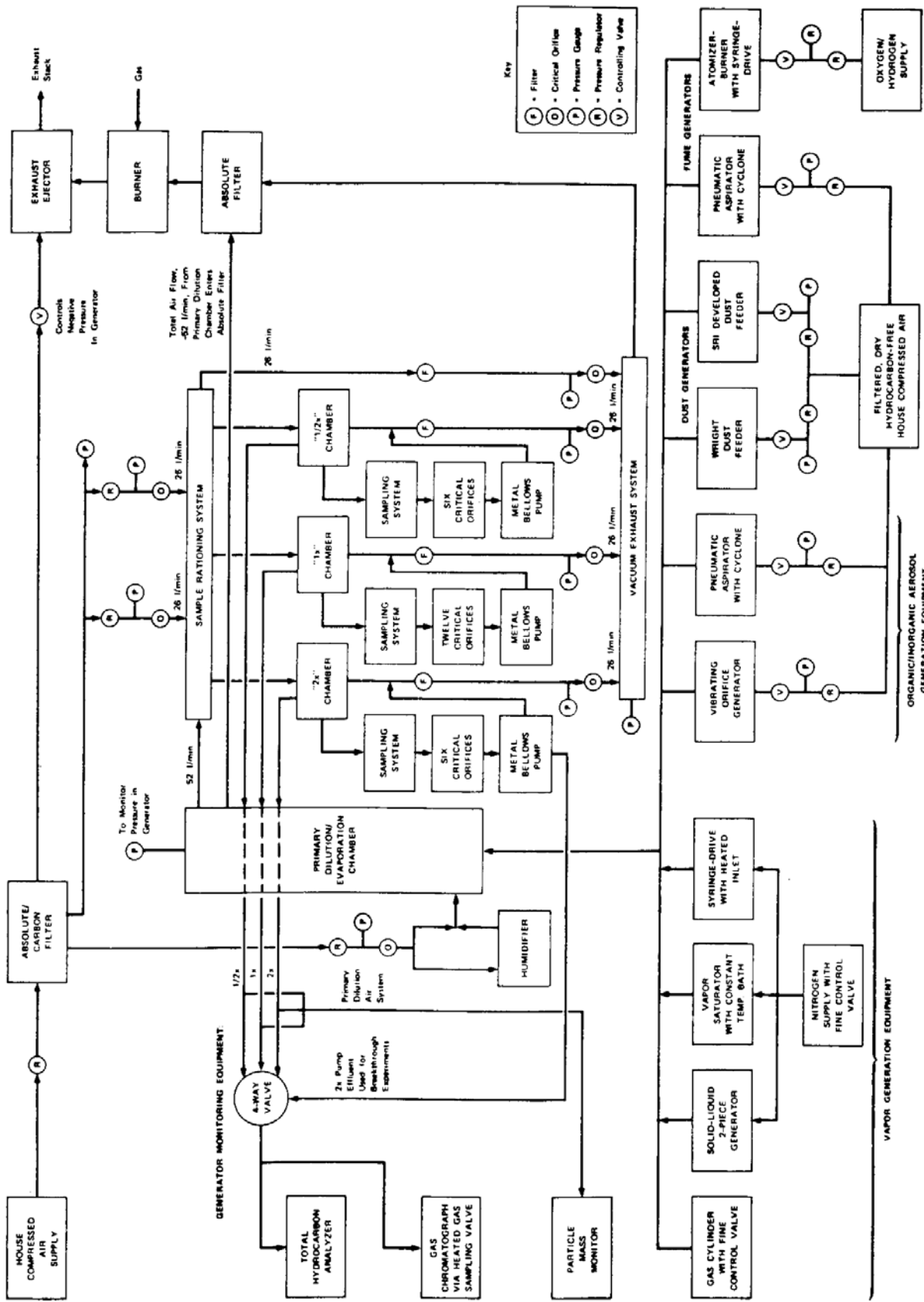
Figure A1. Schematic of sample generation facilities

The dilution ratios from chamber to chamber can also be varied by simply changing the amount of dilution air that is added. This is particularly advantageous in generating aerosols, where wall deposition of particles in the rationing system can be offset by changing the rate of addition of dilution air.

