-CR Toxic level hypergolic
33 vapor detection sensor
development.

NASA CONTRACT REPORT CR-154633

TOXIC LEVEL HYPERGOLIC VAPOR DETECTION SENDOR DEVELOPMENT

JOSEPH R. STETTER, YING-KIT LAU, RAYMOND B. CROMER

NOVEMBER 28, 1979

PREPARED BY:
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15. Abstract

The space shuttle program at Kennedy Space Center will involve the use and handling of large quantities of hypergolic propellants including hydrazine (H), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). Hydrazine compounds (H, MMH, and UDMH) are highly toxic, and threshold limit values (TLV) have been established by OSHA at 1.0 ppm H, 0.2 ppm MMH and 0.5 ppm UDMH.

There are not toxic level hydrazine vapor monitors commercially available meeting KSC's requirement for a low cost, accurate, reliable and simple to operate and maintain instrument which can read in the parts-per-billion range. The objectives of NAS 10-9492 are: 1) to develop electrochemical sensor technology capable of PPB level hypergolic vapor sensing, and 2) to design, fabricate and deliver to KSC one portable instrument capable of meeting the design goals. A report of the completing of this contract is the subject of this final report.

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TOXIC LEVEL HYPERGOLIC VAPOR DETECTION SENSOR DEVELOPMENT

FINAL REPORT — NOVEMBER 28, 1979

NASA CONTRACT NAS 10-9492

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SUBJECT: Toxic Level Hypergolic Vapor Detection Sensor Development, Final Report, NAS 10-9492

The subject report is enclosed for your information. DL-DED-32, in a joint NASA/USAF effort, will be performing additional testing and evaluating the new instrument. Plans are to procure additional instruments for use in this effort.

Please contact Mr. Scott (305-867-3842), or the undersigned if you have any questions.

Perry M. Rogers

Perry M. Rogers

Enclosure: as

TITLE: TOXIC LEVEL HYPERGOLIC VAPOR DETECTION SENSOR DEVELOPMENT

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SUBMITTED TO:
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FINAL REPORT

NOVEMBER 28, 1979

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This report was prepared for the National Aeronautics and Space Administration, Kennedy Space Center by Energetics Science, Division of Becton Dickinson and Company under contract NAS 10-9492 during the period October 25, 1978 to November 28, 1979. The contract was entitled "Toxic Level Hydrazine Analyzer Development". The ES Program Manager and Principal Investigator was Dr. Joseph R. Stetter, and the NASA contract Technical Manager was Mr. Perry M. Rogers, Technical Representative, NASA, Kennedy Space Center, Florida.

Acknowledgements for the success of the work performed under this contract must include the entire ES staff but in particular Joseph C. Delfino, Louis Metzger, Howard W. Bay, and Sydney Krivin for engineering, design, and documentation of the prototype instrument which was constructed. Further, this program could not have achieved its goals without the full support, cooperation, and encouragement of Energetics Science management, Mr. Robert E. Lieb, President.

Expert consultations with the NASA Technical Representatives; particularly Mr. Perry M. Rogers and Mr. Marshall Scott, and the Naval Research Laboratory, particularly, Dr. Raymond Saunders and Dr. James J. DeCorpo were invaluable during the conduct of this program.

SUMMARY

The space shuttle program at Kennedy Space Center will involve the use and handling of large quantities of hypergolic propellants including hydrazine (H), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). Hydrazine compounds (H, MMH, and UDMH) are highly toxic, and threshold limit values (TLV) have been established by OSHA at 1.0 ppm H, 0.2 ppm MMH and 0.5 ppm UDMH.

Original investigations (see references 10 and 11) focused upon the adaptation of existing Energetics Science technology (U.S. Patents #4,001,103, 4,042,464) for hydrazines monitoring. This cooperative NASA and Energetics Science effort resulted in successful commercial instrumentation for monitoring hydrazines at the PPM level (Energetics Science U.S. Patent appln. #916,296, NASA case # KSC-11082). This instrumentation however does not meet the current need for a ppb level detector for MMH.

There are not toxic level hydrazine vapor monitors commercially available meeting KSC's requirement for a low cost, accurate, reliable and simple to operate and maintain instrument which can read in the parts-per-billion range.

The objectives of NAS 10-9492 are: 1) to develop electrochemical sensor technology capable of PPB level hypergolic vapor sensing, and 2) to design, fabricate and deliver to KSC one portable instrument capable of meeting the design goals.

A report of the completion of this contract is the subject of this final report. In summary, the following tasks were completed within the scope of this work.

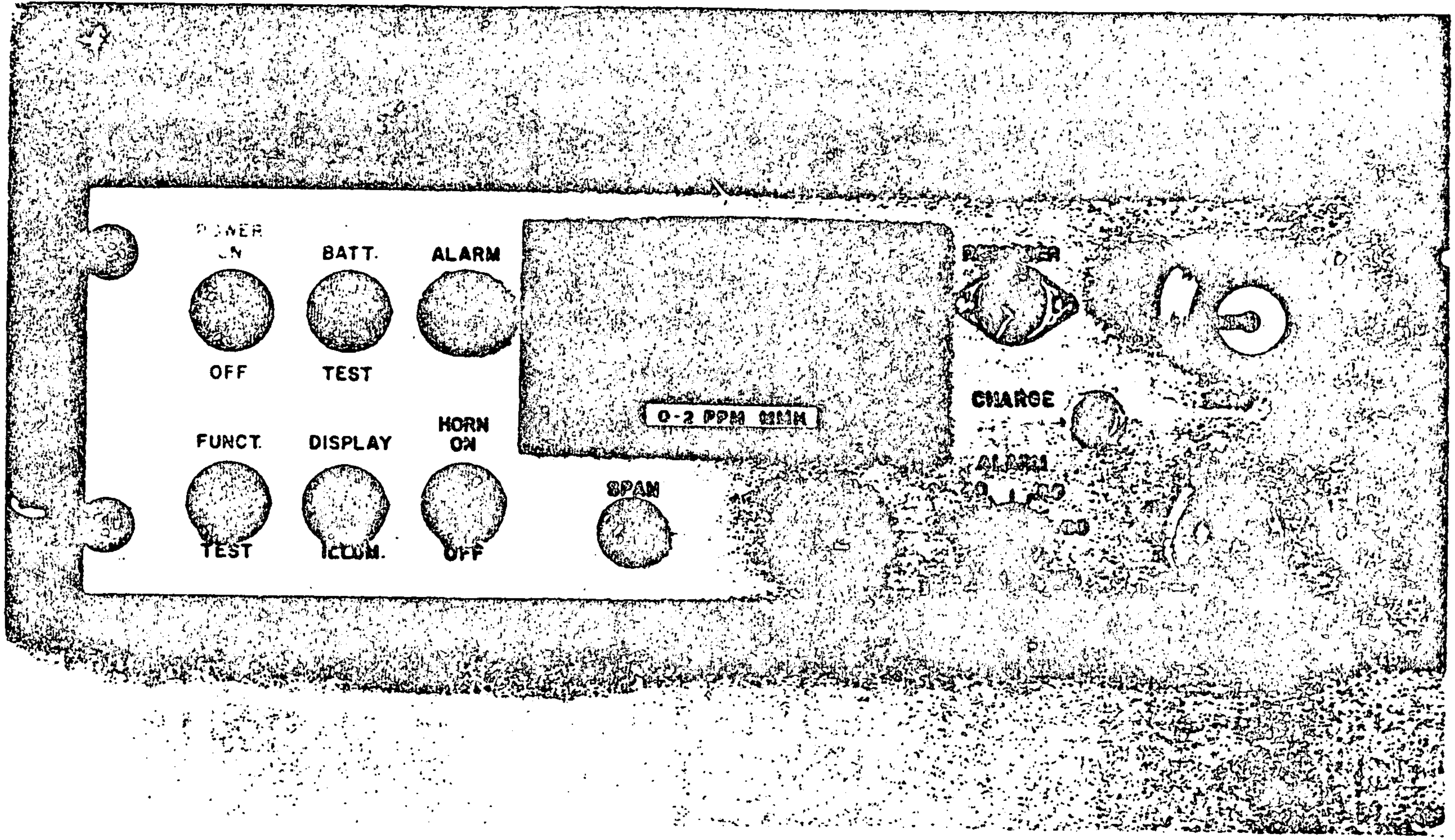
TASK I	Development of Electrode/Electrolyte/Potential conditions for the ppb level Hydrazine Sensing Reaction.
TASK II	Development of the Electrochemical Cell Design.
TASK III	Complete Design of Instrument Electronics.
TASK IV	Complete Design of Instrument Hardware.
TASK V	Fabrication and Evaluation Testing of Hydrazines Instrument.
TASK VI	Evaluation of Instrument Calibration and Hydrazine Handling Techniques for Low Concentration (ppb) of Hydrazine.
TASK VII	Delivery of Instrumentation and Documentation.

