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LOW LEVEL VAPOR VERIFICATION OF MONOMETHYL HYDRAZINE

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ABSTRACT

The purpose of this summer project was to evaluate the vapor scrubbing system and the coulometric test procedure for the low level vapor verification of monomethyl hydrazine (MMH). Experimental data on precision, efficiency of the scrubbing liquid, instrument response, detection and reliable quantitation limits, stability of the vapor scrubbed solution and interference were obtained to assess the applicability of the method for the low ppb level detection of the analyte vapor in air. The results indicated that the analyte vapor scrubbing system and the coulometric test procedure can be utilized for the quantitative detection of low ppb level vapor of MMH in air.

SUMMARY

American Conference of Governamental Industrial Hygienists on toxic vapors has recently proposed to reduce the Threshold Limit Value (TLV) of hydrazines to 10 ppb level in air. NASA's Toxic Vapor Detection (TVD) group at the Kennedy Space Center (KSC) is working on to develop sensors for meeting this requirement. For the testing of the potential sensors, test vapor of the analyte must be verified at the low ppb level of concentration. TVD group has opted to use the coulometric titration method for the vapor verification of hydrazines since it is a routine TVD lab's procedure for the detection of hydrazines at the ppm levels. In this project, experimental data is obtained to assess the applicability of the coulometric test procedure at low ppb level after scrubbing the monomethyl hydrazine (MMH) vapor in acidic absorbing solution.

0.1 M H_2SO_4 is found to be an effective scrubbing medium for absorbing MMH vapors without any carry-over loss of the analyte. Coulometric response to MMH is found to be linear and consistent in the low ppb concentration range. The acidic solution containing scrubbed MMH vapors is stable up to a period of 3-day and a slight loss of the analyte is detected after seven days. Ammonia gas is found to be a potential negative interferent at twice its TLV value and higher. Experimental data obtained demonstrate that the vapor scrubbing system and the coulometric titration test procedure can be utilized for the low ppb level verification of MMH vapor in air.

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I - INTRODUCTION

Hydrazines are used as hypergolic propellants for the in-flight shuttle maneuvering systems. Their vapors are highly toxic at low parts per million (ppm) levels and form hazardous explosive air mixtures at higher concentrations. These fuels affect the performance capabilities of humans and have been shown to cause tetragenic and mutagenic activity.

The American Conference of Governmental Industrial Hygienists (ACGIH) has proposed to reduce in 1991 the Threshold Limit Value (TLV) of hydrazine (N_2H_4) and monomethyl hydrazine (MMH) to 10 parts per billion (ppb) level from their respective 100 and 200 ppb levels. NASA's Toxic Vapor Detection (TVD) Group of the Instrumentation Branch at the Kennedy Space Center (KSC) has been working to develop sensors to meet this new requirement.

Prior to the testing of the potential sensors, test vapors must be accurately analyzed for hydrazines. A coulometric titration procedure has been in use at KSC for many years for the detection of ppm concentration level of hydrazines. Due to its simplicity and accuracy, the TVD group has opted to use this method; however, use of this test procedure requires experimental data on precision, accuracy, efficiency, etc., to assess the applicability of the method for the ppb level detection of hydrazines. This project focussed on the evaluation of the vapor scrubbing system and the coulometric titration test procedure for the ppb level vapor verification of MMH in air.

II - MATERIALS AND METHODS

2.1 MMH Vapor Generator System:

Kin-Tek's Span Pac 361 Precision Standard Vapor Generator is used in conjuction with Miller-Nelson HCS-301 flow-humidity-temperature control system for the generation of the MMH vapors.

Span-Pac consists of three permeation devices housed in three temperature-controlled ovens. Each permeation device is a stainless steel dewar containing a coil of polymeric capillary tube submerged in MMH. Nitrogen flows through the polymeric tubes at all times. Standard vapor of the analyte at various levels of relative humidities may be generated by diluting the analyte-nitrogen mixture with varying conditioned air from Miller-Nelson unit. Activating the SPAN or ZERO mode in conjuction with activating a combination of channel switches of the permeation devices on the Kin-Tek vapor generator, zero air and various concentration levels of the analyte in vapor phase may be generated at various levels of percent relative humidity.

2.1.1 MMH Vapor Standards

Using the standard laboratory set-up, the system generated MMH vapors in the concentration range of 3-149 ppb in air at approximately 80% relative humidity, a requirement for meeting the OSHA's protocol for the development of a new methodology[1,2].

2.1.2 MMH Scrub Solutions for Spiking

0.1 M H_2SO_4 scrubbing solutions containing MMH were prepared using a 10% solution of high purity MMH supplied by Wiltech Corporation in KSC. 25 ml of these solutions were spiked with various MMH standard vapors for recovery, detection and reliable quantitation limits. Actual concentration of MMH present in these scrubbing solutions was determined by coulometric titration[3] method using the following formula:

$$\underset{\text{(in liquid)}}{\text{ppb}} = \frac{10^{-4}\text{ amp} \times (\text{distance in cm} \times 60\text{ sec}/2\text{ cm}) \times (46 \times 10^{6}\text{ ug / mole of MMH})}{(9.6484 \times 10^{4}\text{ amp-seconds / mole e}^{-}) \times 4\text{ mole e}^{-}\text{ / mole MMH} \times \text{sample volume, Lit's.}}$$

2.1.3 Interference Study

Interference by ammonia gas present in the sample stream on the detection of MMH vapor in the scrubbed liquid was determined. K-bottle containing known concentration of ammonia in nitrogen was connected into the air inlet of the MMH vapor generating system. Outlet flow of the K-bottle was controlled so that the standard MMH vapor produced by the system contained approximately 50 ppm (2xTLV) and higher concentration of ammonia gas.

2.2 Vapor Collection System:

Cole-Palmer masterflex peristallic type air sampling pump with variable control speed was used for scrubbing the standard MMH vapors for having the experimental data to assess the applicability of the coulometric method for the ppb level detection of MMH. MMH vapors were scrubbed through a glass straight tube impingers having 25 ml of 0.1 M H_2SO_4 as the scrubbing solution at a rate of about 0.8-1 liter per minute. At all times, the volume of the MMH vapor passing through the impingers was calculated from the wet test meter readings. 15 liters of the MMH vapors were scrubbed for all the standards except for the low level concentration standards (< 10 ppb) where 30 liters of the vapors were also scrubbed to have a readable titration time (net chart distance) in the coulometric analysis over blank (bkg) reading.

Most of the scrubbing was done using single impingers; however, two impingers were also used in series to determine the absorbing efficiency of the scrubbing solution for the MMH vapors. The standard laboratory sampling setup is presented in Figure 2-1.

2.3 Coulometric Titration System

The circuits of a typical standard coulometric titration system[4] is shown in Figure 2-2. The oxidant generator circuit consists of a platinum anode (+), an auxiliary platinum cathode (-) and a constant-current power supply. The potential monitoring circuit contains a platinum indicator electrode, a reference electrode and a strip chart recorder. The schematics and the list of the components of a NRL coulometer used for this study are presented in the Appendix A.