The cylindrical section at the base of each sampling chamber contains the fittings necessary to collect samples, using any of a variety of sampling media--solid sorbent tubes, filters, liquid scrubbers, or a combination of these. Six to twelve samples each at three concentration levels can be collected simultaneously. A metal bellows vacuum pump is used for sampling from each chamber. Separate critical flow orifices are used for each sample.

Air taken from the chamber during sampling is returned via the sampling pump exhaust line to the chamber outlet line, thus preserving the proper air flows during the time of sampling. The sampling rate therefore does not affect the concentration of material in any of the chambers.

The entire system is maintained at 1-inch water vacuum to prevent toxic materials from escaping into the laboratory. All exhaust air streams (from the vacuum exhaust system and excess from the primary dilution chamber) are fed into a combustion chamber where all toxic materials present are burned before entering the atmosphere.

A diagram of the apparatus used for generating high humidity atmospheres is shown below:
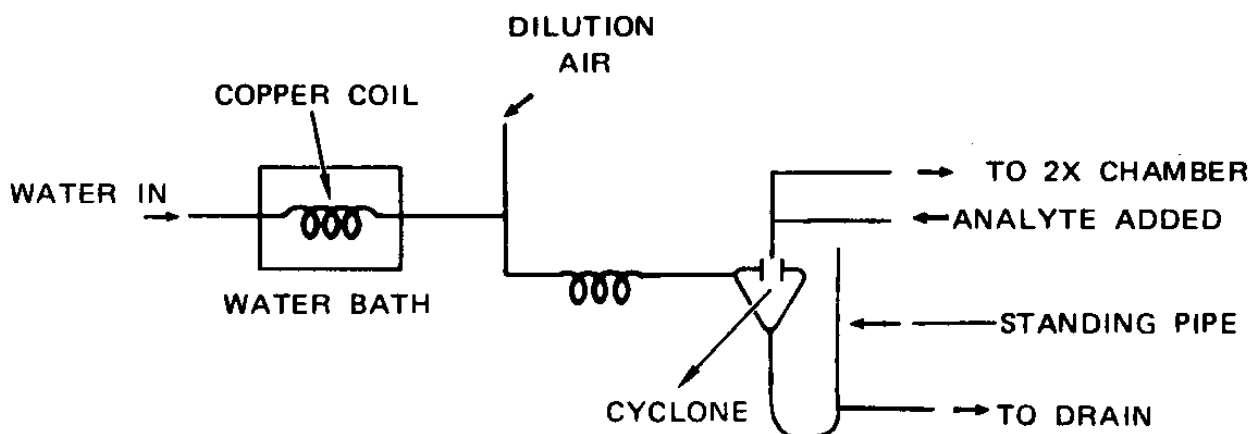

Figure B1. High humidity generation

A regulated flow of tap water at approximately 15°C flows through a copper coil contained in a thermostated water bath. After emerging from the water bath it enters a 5-foot length of 5/16-inch Tygon tubing. The dilution air is introduced into this same tubing and becomes water saturated at the temperature of the bath.

This water-air mixture passes into a cyclone, where excess water is removed from the air stream and drains from the bottom of the cyclone. The U-shaped tube and standing pipe provide a water seal at the bottom of the cyclone to prevent loss of air by this route. The humid air passes through the top of the cyclone. A controlled flow of the analyte enters the air stream at the outlet of the cyclone at a rate such that the 2X concentration is obtained.

The temperature of the water bath is kept 1°C lower than the temperature of the room. Thus, the air is saturated with water vapor at the lower temperature and reaches a relative humidity of less than 100% as it warms to room temperature after leaving the cyclone.

The relative humidity of the air in the sampling chamber is measured by the dry and wet bulb thermometer method. A flow of 32 liters/minute of the test atmosphere is drawn from the sampling chamber over the thermometers.

To ensure that a sufficiently high flow rate of air passes over the thermometers to give an accurate measurement, both thermometers are enclosed in glass tubing with an internal diameter of 11 mm.

From the readings of the relative temperatures of these two thermometers, the relative humidity at the temperature of the dry thermometer is found by consulting relative humidity tables.