The prototype toxic level analyzer is the first instrument of its kind that is capable of performing cost-effective and reliable measurements for PPB level hydrazine vapors. The prototype toxic level analyzer either meets or exceeds this programs required design and performance goals for every category except response time at the lowest levels.

The permeation tube method of preparation of low concentration of hydrazines were evaluated and reliability for this technique was established by comparison with acceptable colorimetric and electrochemical methods.

Results indicate that the electrochemical method is more selective than the colorimetric method towards MMH detection and can be used at lower levels. Calibration of the prototype instrument is recommended to be done with hydrazine mixtures in nitrogen as oxidative decomposition of hydrazines in air had been shown to occur. Further applications of electrochemical sensing technology can be made in the development of analytical instrumentation for dosimeters and safety monitoring of hypergolic vapors.

0-2 PPM MONOMETHYLHYDRAZINE ANALYZER



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I. INTRODUCTION

The Space Shuttle program at Kennedy Space Center will involve the use and handling of large quantities of hypergolic propellants including hydrazine (H), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). The toxicity of these compounds is well known and current recommended exposure levels (TLV) are 0.1, 0.2 and 0.5 ppm V/v in air for H, MMH, and UDMH, respectively (1). Skin and respiratory exposure can yield a wide variety of effects, from nausea to carcinomas (2).

Methods for determination of these three hydrazines (H, MMH and UDMH) include colorimetry (3,4), titration with standard potassium iodate solution (5), an acid-base method (6), gas chromatography (7), derivative chromatography (8) and chemiluminescence (9). However, these methods are not widely used, since they suffer from various drawbacks such as complexity, insufficient sensitivity or lack of portability of the instrumentation (making them not easily adapted for use in a field instrument).

An electrochemical cell has been developed which, when coupled with an instrument system, can provide fast, accurate, sensitive and real-time determination of MMH, H and UDMH vapors at ppb levels.

This final report covers work performed under contract NAS 10-9492 for the period October 25, 1978 to November 30, 1979. The objectives of NAS 10-9492 are: 1) to develop electrochemical technology capable of PPB level hypergolic vapor sensing and 2) to design, fabricate and deliver to KSC one portable instrument meeting the design goals. The objective of this report is to summarize the major findings of this work.

Two prior reports (10, 11) detail the electrochemical technology which was used to develop the fixed installation and portable instrumentation for hydrazines sensing. A similar approach has been taken in this program for the development of instrumentation capable of sensing in real-time at the ppb level.

In summary, the following tasks were completed within the scope of this work:

TASK I	Development of Electrode/Electrolyte/Potential conditions for the ppb level Hydrazine Sensing Reaction.
TASK II	Development of the Electrochemical Cell Design.
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TASK IV	Complete Design of Instrument Hardware.
TASK V	Fabrication and Evaluation Testing of Hydrazine Instrument.
TASK VI	Evaluation of Instrument Calibration and Hydrazine Handling Techniques for low Concentration (ppb) of Hydrazine.
TASK VII	Delivery of Instrumentation and Documentation.

The design and performance goals for the portable PPB instrumentation for MMH are given in Table I and Table II respectively.

The following report discusses the effort necessary to meet these instrument design objectives and successfully complete the major tasks of this work.

II. EXPERIMENTAL

The fundamental design of these instruments include an electrochemical cell as the vapor detector. A complete description of this technique has been reported (10, 11) and therefore only a summary of the experimental techniques used for development of the instrumentation is discussed here.

TABLE I

DESIGN GOALS
PORTABLE HYPERGOLIC VAPOR DETECTION INSTRUMENT

	GOAL
INSTRUMENT TYPE:	Portable, Single Readout of Hydrazine Vapor Conc. in Air.
SPECIFICITY	Sensor responds to all Hydrazine types (H, MMH and UDMH), but need not differentiate between them.
RANGE:	0-2 PPM with 1 PPB resolution.
SENSITIVITY:	0.05 PPM minimum detectable conc. readable to ± 1 PPB.
TEMPERATURE RANGE:	0-40°C.
RELATIVE HUMIDITY:	10-95%.
DIMENSIONS (Maximum):	8" x 8" x 16".
WEIGHT:	< 12 lbs.
READOUT:	Digital, readable in sunlight 3 digit resolution. Also provide a recorder output.
CONSTRUCTION:	Ruggedized, hazard proofed, insensitive to changes in position.
POWER:	Battery, 8 hours continuous, with provision for 105-125V AC power/recharge jack.
ALARM:	Audible alarm and light alarm, adjustable trigger level.

TABLE II

INSTRUMENT PERFORMANCE GOALS

	GOAL
RESPONSE TIME (to 90% of reading change at 0.1 PPM or above):	30 seconds
ACCURACY (at 0.1 PPM or above):	± 10%
PRECISION:	± 1% F.S.
ZERO DRIFT:	< 1% F.S. per day
SPAN DRIFT:	< 1% F.S. per day
NOISE:	± 1% F.S. per day
INTERFERENCES:	The following gases will give the interference ratio shown or greater:
GAS	INTERFERENCE RATIO GOAL
NH_3	100:1
NO_2	100:1
FREON	1,000:1
CO	1,000:1
N_2, O_2, H_2, Ar, He, CH_4 and CO_2	No Response

A schematic diagram of the electrochemical sensor design is shown in Figure 1. The three electrodes are all Teflon-bonded diffusion electrodes prepared by fabricating the catalyst onto a hydrophobic Teflon film. The platinum and gold catalyst used were of high purity. These electrodes were sealed inside a polypropylene chamber which was subsequently filled with electrolyte. The alkaline gel electrolyte was prepared from reagent grade materials and distilled water.

Gold and platinum leads from the sensor electrodes were attached to a potentiostat (Figure 2) and hydrazine sensing electrodes were potentiostatically controlled at 0.000 V with respect to the Pt/Air reference electrode. The reference electrode, Pt/Air was stable to ± 0.01V at approximately 1.0 ± .010V in basic electrolyte with respect to the normal hydrogen electrode.