2.3.1 Coulometric Titration Method:

Following vapor absorption, MMH concentration was determined by constant-current coulometric titration method.

> Hydrazines are titrated in acidic solution with electrically-generated bromine. Coulometric method analyzes hydrazines collectively. Quantification of hydrazines are obtained by counting the electrons produced by the oxidation of the analyte since each mole of hydrazines produces four moles of electrons. The electrons produced during the titration enter an electric circuit and are counted by integrating the electric current as a function of time since time and current are related to the number of electrons by Faradays constant (96484.56 amp-sec per mole). In other words, time or net recorder chart distance required for the titration is directly related to the analyte concentration in the scrubbed solution.

Basically, NASA's TVD lab's analysis procedure TVD-00003-GP was followed for the titration of the MMH vapor in the scrubbed solutions and is presented in Appendix B. A small amount of potassium bromide (KBr) crystals were dissolved in the vapor-absorbed scrubbing solution. A direct electric current passing through the solution electrolyzed KBr at the anode (+) to produce bromine (Br_2) which immediately oxidized MMH present in the scrubbing solution. The length of the titration (Figure 2-3) reflected the amount of MMH present in the solution. Soltec 1241 recorder having a chart speed of 2 cm / min at a recorder sensitivity of 100mv was used for all the coulometric titration runs. Proper coulometric operation was checked by titrating standard solutions of MMH and hydrazine prepared in the laboratory.

Analyte vapor concentration was calculated using the following simple formula:

$$\underset{\text{(in air)}}{\text{ppb}} = \frac{\text{Net titration length in cm} \times 0.38 \times 10^3}{\text{Chart speed (cm / min)} \times \text{Liters of vapor scrubbed}}$$

$$\text{where} \quad 0.38 = \frac{(10^{-4}\ \text{amp}) \times (60\ \text{sec / min}) \times (24.5\ \text{Lit / mole}) \times (10^6\ \text{ul / Lit})}{(9.65 \times 10^4\ \text{amp-sec / mole e}^-) \times (4\ \text{mole e}^- / \text{mole MMH})}$$

No volume correction was applied since all the MMH vapor scrubbing was done at 23-25 ^{0}C and at one atmospheric pressure. However, the following formula may be used for obtaining the correct sample volume if significant variation in temperature and pressure exists.

$$\text{Volume, Liters} = \frac{\text{Volume scrubbed, Liters} \times (273 + {}^{o}\text{C}) \times 760\ \text{mm of Hg}}{\text{Pressure in mm of Hg} \times 298}$$

2.3.2 Chemical Reaction in Coulometric Titration

N_2H_4 and its alkylated derivative (MMH) do not go oxidation at anode (+) spontaneously given by the equations

$$N_2H_4 \not\longrightarrow N_2 + 4H^+ + 4e^-$$

$$CH_3HN_2H_2 + H_2O \not\rightarrow CH_3OH + N_2 + 4H^+ + 4e^-$$

They are forced to do so by applying potential across the solution between two oppositely-charged electrodes. As the scrubbing solution is acidic, H^+ are reduced to H_2 at cathode (-).

$$4H^+ + 4e^- \longrightarrow 2H_2$$

Hydrazines are protonated in acidic scrubbing solution as follows

$$N_2H_4 + H^+ \longrightarrow N_2H_5^+$$

$$CH_3HN_2H_2 + H^+ \longrightarrow CH_3HN_2H_3^+$$

Protonated hydrazines are not oxidized directly on an anode (+). An intermediate electrolyte is used which oxidizes easily at the anode (+) and then oxidizes hydrazines. KBr is used for this purpose.

$$4KBr \longrightarrow 2Br_2 + 4e^- + 4K^+$$

Liberated oxidant, Br_2, immediately oxidizes hydrazines

$$N_2H_5^+ + 2Br_2 \longrightarrow N_2 + 5H^+ + 4Br^-$$

$$CH_3HN_2H_3^+ + 2Br_2 + H_2O \longrightarrow CH_3OH + N_2 + 5H^+ + 4Br^-$$

Each mole of hydrazine or MMH produces four moles of electrons. Hydrazines are titrated with electrons which act as a universal standard. There is no need of an external standard. Moreover, there are no reference standards available from National Institute of Standards and Technology (NIST).

III - RESULTS AND DISCUSSIONS

3.1 Efficiency of the Vapor Scrubbing Solution

The results obtained for the scrubbing of the various MMH vapor standards into the 25 ml of the 0.1 M H_2SO_4 absorbing solutions under the standard laboratory setup are presented in Table 3-1. Scrubbing of 15 liters over 10 ppb level and 30 liters under 10 ppb level MMH standard vapors did not show any carryover of the analyte vapor into the second impinger except for the 149 ppb level MMH standard where a slight carryover of MMH vapors was observed into the second impinger. Higher scrubbing volume (overnight run) resulted in the carryover of the MMH vapor into the second impinger for the standards having 42 ppb MMH and above. The data indicate that 15 liters over 10 ppb level and 30 liters under 10 ppb level are the optimum scrubbing volumes and that 0.1 M H_2SO_4 is an efficient scrubbing medium for absorbing the MMH vapors at low ppb levels without any carryover losses.

3.2 Precision of the Analytical Procedure

The precision of the analytical procedure for the MMH vapor verification study includes the sample collection system as well as the coulometric titration analysis. Data obtained for a series of MMH vapor standards scrubbed and analyzed by the coulometric method are presented in Table 3-2. The variation in the results of the MMH concentration found in the scrubbed solutions for most of the vapor standards was found to be approximately 10%. The scattering in the data obtained for the 15 liter vapor scrubbing done for std-20 on June 11 was found to be higher; however, another run of July 3 of the same standard for the same scrubbing volume was found to be less than 10%. The variation of approximately 30% on June 11 may be attributed to the air inlet pressure fluctuations in the standard vapor generation system observed during the early part of this investigation. Scattering in the data is also observed for the higher MMH vapor standards but the variation is less compared to std-20.

The calculated percent coefficient of variation for all the standards was found to be 10% or less except for std-20 scrubbed on June 11. Using 30 liters scrubbed volume for std-7.5 and std-20, and 15 liters scrubbed volume for all other standards, the calculated pooled percent coefficient of variation was found to be 6.7% which is better than 8% required by OSHA for the development of a new methodology .

3.3 Instrument Response to MMH

The linear curve obtained for the net chart distance obtained in cm at a chart speed of 2 cm / min in the coulometric analysis versus the average MMH vapor concentration determined experimentally by scrubbing is presented in Figure 3-1. The curve demonstrates the consistency in the coulometric response in determining MMH in the absorbing solution after scrubbing. It also demonstrates a linear response of the analytical method to the concentration range (3-149 ppb) of the analyte vapor scrubbed and analyzed under the prescribed conditions of the test procedure.