The hydrazine cells used 0.25% gel, 23% KOH solution as electrolyte. During sensor evaluation, hydrazine mixtures were passed over the back (gas) side of the sensing electrode at constant flowrate, typically 400 cc/min. and the current produced by electrochemical reaction in the sensor flowing between the sensing and counter electrodes was monitored. The sensors currents were measured by monitoring the voltage drop across a precision resistor (typically 1K) in series with the sensing electrode and displaying this voltage on a LCD. Background currents were measured for the sensor in a 'static' condition (no gas flow through the sensor) and in a dynamic vs "steady state" condition, i.e., with a constant gas flow of Zero grade air (79% N_2, 21% O_2) through the sensor. Signals for the various gas mixtures (< 2 ppm MMH) were obtained directly from the permeation device gas outlet or from a sample bag for higher MMH concentrations by using an air sampling pump, drawing the gas into the sensor at flowrates which were constant for each analysis. In this manner the sensor signal (current) was measured as the difference in sensor output at steady-state between zero air and the pollutant gas mixture.

FIGURE I SCHEMATIC OF ELECTROCHEMICAL SENSOR

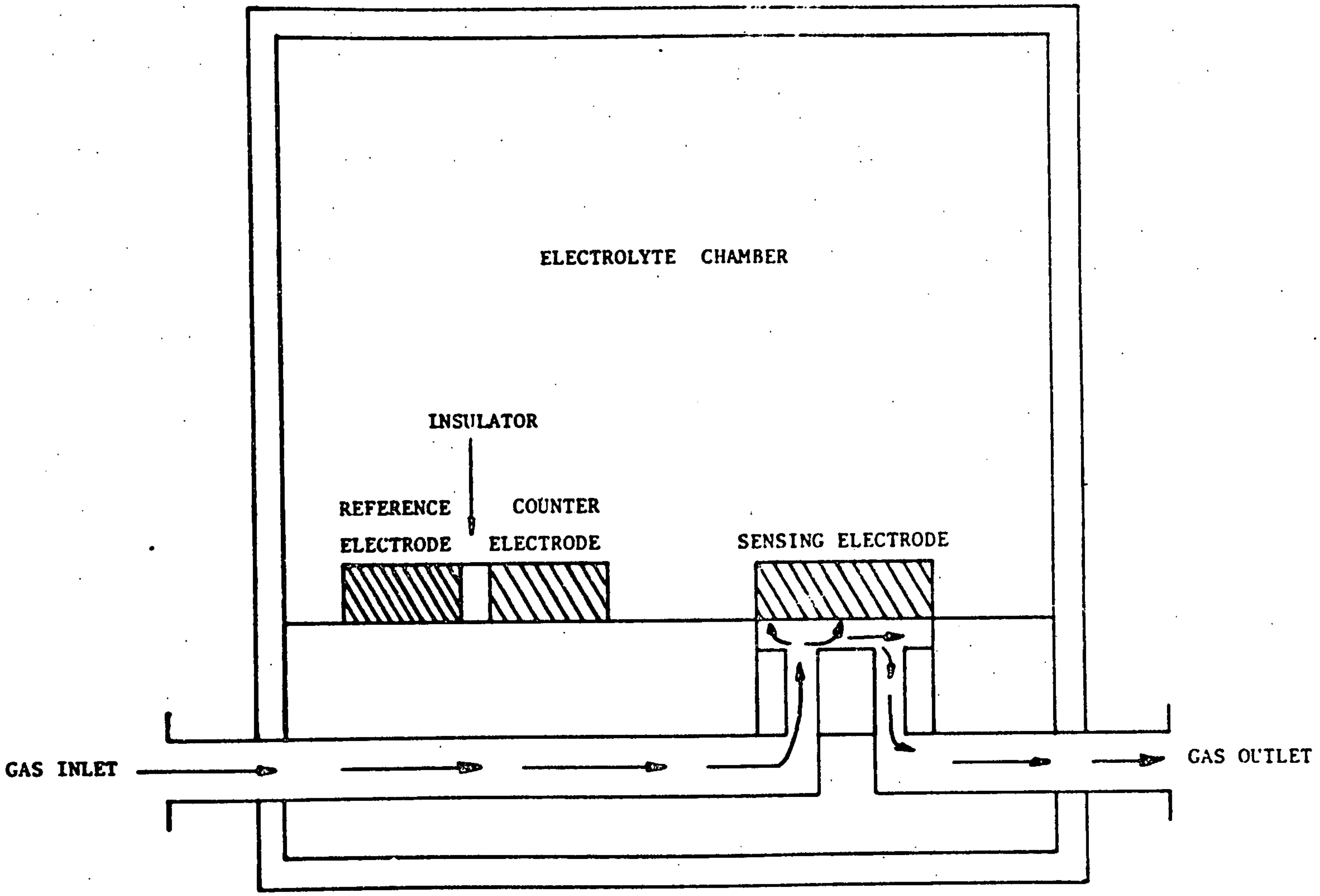
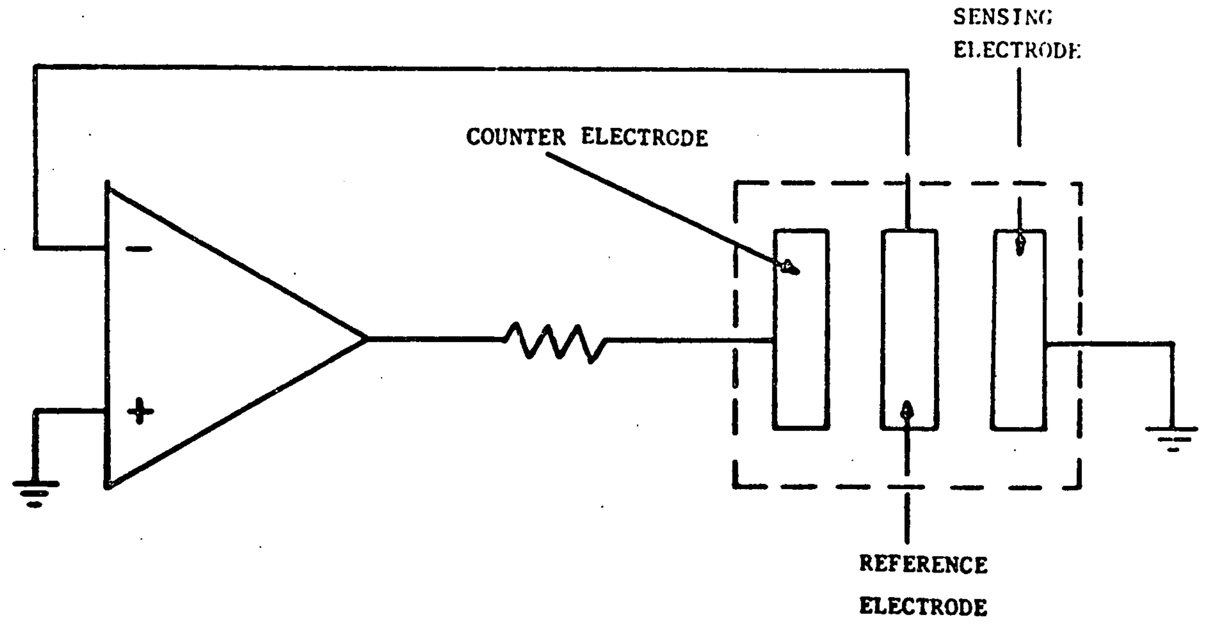


FIGURE 2 POTENTIOSTAT AND SENSOR ELECTRODES



A permeation tube calibration system (Model 670 Kin-Tek Precision Calibration System) was used for continuous generation of hydrazines vapor mixtures between 0.010 PPM and 2.000 PPM, The system operates by maintaining a constant temperature at which a permeation tube emits a known weight of the vapor at a constant rate into a diluent stream of 99.9998% N_2. N_2 was most frequently used as the diluent since hydrazines vapors were found to be more stable in N_2 than air.

A controlled flow of the diluent gas passes through a preheating chamber which is used to warm the gas to the same temperature at which the tube is thermostatted. It then passes through the permeation tube glass chamber where it picks up and mixes with the vapor. The blended vapor then exits the system and is connected directly to the analyzer via a manifold which allows venting of excess calibration gas through a scrubber. By the temperature control, number of permeation tubes used, and by adjusting the flowrate of diluent gas, a variety of mixtures from 10 ppb - 2000 ppb can be generated. For a detailed procedure for the set up and operation of the permeation tube calibration system, See Appendix I.

The dynamic dilution apparatus as described in a previous report (11) was used to synthesize high concentrations (> 2 ppm) mixtures of Hydrazine, MMH and UDMH in both N_2 and Air. For a detailed procedure for the operation of the dilution apparatus, See Appendix II. Whenever possible available standard gas mixtures were obtained, for NO/N_2, NO_2/Air, H_2/Air, CO/Air, NH_3/N_2, H_2S/N_2, SO_2/Air, C_2H_4/Air, Freon-12/N_2 samples, mixtures were obtained commercially at various PPM level concentrations, while CO_2, N_2, O_2 and Air were obtained as pure gases.

The permeation tube method of preparation of low concentration of hydrazines was evaluated for its reliability by comparison with the established specific colorimetric method. Vapors emitted from the permeation tube at 60°C were collected for 2 hours into a midget impinger. Hydrazine vapors were collected in 0.1N HCl, MMH vapors in 0.1N H_2SO_4 and UDMH vapors in a Citric Acid/Na_2 HPO_4 buffer solution. As the detailed procedures have been reported previously (11), only a brief summary will be described here. For the detailed procedures, See Appendix III, A,B,C.

The analyses of aqueous samples of hydrazine and MMH involves the reaction with p-dimethyl aminobenzaldehyde to form a yellow dye, for UDMH, reaction with trisodium-dimethylaminopentacyanoferrate to form a red solution. The concentrations of the hydrazines were determined colorimetrically at a wavelength of 457 nm for N_2H_4 and MMH, and at 500 nm for UDMH. Standard solutions of H, MMH and UDMH were prepared gravimetrically from the appropriate salts of the hydrazine compounds. Calculation of the emission rate in nanograms per minute from the colorimetry yields results in excellent agreement with those specified by the permeation tube manufacturer.

RESULTS AND DISCUSSIONS

For the purpose of clarity, this section of the report is divided into the following sections:

A. Membrane

B. Electrolyte

C. Sensors

D. Optimum Operation Conditions
  i. Temperature Compensation
  ii. Response Time
  iii. Saturation

E. Analysis and Handling of Hypergolic Vapors

F. Prototype Instrument

A. MEMBRANE

The initial phase in the development of this instrument was the evaluation of the different types of diffusion membranes. Electrochemical cells were constructed using different types of diffusion membrane numbers EX-122, EX-Q1, EX-10 and their suitability determined. A diffusion membrane must possess the following properties in order to optimize the MMH sensors response:

a) Ruggedness, b) compatibility with electrode, c) high permeability, d) low evaporation, i.e., little water loss from the electrolyte.

An experimental sensor membrane electrode was evaluated for ruggedness by manufacturing several HF design sensors filling them with free KOH and gelled KOH, placing them at -5°C and subsequently dropping them from heights of 8 ft. None of the sensors included in this test failed due to rupture of the membrane. Increasing the dropping height to 15 ft, the EX-122 membrane electrode failed the ruggedness test and the membrane was ruptured. Further tests to evaluate the suitability of the membrane indicated that the EX-Q1 membrane gave the optimum overall performance; hence all further electrodes were made using the EX-Q1 membrane. The results on the membrane evaluation are summarized in Table III.

B. ELECTROLYTE

An electrolyte must possess the following properties to be useful in our ppb level MMH detection sensor: a) stability - biological, chemical, b) compatibility with electrode, c) non reactivity at potential employed, d) conductivity.

In the initial phase of this program, ten electrolytes were prepared and evaluated as potential electrolytes for the sensor system. A special conductivity cell was constructed for evaluation of the electrolytes. Their contribution to the electrochemical cell conductivity was measured using a YSI Model 31 conductivity bridge. All chemicals were reagent grade where possible and all solutions

TABLE III

EVALUATION OF MEMBRANE PERFORMANCE

TYPE (ZITEX)	TENSILE STRENGTH (lbs/inch width)	µA/PPM MMH	WT. LOSS on 0% RH (GRAM/DAY)
G-Q1	3.1 - 4.1	12.0	0.60
G-10	5 - 6	6.0	0.30
606-122	.6 - 1.2	8.0	0.86

were made using triply distilled water. Table IV shows the approximate contributions using a Model 6956 type electrochemical cell of various electrolytes to the overall cell impedance. Halide salts were not stable for even short periods but K_2CO_3, $KHCO_3$, and the usual KOH exhibited the most promising behavior.

These electrolytes were further tested for selectivity towards MMH detection. KOH exhibited the most favorable behavior in terms of signal stability and specificity towards MMH. K_2CO_3 electrolyte does not offer good selectivity with respect to NO, NO_2, NH_3 or SO_2, and signals obtained for MMH with H_2SO_4 electrolyte deteriorated to less than 10% of their initial value within 24 hours. Table V summarizes the electrolyte evaluation in terms of signal stability and specificity towards MMH.

In order to develop attitude insensitive HF design sensors, gelled KOH electrolytes were used. These sensors were evaluated by operating them in various positions while sampling MMH. No change in signal magnitude or response characteristics were observed over the 15 minute sampling period used in the experiments. The short term stability of two 10% KOH gel sensors was determined after one month of intermittent use. MMH signals did not change appreciably but response times and selectivity improved with time as shown in Table VI.

However, in continuous monitoring for 8 hours, the sensor with 10% KOH, 2% gel electrolyte lost its sensitivity due to 'skin' formation on the electrode surface. This is mainly due to the drying up of the gel at the electrode which then causes the conductivity between the electrode and electrolyte to drop significantly. In order to bypass this evaporation problem, a 23% KOH with 0.25% gel electrolyte was used. Its 'superior' improvement as referenced to long-term stability is indicated in Table VII. For approximately 100 hours of continuous monitoring, the MMH signal has only varied by less than 10%. From the long-term stability under continuous use and its attitude insensitive response, the 23% KOH with 0.25% gel was chosen to be the electrolyte used for the ppb MMH analyzer.

TABLE IV

EVALUATION OF ELECTROLYTE IMPEDANCE

ELECTROLYTE	CONTRIBUTION TO THE IMPEDANCE OF A MODEL 6956 ELECTROCHEMICAL CELL - OHMS -
5.0 N KOH	< 2
1.0 N KCL	15
2.0 N H_3BO_3	2100
1.0 N KBr	15
1.0 N NaCl	20
1.0 N K_2CO_3	21
1.0 N LiCl	24
0.4 N $Na_2B_4O_2$	87.4
1.0 N KNO_3	19
1.0 N $NaNO_3$	23
1.0 N $NaNO_2$	22

TABLE V

ELECTROLYTE EVALUATION ON H.P. GOLD @ 0.000 VOLTS VS. Pt/AIR REFERENCE

	23% KOH	20% K_2CO_3	28% H_2SO_4
GAS	SIGNAL OR INTERFERENCE EQUIV.	SIGNAL OR INTERFERENCE EQUIV.	SIGNAL OR INTERFERENCE EQUIV.
Zero Air (Static)	0.1 µA	1.8 µA	0 µA
Zero Air (Dynamic)	0.1 µA	1.8 µA	0 µA
N_2	0.1 µA	1.8 µA	0 µA
0.15 ppm MMH	11.8 µA/ppm	4.7 µA/ppm	*3.3 µA/ppm
1000 ppm CO	15,500:1	25,253:1	NONE DETECTED
12 ppm NO_2	1,200:-1	193:-1	233:-1
50 ppm NH_3	3,278:1	332:1	2,081:1
23.5 ppm NO	NONE DETECTED	4.3:1	65:1
20.5 ppm SO_2	NONE DETECTED	0.3:1	6:1

* MMH signal drops to 0.1 µA/ppm after 24 hours.