3.4 Spiking of the Scrubbing Solution Containing MMH

Spiking of the various MMH vapor standards was done into 0.1 H_2SO_4 scrubbing solutions containing 72 and 7.9 ppb average concentration levels of MMH. The purpose was to evaluate if we could recover the amount of MMH vapors spiked into a scrubbing solution containing MMH. Data obtained for this spiking are presented in Tables 3-3 and 3-4. The results reflect that the average %recovery for all of the standard MMH vapors spiked into the scrubbing solution containing a known amount of the analyte was in the range of 81-113% for 15 or 30 liters of sample volume scrubbed except for the std-20 where average %recovery was found to be 71% for 15 liter scrubbing volume. No explanation can be given for this low recovery except to attribute this to the air pressure fluctuations in the vapor generation system; however, 30 liter scrubbing volume of std-20 gave 105 and 103 average percent recovery for scrubbing solutions containing 72 and 7.9 ppb average concentration of the analyte respectively.

3.5 Detection Limits

3.5.1 Detection Limit of the Analytical Procedure

Detection limit of an analytical procedure is normally a factor of the base-line noise in any analytical instrumentation. In coulometric analysis, the type of base-line (bkg) information obtained is a line trace. It was decided to use the detection limit equal to the blank line trace obtained by running the scrubbing solution through the coulometric titration procedure. 0.1 M H_2SO_4 scrubbing solutions gave an average chart distance of approximately 0.4 cm at a chart speed of 2 cm / min which when calculated using the standard formula gave an equivalent value of approximately 5 ppb. Hence 5 ppb was selected as a detection limit of the analytical procedure.

3.5.2 Detection Limit of the Overall Procedure

The detection limit of the overall procedure is the amount of the analyte spiked which allows recovery equivalent to the detection limit of the analytical procedure. Figure 3-2 is a recovery curve of the MMH vapor concentration recovered versus average MMH vapor concentration of various spiked standards. Data used for the preparation of this recovery curve is the spiking data presented in Table 3-4. The detection limit of the overall procedure was found to be 5 ppb. It was decided to evaluate if we can go below 5 ppb as the detection limit of the overall procedure. A set of six absorbing solutions having 2.1 ppb average MMH concentration were spiked with a 2.7 ppb average MMH vapor concentration standard using 30 liters of the scrubbing volume. MMH concentrations recovered in this test are also plotted on to Figure 3-2 and are presented in Table 3-5. It demonstrates that we can detect less than 5 ppb level of MMH vapor absorbed in 0.1 H_2SO_4. So we may conclude that the detection limit of the overall procedure is less than 5 ppb.

3.6 Reliable MMH Quantitation Limit

The reliable quantitation limit is the smallest amount of the analyte which can be quantitated with at least 75% recovery and a precision (∓ 1.96 Std Dev) of ∓ 25% or better. The data obtained (Table 3-5) for spiking 30 liters of MMH vapor std-20 into six of 0.1 M H_2SO_4 absorbing solutions containing 7.9 ppb concentration level of MMH were used to calculate the reliable quantitation limit. The average percent recovery of six runs was found to be 103% and a precision of ∓ 12%. As the precision obtained was better than required for OSHA methodology, it was decided to use the scrubbing data of 30 liters of the MMH vapor standard having 2.7 ppb average MMH vapor concentration spiked individually into six absorbing solutions having 2.1 ppb average MMH concentration (Table 3-5). The average percent recovery was found to be 87% with a precision of +20%. Hence it is appropriate to consider 3 ppb as the reliable quantitation limit of the analytical method.

3.7 Stability of the MMH Vapor Scrubbed Solutions

30 liters of std-20 was spiked into each of the six absorbing solutions and the MMH concentration was determined at an interval of three and seven days. The scrubbed solutions were stored at the room temperature and analyzed at the required time interval. No variation in the average MMH concentration in the three scrubbed solutions was found after three days; however, an average decrease of approximately 15% was observed in the other three solutions after a period of 7-day; average concentration of 6.1 ppb (6.3 ppb, 5.7 ppb and 6.3 ppb) MMH versus 7.2 ppb MMH.

3.8 Determination of MMH vapor in the presence of ammonia as interferent

The study indicates that ammonia is a negative interferent. The higher the concentration of ammonia in the stream of the MMH vapor for scrubbing, the lower is the MMH concentration detected in the scrubbed solution. 50 ppm of ammonia gas present in the MMH vapor std-20 stream resulted in a 25% average detection loss of MMH in the scrubbed solution while for 588 ppm ammonia, the loss was found to be 58% of the original concentration. The results obtained are as follows:

NH_3, ppm	Std-20 MMH, ppb	MMH, ppb detected	Av MMH detected	% MMH loss
50	7.2	5.4 5.4	5.4	25%
588	7.2	2.9 3.2 2.9	3.0	58%

IV - CONCLUSIONS

1. 0.1 M $H2SO_4$ is an effective scrubbing solution for absorbing MMH vapors at low ppb levels. 15-30 liters scrubbing of the vapor sample at approximately 0.8-1 liter / min is optimum without any carry-over loss of the analyte.
2. The pooled percent coefficient of variation of the method (sample collection system and the coulometric analysis) is found to be 6.7.
3. Coulometric response to MMH in the absorbing solution is found to be linear and consistent in the concentration range of 3-149 ppb under the prescribed conditions of the test procedure.
4. The average percent recovery of the spiked MMH vapor standards into the scrubbing solutions having various levels of MMH is found to be in the range of 71-113%.
5. The detection limit of the overall procedure and the reliable quantitation limit are found to be less than 5 ppb and 3 ppb respectively.
6. No variation in the average concentration of MMH vapor in the scrubbed liquids is found for std-20 after three days; however, a slight reduction in the detection of the analyte is observed after a period of 7-day.
7. Ammonia is found to be a potential negative interferent. The higher the ammonia in the sample stream, the lower is the amount of the analyte detected in the scrubbed solutions i.e. 25% and 58% average detection loss at 50 ppm and 588 ppm levels of ammonia respectively.
8. The present study demonstrates that the analyte vapor scrubbing system and the coulometric titration test procedure can be utilized for the quantitative analytical low ppb level detection of MMH vapor in air.

V - RECOMMENDATIONS

1. For the testing of any potential sensor at low ppb level detection of MMH vapor using the Span-Pac MMH vapor generator system, the following is recommended
   - The vapor generator system should be optimized with a constant air flow and a standard laboratory setup procedure.
   - There should not be any interference with the test setup during the course of the investigation for having a constant and reliable analyte vapor concentration.
2. Interference study using H_2S, alcohols and other interferents should be carried out to have information about the impact of the interferents on the detection of MMH in the scrubbed solution.
3. Since hydrazine behaves like MMH in acidic solution for the coulometric titration analysis, the data obtained in this study may also be utilized for the vapor verification of hydrazine at low ppb level. However, it is worth to generate independent experimental data in the laboratory for the detection of hydrazine at low ppb level.

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2. Hull, R. D., "Development and Evaluation of Methods," NIOSH / DPSE.

3. Johnson, R. P. and Miller, E. L., "Quantitation of Hydrazines and Hydrazones," Lockheed E & M Service Company, NASA / Johnson Space Center, Los Cruces, New Mexico.