TABLE VI

STABILITY OF 10% KOH, 2% GEL ELECTROLYTE

GAS	EHPG-1		MHPG-2	
	SIGNAL OR INTERFERENCE EQUIV.		SIGNAL OR INTERFERENCE EQUIV.*	
	3-19	4-19	3-19	4-19
Zero Air (Static)	0.9 µA	0 µA	0.2 µA	0 µA
Zero Air (Dynamic)	0.9 µA	0 µA	0.2 µA	0 µA
N_2	0.9 µA	0 µA	0.2 µA	0 µA
0.15 ppm MMH	6.7 µA/ppm	7.5 µA/ppm	3.7 µA/ppm	3.5 µA/ppm
1040 ppm CO	5,098:1	16,250:1	5,728:1	20,222:1
38.4 ppm NO_2	927:-1	1,309:-1	939:-1	1,315:-1
50 ppm NH_3	303:1	5,357:1	141:1	2,188:1
23.5 ppm NO	NOT DETECTED	NOT DETECTED	288:1	NOT DETECTED
20.5 ppm SO_2	350:1	NOT DETECTED	NOT DETECTED	NOT DETECTED
[illegible]0 ppm Freon-12	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
50% CO_2	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED
2931 ppm H_2	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED

	TIME TO 90% SIGNAL		TIME TO 90% SIGNAL	
	3-19	4-19	3-19	4-19
0.15 ppm MMH	180 Sec.	80 Sec.	220 Sec.	105 Sec.

* Intermittent use for 1 Month @ 0.000 Volts vs. Pt/Air Reference

TABLE VII

LONG TERM ZERO AND SPAN STABILITY TOWARDS MMH USING 23% KOH, .25% GEL AS ELECTROLYTE

HOURS	ZERO (DRIFT) (ppb)	LCD DISPLAY MMH (ppb)
0	0	291
24	13	322
48	4	295
96	8	290

C. SENSORS

In the initial phase of this program several types of experimental electrode materials were fabricated and tested for improved background and signal specificity characteristics. Table VIII summarizes the performance of these cells. Rhodium, nickel and silver electrodes did not exhibit good selectivity towards NO_2. Further, the high µA/ppm MMH signal, high signal to background ratio, ease of fabrication, and extensive prior experience with the gold electrode, lead us to choose gold as the electrode material.

Gold Electrodes

Two types of gold electrodes were used to test electrode performance, namely, standard (as in previous sensors) (10,11) and high purity. Table IX shows the results of these cells, one with a standard Au electrode and two experimental electrodes of high purity Au. The two high-purity gold experimental cells were more selective under the experimental conditions then corresponding standard gold electrode as indicated by their much larger interference ratios for CO, NO_2, and NO. To determine if the selectivity ratio observed with the high purity gold electrode is reproducible, several samples of the experimental high purity Au used for the experiment were prepared. Results are summarized in Table X for an electrode potentiostated at 0.00V vs the Pt/Air reference electrode. Excellent selectivity is again observed for all gases except H_2S, which always gave an equivalent signal to MMH.

Since high purity gold electrodes fabricated onto a rugged Teflon membrane have been established to offer the most promising results for use as ppb level MMH sensors, later efforts have been placed on optimization of this system. In an attempt to improve the response characteristics of the electrochemical sensor towards low level hydrazine detection, a study of the effect of the catalyst loading was undertaken with special emphasis upon response time. Electrode catalyst loadings of

TABLE VIII

EVALUATION OF DIFFERENT TYPES OF ELECTRODES MATERIALS FOR SENSOR PERFORMANCE

Electrolyte: 23% KOH
Potential (vs Pt/Air): 0.000V

GAS/VAPOR CONCENTRATION TESTED	ELECTRODE MATERIAL: Ni	Rhodium	Gold	Silver
7.0 ppm MMH/N_2 (µA/ppm)	6.97	14.79	15.7	2.2
Zero Air Static (µA)	9.6	13.5	-0.8	7.2
Zero Air Dynamic (µA)	9.4	12.0	---	---
Pure N_2 (µA)	9.2	15.5	2.4	7.2
50 ppm NH_3 (ppm:MMH)	NOT DETECTED	135:1	13.6:1	55:1
1000 ppm CO	NOT DETECTED	1842:1	303:1	2157:1
40 ppm NO_2	-3:1	-4.5:1	-8.3:1	-6.9:1
26 ppm H_2S/N_2	0.67:1	1.1:1	0.98:1	---
23.5 ppm NO/N_2	NOT DETECTED	37:1	180:1	---
20.5 ppm SO_2/N_2	NOT DETECTED	5.5:1	386:1	---
Rise Time (90% at 7 ppm MMH)	12 sec.	81 sec.	9-11 sec	---

TABLE IX

ELECTROCHEMICAL CHARACTERISTICS OF STANDARD AND HIGH PURITY GOLD ELECTRODE SENSOR

CELL SIGNALS[1]

GAS/VAPOR CONCENTRATION TESTED	Au-1[2]	Au-2[3]	Au-3[4]
	BIAS MV 0.00	BIAS MV 0.00	BIAS MV 0.00
7.0 ppm MMH/N_2 µA/ppm	15.7	1.9	8.5
ZERO AIR - µA	-0.8	1.3	0.52
PURE N_2^- - µA	+2.4	1.3	0.51
50 PPM NH_3/N_2	13.6:1	32:1	64:1
1000 ppm CO/Air	303:1	94,500:1	47,333:1
40 ppm NO_2/Air	-8.3:1	-1,454:1	-1,639:1
8 ppm NO/N_2	180:1	NO SIGNAL	NO SIGNAL
25 ppm SO_2/Air	386:1	33:1	NO SIGNAL
25 ppm H_2S/N_2	0.98:1	0.9:1	1.6:1

[1] ALL THE RATIOS IN THE TABLE ARE: PPM GAS/PPM MMH

[2] Au-1 = Membrane: 606-122, Electrode: STD. Au

[3] Au-2 = Membrane: 606-122, Electrode: EXP-HP-Au

[4] Au-3 = Membrane: 606-123, Electrode: EXP-HP-Au

TABLE X

PERFORMANCE OF A HIGH PURITY GOLD WORKING ELECTRODE (EXP-EHP-1) SENSOR

GAS	SIGNAL OR INTERFERENCE RATIO		TIME TO 90% RISE
Zero Air (Static)	3.3 µA	(-0.5)[1]	
Zero Air (Dynamic)	3.4 µA	---	
7 ppm MMH	7 ppm		10.5 Sec
0.15 ppm MMH	0.15 ppm		150 Sec
206 ppm CO	14,237:1	(12500:1)[1]	
23.5 ppm NO	219:1	(not detected)[1]	
38.4 ppm NO_2	-1,196:1	(1450:1)[1]	
50 ppm NH_3	142:1	(945:1)[1]	
20.5 ppm SO_2	18:1	(not detected)[1]	
26 ppm H_2S	0.8:1	------------	
1160 ppm Freon	----	(not detected)[1]	
50% CO_2	----	(not detected)[1]	
2931 ppm H_2	----	(not detected)[1]	

1) Performed at potential 150 mV lower.

1.2, 2.5 and 5.0 mg/cm^2 were evaluated. The results in Table XI indicate that the response to 1.1 ppm MMH was optimized at 45 seconds to 90% with 2.5 mg/cm^2 catalyst loadings.