4. Willard et. al., Instrumental Methods of Analysis, 5th ed. New York: D. Van Nostrand Co., 1974.

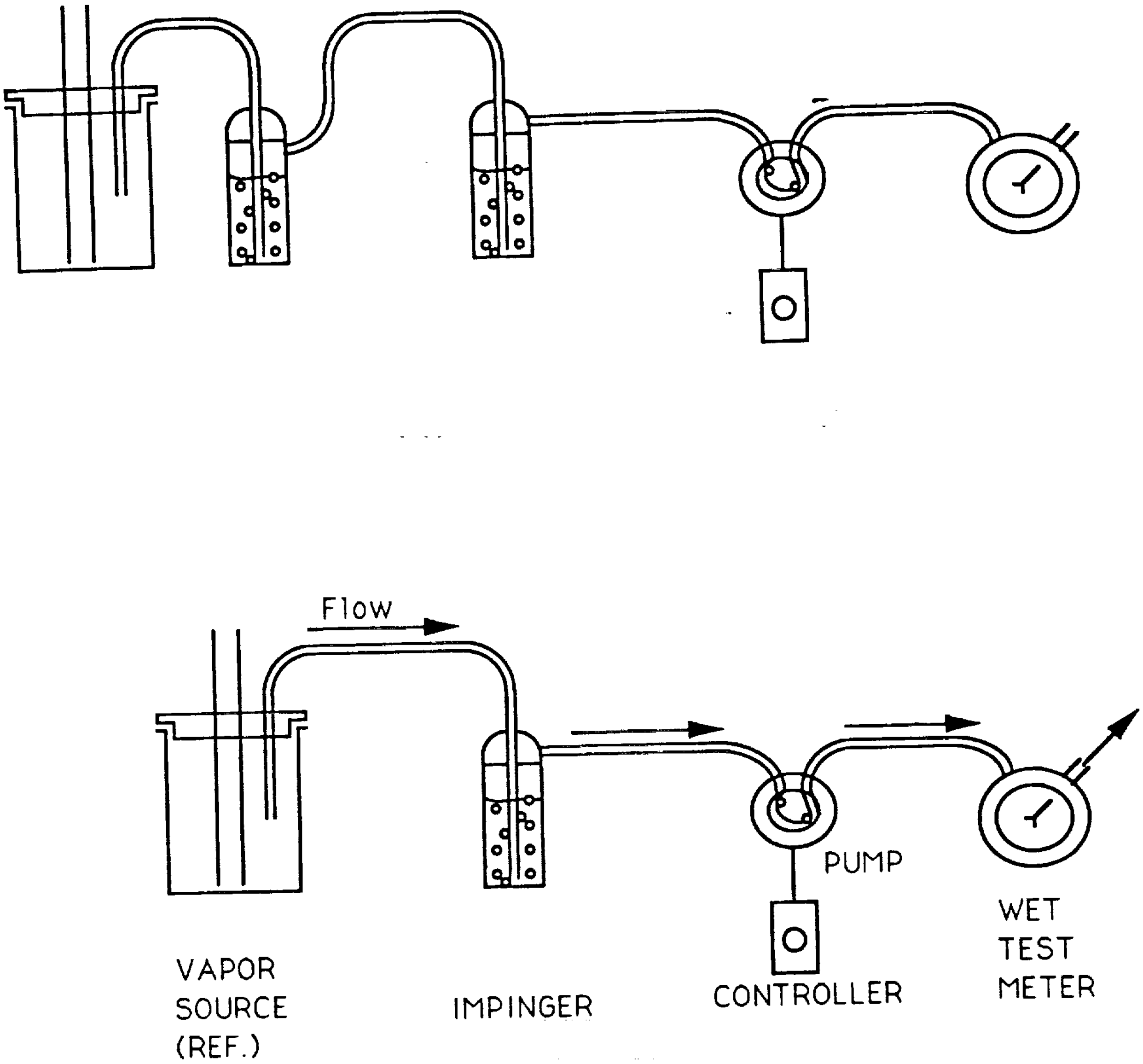


Figure 2-1 Vapor Collection System Setup

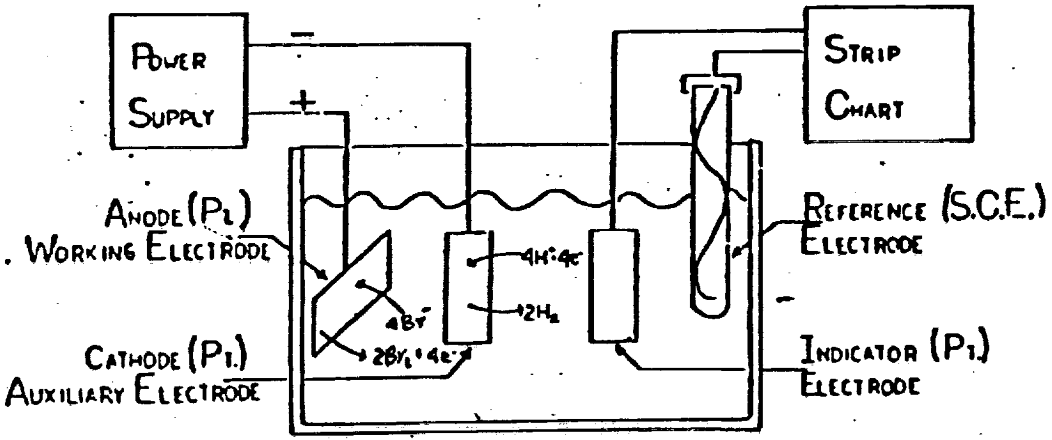


Figure 2-2 Typical Standard Coulometric Titration System

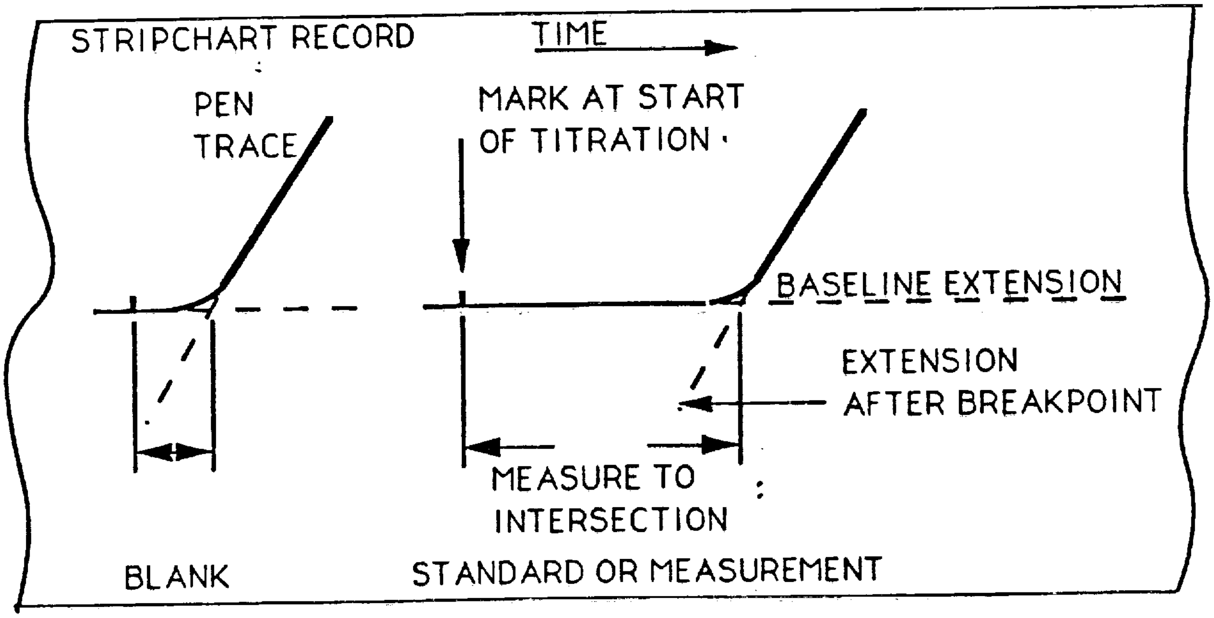


Figure 2-3 Measurement of Coulometric Titration Length

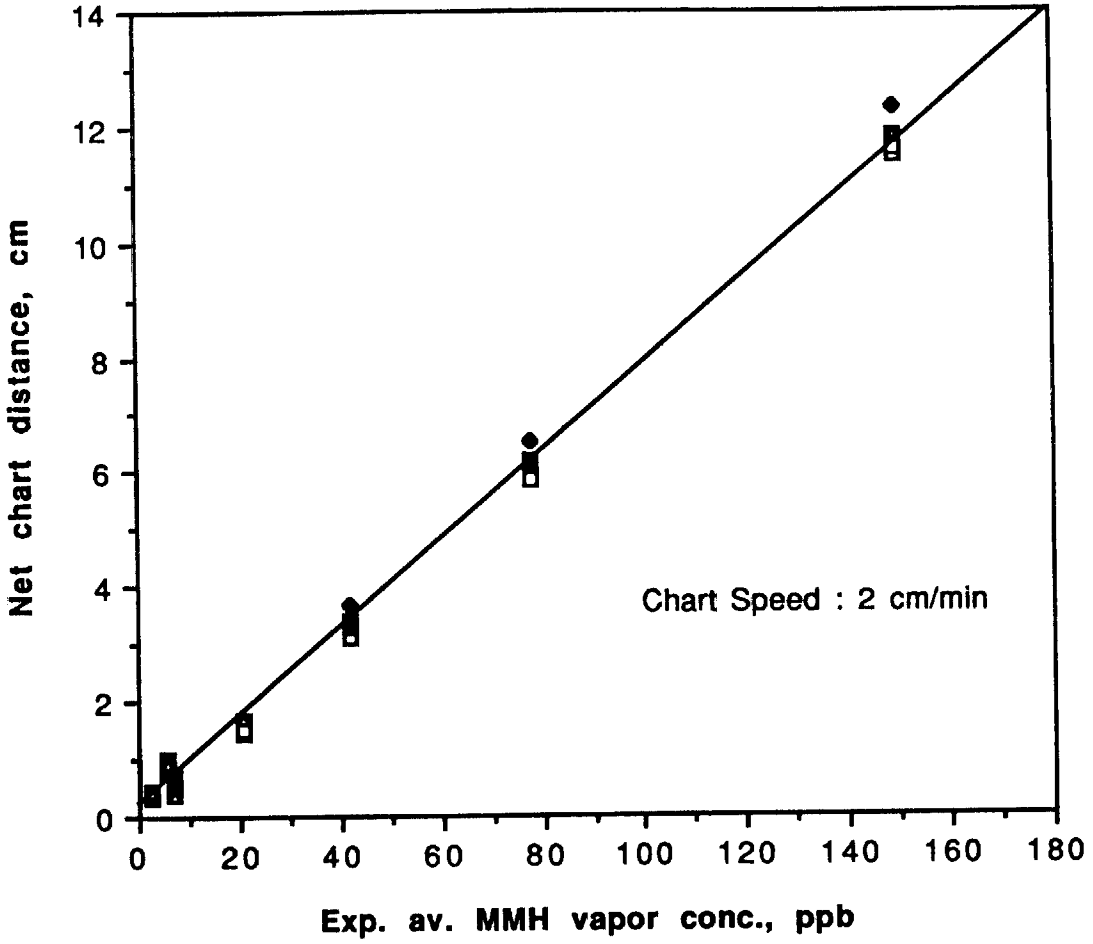
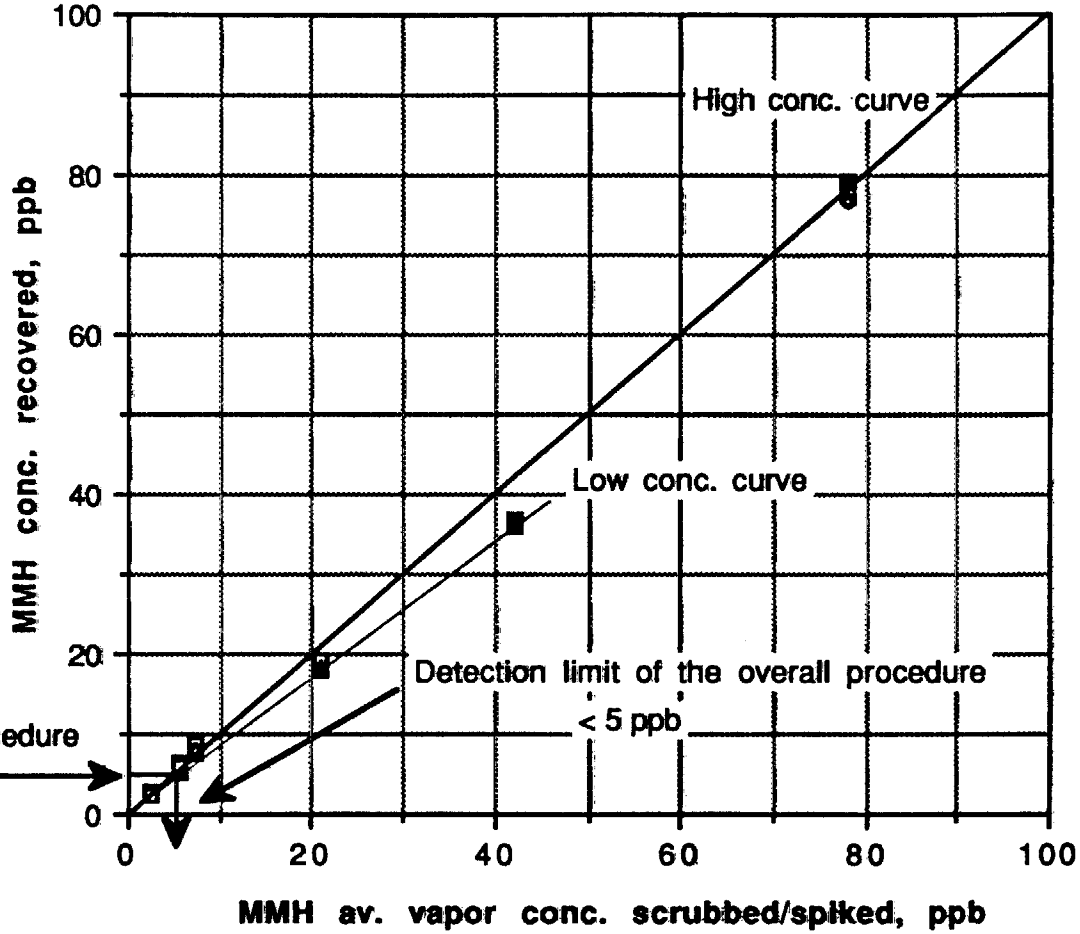


Figure 3-1. Instrument (Coulometer) Response to MMH



Detection limit of the analytical procedure
= Blank (coulometric) line trace
≅ 0.4 cm at a chart speed of 2cm / min
which is equivalent to 5 ppb

In exp work, scrubbing solution having 7.9 ppb MMH was spiked with various MMH vapor standards

AND

Scrubbing solution having 2.1 ppb MMH was also spiked with a 2.7 ppb MMH vapor std to see how low we can detect MMH.