To further establish the optimum operating conditions for the high purity gold electrode, the electrochemical specificity was studied as a function of potential settings. Table XII is a summary of the results based on the typical response of eight sensors. Optimum specificity is obtained at a potential of 0.000 Volts vs the Pt/Air reference in our gel electrolyte. This potential has then been selected for use in all subsequent prototype instrumentation testings.

In order to improve the sensors' lifetime, i.e., minimize the rate of evaporation, and to improve the response characteristics of the electrochemical sensor, a new configuration of the electrodes is employed. Figure I illustrates the new configuration. This new configuration minimizes the distance between electrodes and therefore maximizes response parameters. In addition, the new sensor configurations will be virtually attitude insensitive. It is also observed that improved response characteristics are obtained when the sample is pulled through the sensor and plumbing before the sensor is as short as possible. (See Table XIII for results). Figure 3 is a modified flow diagram of the flow scheme which is incorporated into the final instrument design.

The steady-state current response of the high purity gold electrode was measured at various flowrates between 0 and 700 cc/min for MMH/N_2 for two different electrode sizes. Results are summarized in Table XIV and shown in Figure 4. It is observed that the sensitivity of the device diminishes rapidly at flowrates below 400 ml/min as does the instrument response time, (See Table XV and Figure 5), therefore, 400 ml/min was selected as the operating flow of the instrument.

TABLE XI

ELECTRODE LOADING STUDY
0.000 VOLTS vs Pt/Air REFERENCE IN GEL ELECTROLYTE

GAS	1.2 mg/cm² SIGNAL OR INTERFERENCE EQUIVALENT	2.5 mg/cm² SIGNAL OR INTERFERENCE EQUIVALENT	5.0 mg/cm² SIGNAL OR INTERFERENCE EQUIVALENT
ZERO (STATIC)	0.05 µA	0.10 µA	0.90 µA
ZERO (DYNAMIC)	0.10 µA	0.20 µA	0.45 µA
N_2	0.20 µA	0.50 µA	1.00 µA
1.1 ppm MMH	14.3 µA/ppm	12.89 µA/ppm	16.56 µA/ppm
1040 ppm CO	28,000:1	15,917:1	9,383:1
9 ppm NO_2	315:-1	659:-1	928:-1
23.5 ppm NO	NOT DETECTED	NOT DETECTED	NOT DETECTED
50 ppm NH_3	3,750:1	1,684:1	358:1
21.5 ppm SO_2	NOT DETECTED	NOT DETECTED	231:1
RESPONSE TO 90%	75 SEC.	45 SEC.	90 SEC.

TABLE XII

SPECIFICITY AS A FUNCTION OF ELECTRODE POTENTIAL*

GAS	-0.200 VOLTS SIGNAL OR INTERFERENCE EQUIVALENT	-0.100 VOLTS SIGNAL OR INTERFERENCE EQUIVALENT	0.000 VOLTS SIGNAL OR INTERFERENCE EQUIVALENT	+0.100 VOLTS SIGNAL OR INTERFERENCE EQUIVALENT	+ 0.200 VOLTS SIGNAL OR INTERFERENCE EQUIVALENT
ZERO (STATIC)	- 2.08 µA	- 0.30 µA	0.01 µA	0.55 µA	1.08 µA
ZERO (DYNAMIC)	- 2.20 µA	- 0.30 µA	0.03 µA	0.59 µA	1.24 µA
N_2	- 0.80 µA	- 0.20 µA	0.17 µA	0.69 µA	1.34 µA
1.10 PPM MMH	9.63 µA/ ppm	13.97 µA/ ppm	15.96 µA/ ppm	18.21 µA/ ppm	13.43 µA/ ppm
1040 PPM CO	79,561:1	64,961:1	35,519:1	57,016:1	61,602:1
9[illegible]PM NO_2	102:-1	367:-1	1,460:-1	9,019:-1	NOT DETECTED
50 PPM NH_3	NOT DETECTED	31,475:1	4,187:1	533:1	1,398:1
23.5 PPM NO	NOT DETECTED	NOT DETECTED	NOT DETECTED	463:1	101:1
21.5 PPM SO_2	NOT DETECTED	NOT DETECTED	NOT DETECTED	74:1	11:1

* Potentials are listed with respect to the Pt/Air reference electrode.

FIGURE I SCHEMATIC OF ELECTROCHEMICAL SENSOR

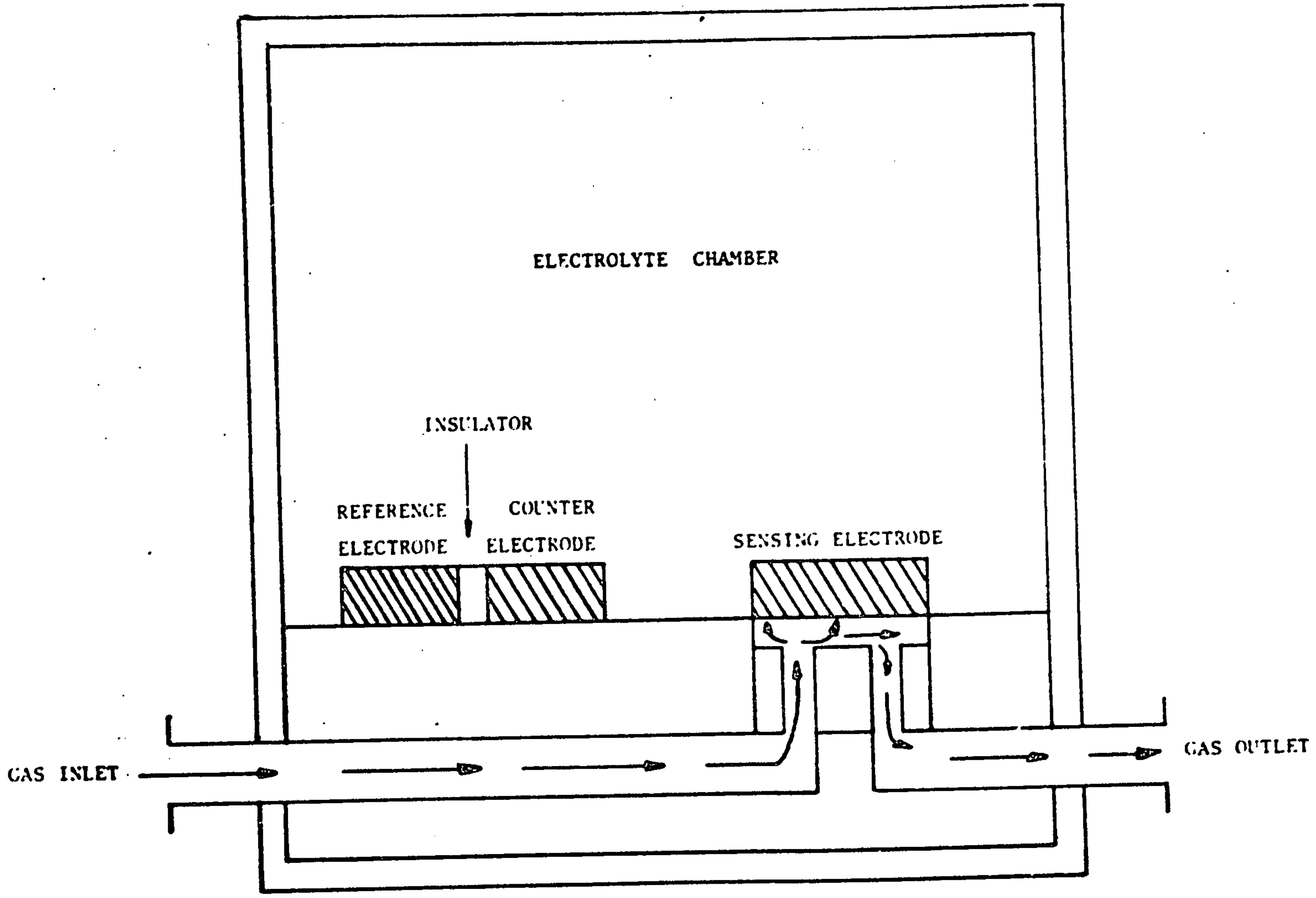


TABLE XIII

EFFECT OF FLOW SCHEME ON INSTRUMENT RESPONSE

FLOW SCHEME	1st 100 ppb MMH SAMPLE	2nd 100 ppb MMH SAMPLE
Push thru sensor (Pump before)	> 600 seconds	150 seconds
Pull thru sensor (Pump after)	130 seconds	95 seconds

(All response times noted are as time to 90% of final signal).