D. L. of the analytical procedure
5 ppb

Figure 3-2. Detection Limit of the Overall Procedure for MMH

TABLE 3-1

MMH Vapor Generated By Span-Pak Under Standard Lab Procedure

Temp : 23-25 C and % R. H. : 80-81
Scrubber (0.1 M H2SO4) Volume : 25 ml
Scrub rate : 0.8-1 liter / min

MMH vapor standard	Liters of vapor scrubbed	Airflow	Av MMH found in Ist impinger ppb	MMH found in 2nd impinger ppb
Std-7.5	30 (July 2)	4+1	2.7	
Std-20	15 (June 11)	4+1	7.2	
	15 (July 3)	4+1	8	
	30 (June 18)	4+1	5.7	
Std-79	15 (June 8)	39+1	21	0
Std-158	15 (June 5)	19+1	42	0
	831 (overnight)		38	<1
Std-316	15 (June 7)	9+1	78	0
	836 (overnight)		84	2
Std-632	15 (June 8)	4+1	149	2

TABLE 3-2

PRECISION OF THE ANALYTICAL PROCEDURE FOR MMH VAPOR VARIFICATION STUDY

(Sample collection and Coulometric Titration Analysis)

Recorder Chart Speed and Sensitivity : 2 cm/min and 100mv
Scrubbing Solution Volume : 25 ml of 0.1 M H2SO4

	Std-7.5	Std-20		Std-20	Std-79	Std-158	Std-316	Std-632
Vap scrub vol	30 Lit	15 Lit		30 Lit	15 Lit	15 Lit	15 Lit	15 Lit
		11-Jun	3-Jul	18-Jun				
Run 1	2.2 ppb	7 ppb	7.6 ppb	6 ppb	22 ppb	42 ppb	79 ppb	146 ppb
2	2.5	7.6	8.2	5.4	22	47	82	156
3	2.5	7	7.6	6.3	20	43	75	150
4	2.9	5.1	8.2	5.7	22	41	79	147
5	2.5	7	8.2	6	19	41	77	147
6	2.9	8.8	8.2	5.1	19	39	74	147
7	2.9	10		5.4		42		
8	2.9	5.1		5.9		44		
Average, ppb	2.7	7.2	8	5.7	21	42	78	149
ppb Variation	2.7+0.2 -0.2	7.2+2.8 -2.1	8+0.2 -0.4	5.7+0.6 -0.6	21+1 -2	42+5 -3	78+4 -4	149+7 -3
% Variation	7%	29-39%	3-5%	11%	5-10%	7-12%	5%	2-5%
Std Deviation	0.27	1.67	0.31	0.4	1.51	2.39	2.94	3.76
% Co Variation	* 10	23.2	3.9	* 7	* 7.2	* 5.7	* 3.8	* 2.5

* Pooled % Coefficient of Variation : 6.7

* Using15 Lit vap scrub vol data for all std's except 30 Lit vap scrub vol data for Std-20 and Std-7.5

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Table 3-3

STUDY OF MMH VAPOR SPIKING-1

Av conc of MMH in the scrubbing solution (by coulometric method) : 72 ppb.
Scrubbing solution volume : 25 ml of 0.1 M H2SO4

Lit's of vapor scrubbed	MMH vapor standard	MMH av conc in scrubbed vapor, ppb	MMH found in solution after scrub, ppb	% Recovery	Average % Recovery
15	Zero gas	0	72+1		
			72+0		
			72+1		
15	Std-20	7.2	72+5.1	71	71
			72+5.1	71	
			72+5.1	71	
30	Std-20	5.7	72+5.7	100	105
			72+6.3	111	
15	Std-79	21	72+17	81	81
			72+15	71	
			72+20	95	
			72+16	76	
15	Std-158	42	72+39	93	88
			72+38	91	
			72+33	79	

Table 3-4

STUDY OF MMH VAPOR SPIKING-2

Av conc of MMH in the scrubbing solution (by coulometric method) : 7.9 ppb
Scrubbing solution volume : 25 ml of 0.1 M H2SO4

Lit's of vapor scrubbed	MMH vapor standard	MMH av conc in scrubbed vapor, ppb	MMH found in solution after scrub, ppb	% Recovery	Average % Recovery
15	Zero gas	0	7.9+0		
			7.9+0		
			7.9+0		
15	Std-20	7.2	7.9+8.9	124	113
			7.9+7.6	106	
			7.9+7.6	106	
			7.9+8.2	114	
30	Std-20	5.7	7.9+6.3	111	103
			7.9+6.0	105	
			7.9+5.3	93	
			7.9+5.7	100	
			7.9+6.0	105	
			7.9+6.0	105	
15	Std-79	21	7.9+19	91	87
			7.9+18	86	
			7.9+18	86	
			7.9+18	86	
15	Std-158	42	7.9+36	86	87
			7.9+36	86	
			7.9+37	88	
			7.9+36	86	
15	Std-316	78	7.9+78	100	100
			7.9+77	99	
			7.9+79	101	
			7.9+77	99	

Table 3-5

RELIABLE QUANTITATION LIMIT FOR MMH

Av conc of MMH in the 0.1 M H2SO4 scrubbing solution : 7.9 ppb
MMH standard vapor scrubbed volume : 30 Liters

MMH conc in scrubbed vap ppb	# Run	MMH found in solution after scrub, ppb	% Recovered after scrub
5.7	1	6.3	111
18-Jun	2	6	105
	3	5.3	93
	4	5.7	100
	5	6	105
	6	6	105
	Average	5.9	103
	Std Deviation		6.1

Precision = ∓ 1.96 Std Deviation = ∓ 12 %

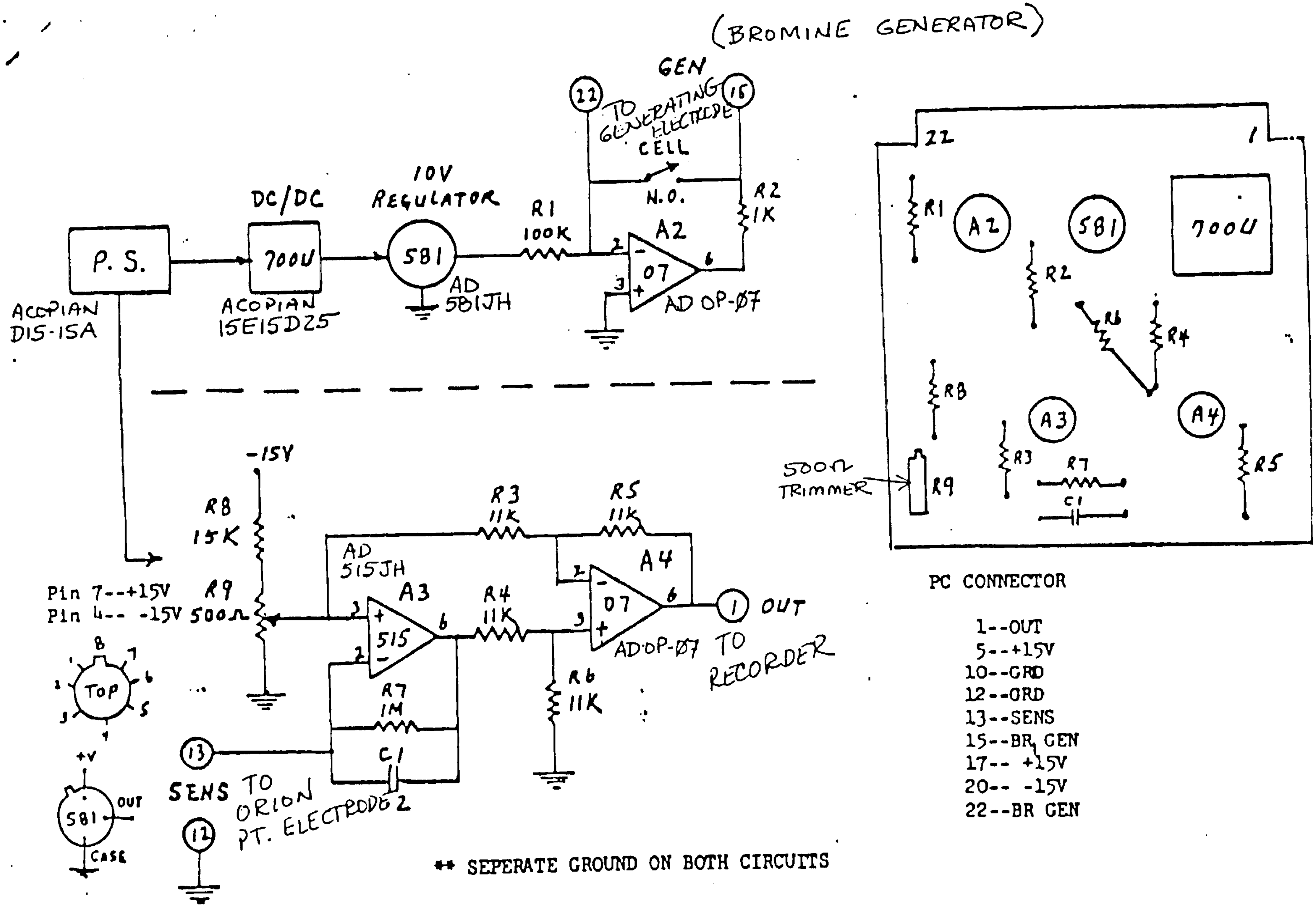
Av conc of MMH in the 0.1 M H2SO4 scrubbing solution : 2.1 ppb
MMH standard vapor scrubbed volume : 30 liters

MMH conc in scrubbed vap ppb	# Run	MMH found in solution after scrub, ppb	% Recovered after scrub
2.7	1	2.9	107
2-Jul	2	2.5	93
	3	2.2	81
	4	2.2	81
	5	2.2	81
	6	2.2	81
	Average		87
	Std Deviation		10

Precision = ∓ 1.96 Std Deviation = ∓ 20 %

PARTS LIST NRL COULOMETER

PART No.	AMT REQ'D	COMPONENT	MFR	MFR'S No.	or equiv.	Net ea $	Cost $	Bckd.
A1	4	REG. DUAL POWER SUPPLY,						
		±15VDC, 0.150A	ACO	D15-15A		79.—	316.—	
A2	4	SOCKET (FOR A1)	"	EL-1		5.—	20.—	
A3	4	ISOLATED DC-DC CONVERTER	"	15E15D25		105.—	420.—	
A4	4	SOCKET (FOR A3)	"	ES-1		5.—	20.—	
A5	12	ULTRA LOW OFFSET VOLTAGE						
		OP AMP	AD	AD OP-07-	DH	3.—	36.—	
A6	6	PRECISION LOW POWER FET INPUT		—				
		ELECTROMETER OP AMP	AD	AD515 —	JH	28.50	171.—	
A7	6	HIGH PRECISION 10V IC REFERENCE	AD	AD581 —	JH	6.90	41.40	
A8	1 pk	RESISTOR, 100K, 1/4W, 5%, (100/pk)	ALL	823-1717		5.04	5.04	
A9	1 pk	" , 1K, " , " , "	ALL	823-1356		5.04	5.04	
A10	1 pk	" , 11K, " , 1%, "	"	832-6528		4.94	~~5.04~~	4.94
A11	1 pk	" , 10K, " , " , "	"	832-6522		4.94	4.94	
A12	1 pk	" , 1M, " , 5%, "	"	823-1877		5.04	5.04	
A13	1 pk	" , 15K, " , " , "	"	823-1550		5.04	5.04	
A14	12	500Ω, TRIMMER POT, PC MOUNT	"	753-4720		1.68	20.16	
A15	12	0.22 μF CAPACITOR	"					
A16	12	SWITCH, MINIATURE, DPDT	"					
A17	12	INSULATED TIP JACK - RED	"	920-0181		.81	9.72	
A18	12	" " " - BLACK	"	920-0182		.81	9.72	
A19	12	" " " - YELLOW	"	920-0208		.81	9.72	
A20	12	" " " - GREEN	"	920-0206		.81	9.72	
A21	12	" " PLUG - RED	"	920-0578		.76	9.12	
A22	12	" " " - BLACK	"	920-0577		.76	9.12	
A23	12	" " " - YELLOW	"	920-0590		.76	9.12	
A24	12	" " " - GREEN	"	920-0580		.76	9.12	
A25	4	BNC CONNECTOR, PANEL MT.	"	885-4160		2.95	11.50	
A26	4	CABINET, 2 1/2 x 15 x 7, STEEL	"	736-3613		16.24	64.96	
A27	4	EDGE CONNECTOR, 44 CONTACT	"	750-1039		17.55	70.20	
A28	4 pr	HANDLES, CHROME, 1 15/16" CTRS	"	736-4366		7.05	28.20	
A29	1 pk	RECESSED BUMPERS, 100/pk	"	839-2439		20.40	20.40	
A30	2 pk	INSULATED BANANA JACK, RED, 5/pk	"	920-1485		1.75	3.50	
A31	2 pk	" " " , BLACK, "	"	920-1519		1.75	3.50	
A32	2 pk	" " " , YELLOW, "	"	920-1526		1.75	3.50	
A33	2 pk	" " " , GREEN, "	"	920-1527		1.75	3.50	
A34	2 pk	" " PLUG, RED, "	"	920-0185		3.85	7.70	
A35	2 pk	" " " , BLACK, "	"	920-0186		3.85	7.70	
A36	2 pk	" " " , YELLOW, "	"	920-0237		3.85	7.70	
A37	2 pk	" " " , GREEN, "	"	920-0233		3.85	7.70	