FIGURE 3 FLOW DIAGRAM FOR THE TOXIC LEVEL INSTRUMENT

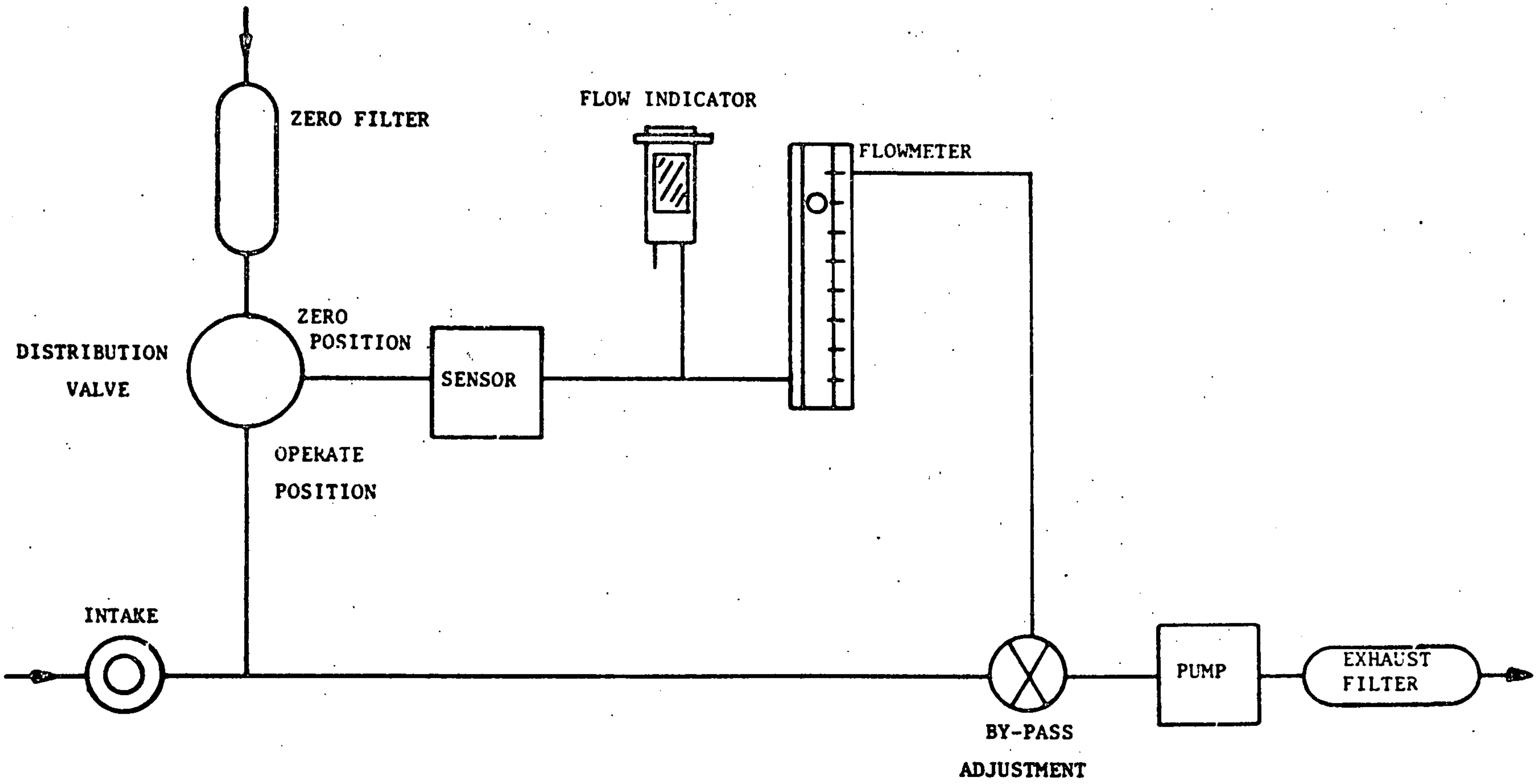


TABLE XIV

HYDRAZINE SENSOR RESPONSE MAGNITUDE AT VARIOUS FLOWRATES

	ELECTRODE GEOMETRIC AREA	
FLOWRATE	0.50 cm^2	1.33 cm^2
(cc/min)	(μA/PPM)*	(μA/PPM)*
50	2.0	4.2
100	2.2	5.9
200	2.5	6.7
400	2.6	8.6
700	2.8	9.5
Response Time (90% Rise)	72 Sec.	105 Sec.

Electrode: High Purity Gold.

Electrolyte: 10% KOH, 2% Gel.

* Average of two separate measurements.