PC CONNECTOR

1--OUT
5--+15V
10--GRD
12--GRD
13--SENS
15--BR GEN
17-- +15V
20-- -15V
22--BR GEN

** SEPERATE GROUND ON BOTH CIRCUITS

Appendix B

2. DETERMINATION OF N2H4 OR MMH VAPOR CONCENTRATION IN NITROGEN OR AIR - COULOMETRIC TITRATION METHOD

2.1 Apparatus

2.1.1 Coulometer, 0.1 ma, 30 mv, with platinum wire electrodes.

2.1.2 Reaction vessel, 100 ml beaker.

2.1.3 Stirring bar and magnetic stirrer.

2.1.4 Recorder, Soltec Model 1241 or equal, calibrated for chart speed.

2.1.5 Pipets, 25 ml volumetric, 10 ml measuring.

2.1.6 Volumetric flasks, 1000 ml, 100 ml.

2.1.7 Wet test meter, Singer AL-17-1 or equal, calibrated.

2.1.8 Air sampling pump, Cole Parmer, masterflex, peristaltic type with variable speed control or equal.

2.1.9 Glass midget impingers, 25 ml, straight tubing.

2.1.10 Autopipet: Eppendorf or equal, 10 ul to 1000 ul adjustable.

2.1.11 Flowmeter, Sensidyne, EZ cal/Digital flowmeter or equal, calibrated.

2.1.12 Scoop, two scoops yield approximately 0.4 g KBr.

2.1.13 Tubings, Bev-A-Line, Tygon, assorted sizes and lengths.

2.1.14 Beaker, 100 ml, containing D.I. water.

2.2 Chemicals

2.2.1 Potassium Bromide (KBr), reagent grade.

2.2.2 Sulfuric acid (H2SO4), concentrated, reagent grade.

2.2.3 D.I. water.

2.2.4 Hydrazine (N2H4), reagent grade.

2.3 Safety

General - Refer to TVD-00004-SP, Toxic Vapor Detection Laboratory Hazards and Safety Manual for safety requirements and specific hazards, precautions, and emergency procedures concerning fire

(paragraph 4.4.1), hypergols (paragraph 4.4.4), acid and base (paragraph 4.4.5) and toxic vapors and solvents (paragraph 4.4.3).

2.3.2 Safety Equipment (Personal)

2.3.2.1 Face shield or safety glasses

2.3.2.2 Laboratory coat or rubber apron.

2.3.2.3 Gloves, chemical resistant.

WARNING

Monomethyl hydrazine and hydrazine are suspected carcinogenic chemicals. The current OSHA maximum allowable concentrations in air ceiling exposure are 0.2 ppm and 0.1 ppm, respectively.

WARNING

Concentrated sulfuric acid is very corrosive. Wear gloves while handling this chemical.

2.3.3 Safety Equipment (Laboratory)

2.3.3.1 Fume hood.

2.3.3.2 Safety shower and eyewash fountain.

2.3.3.3 MMH and N2H4 vapor concentration monitoring devices.

2.3.3.4 Fire extinguisher.

WARNING

Handle MMH and N2H4 in a fume hood. Avoid all oxidizing agents. Wear personal safety equipment. Note location of the closest fire extinguisher, safety shower, and eyewash fountain. Ensure test area conforms to good housekeeping standards. Monitor working area MMH and N2H4 concentrations with a calibrated monitoring device.

2.4 Preparation of Reagents

2.4.1 Sulfuric acid 0.1M - Pipet 5.6 ml of H2SO4 conc. into a 1000 ml volumetric flask containing approximately 700 ml of D.I. water. Add D.I. water to the mark. Mix well.

2.4.2 Hydrazine Stock Solution 100 ppm - Fill a 100 ml volumetric flask to the mark with 0.1 M H2SO4 solution. Add, below the surface, 10 ul of N2H4 into the solution. Mix well. Solution is stable for one month.

2.5 Sampling of N2H4 or MMH Vapor.

2.5.1 Set up the sampling apparatus as in Figure 1.

2.5.2 Pipet 25 ml of 0.1 M H2SO4 into the impinger. Stopper the impinger and water seal.

2.5.3 Turn on the air pump and adjust the flow control valve for 0.5 liter per minute flow. The flowrate shall be verified by calibrated EZ cal digital flowmeter.

2.5.4 Attach the inlet of impinger to vapor source using Bev-A-Line tubing.

2.5.5 As a guide, sample 6 liters for less than 0.5 ppm concentration of vapor, sample 3 liters for more 1.0 ppm concentration.

2.6 Analysis of Sample

2.6.1 Set recorder parameters as follows:

Range - 500 mV
Speed - 60 cm per hour

2.6.2 Turn coulometer power on.

2.6.3 Fill the reaction vessel containing a stirring bar to 40 ml mark with 0.1M H2SO4.

2.6.4 Place the raction vessel on the magnetic stirrer. Stir at medium speed.

2.6.5 Add 0.5 scoops of KBr to the solution. Stir until KBr is dissolved.

2.6.6 Place the electrodes in the solution. Ensure the electrolyte (0.1M H2SO4) in the Bromine generating electrode is approximately 1 inch above the solution in the vessel.

2.6.7 Turn on the recorder and lower the pen to start recording. When the line on the chart paper is level, simultaneously activate the coulometer CELL switch and the recorder marker.

2.6.8 When the recording line deflects upward approximately 1-1/2 inches (see figure 2), deactivate the cell switch, lift up the recorder pen, and promptly place the electrode in clean D.I. water.

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OF POOR QUALITY

2.6.9 Discard the solution in the vessel; rinse the vessel with D.I. water, then with 0.1M H2SO4.

2.6.10 Measure the reaction time in terms of distance in cm as in figure 2.

2.6.11 Repeat paragraphs 2.6.3 through 2.6.10 until three consecutive runs indicate the same distance. This is the blank value.

2.6.12 To ensure that the instrument is functioning properly, repeat pararaphs 2.6.3 to 2.6.10 with 30 ul of N2H4 stock solution added to 0.1 M H2SO4 in the vessel. The measured distance should be 6.0 cm ±0.1 cm. If this distance cannot be achieved, notify supervisor.

2.6.13 Quantitatively transfer (or take an aliquot of) the sample in the impingers to the glass vessel. Add 0.1M H2SO4 to 40 ml mark of the vessel. Repeat paragraphs 2.6.4 to 2.6.10.

2.7 Calculation

ppm MMH or N2H4 in air (or nitrogen) =

$$\frac{[\text{Sample (cm)} - \text{blank (cm)}] \times 0.38 \times \text{aliquot factor}}{\text{volume sampled (l)}}$$