FIGURE 4 HYDRAZINE SENSOR RESPONSE AT VARIOUS FLOWRATES

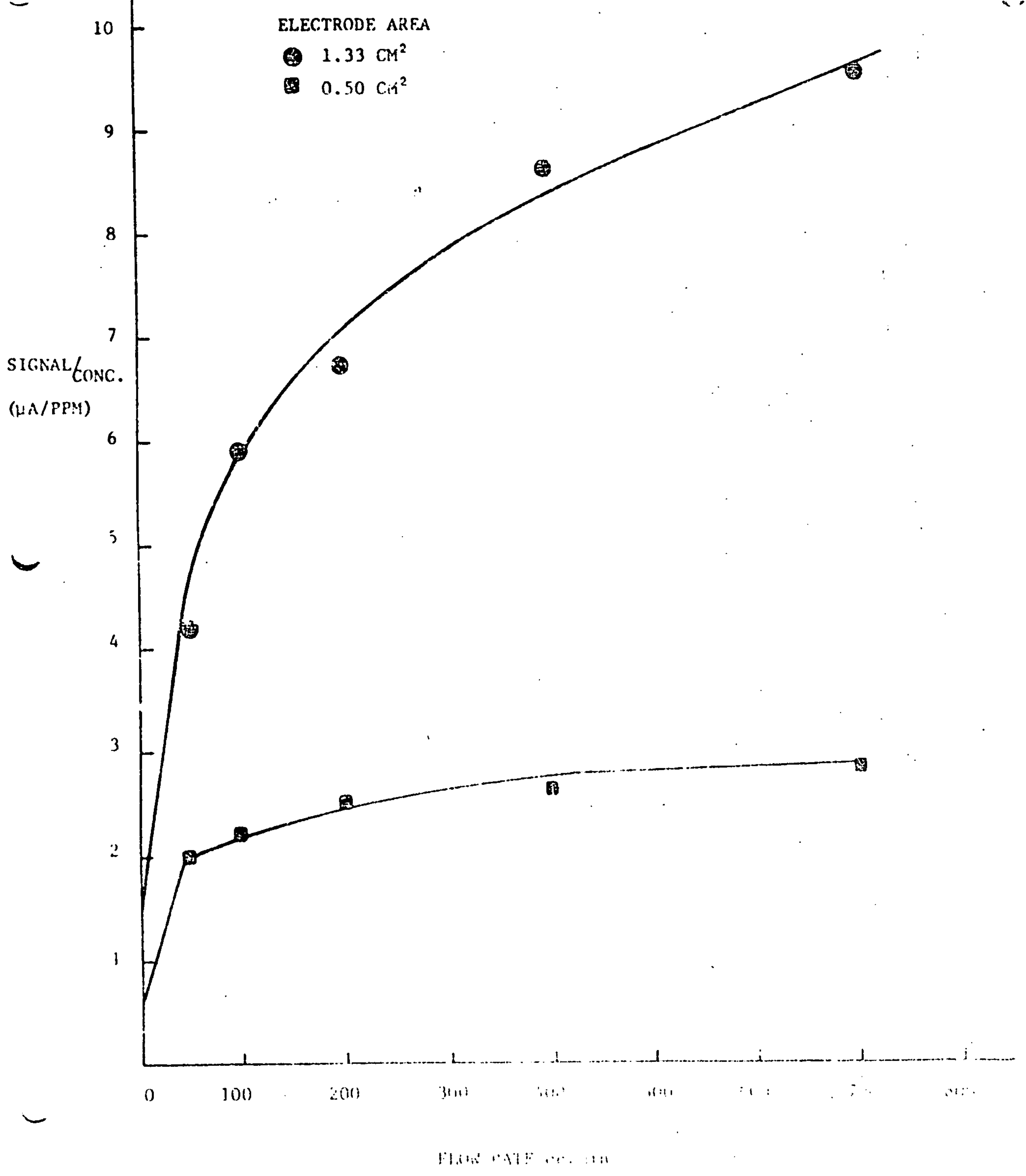
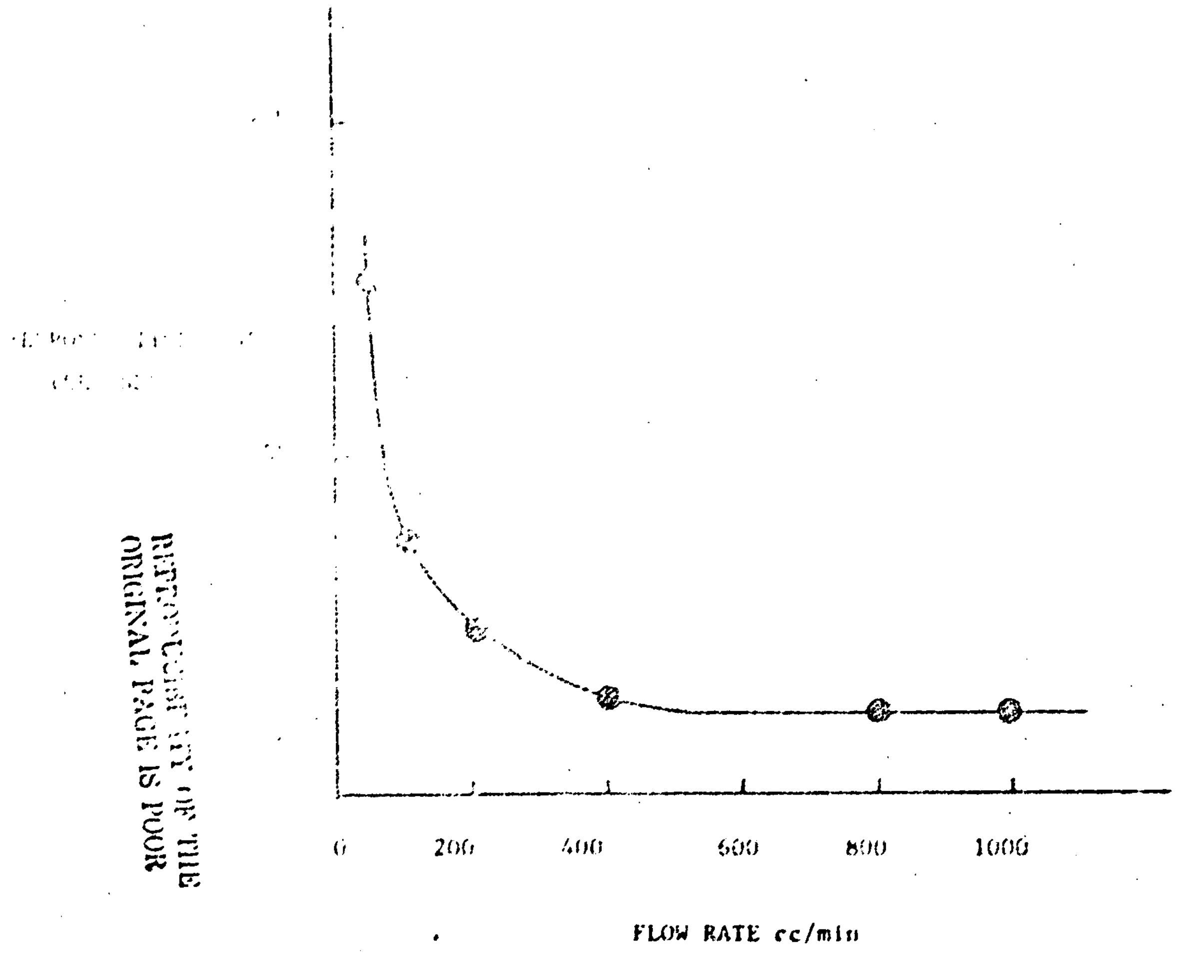


TABLE XV

HYDRAZINE SENSOR RESPONSE TIME AT VARIOUS FLOWRATES

FLOWRATE (cc/min)	SIGNAL (μA)	RESPONSE TIME (90% RISE)
50	28.2	76
100	39.1	37.5
200	48.2	24
400	56.3	14
800	61.4	12
1000	62.4	12

FIGURE [illegible] HYDRAZINE SENSOR RESPONSE TIME AT VARIOUS FLOWRATES



In order for this device to be useful for field measurements the instrument must be able to possess environmental stability. That is, the instrument must retain its sensitivity and accuracy over long periods of time and exhibit minimum sensitivity to fluctuations in ambient conditions. The zero and span drift of a typical ppb level MMH analyzer was monitored over a 23 test day period and the results are summarized in Figure 6. For breadboard instrument prototype, the zero and span was monitored intermittently for the first 12 days, both zero and span drift by no more than ± .02 ppm. At day 15, the instrument was put on continuous testing for zero and span drift, after 72 hours of continuous monitoring, again the zero and span did not drift by more than ± .02 ppm for MMH concentration of .288 ppm. Short term fluctuations have not been monitored in this experiment but the short term effects of the instrument zero can always be minimized by adjusting the instrument zero immediately prior to measurements by admitting a sample of pure air or switching valve to zero position to remove the electrochemically active gases from the inflowing sample.

D. OPTIMUM OPERATION CONDITIONS

1. Temperature Compensation

A Tenney Environmental Chamber was used to evaluate performance as a function of temperature.

The first breadboard prototype model ppb level hydrazine analyzer based on the electrochemical oxidation of the vapor was evaluated for the effects of temperature over the range of 0 to 40°C. The sensor and instrument output were monitored using 0, 0.23 and 0.66 ppm of MMH. When cycled between 25°C and 40°C zero shifted up 0.023 ppm and span was 5% higher with both concentrations tested. When cycled between 25°C and 0°C zero shifted down 0.016 ppm and span was 15% lower with both concentrations tested. After cycling, room temperature (25°C) zero was within 0.005 ppm and span was within 2% of their original values. These results indicated the need for minimal electronic temperature compensation in this instrument, (See Figure 7). However after further development of the sensor, this experiment was repeated and different re

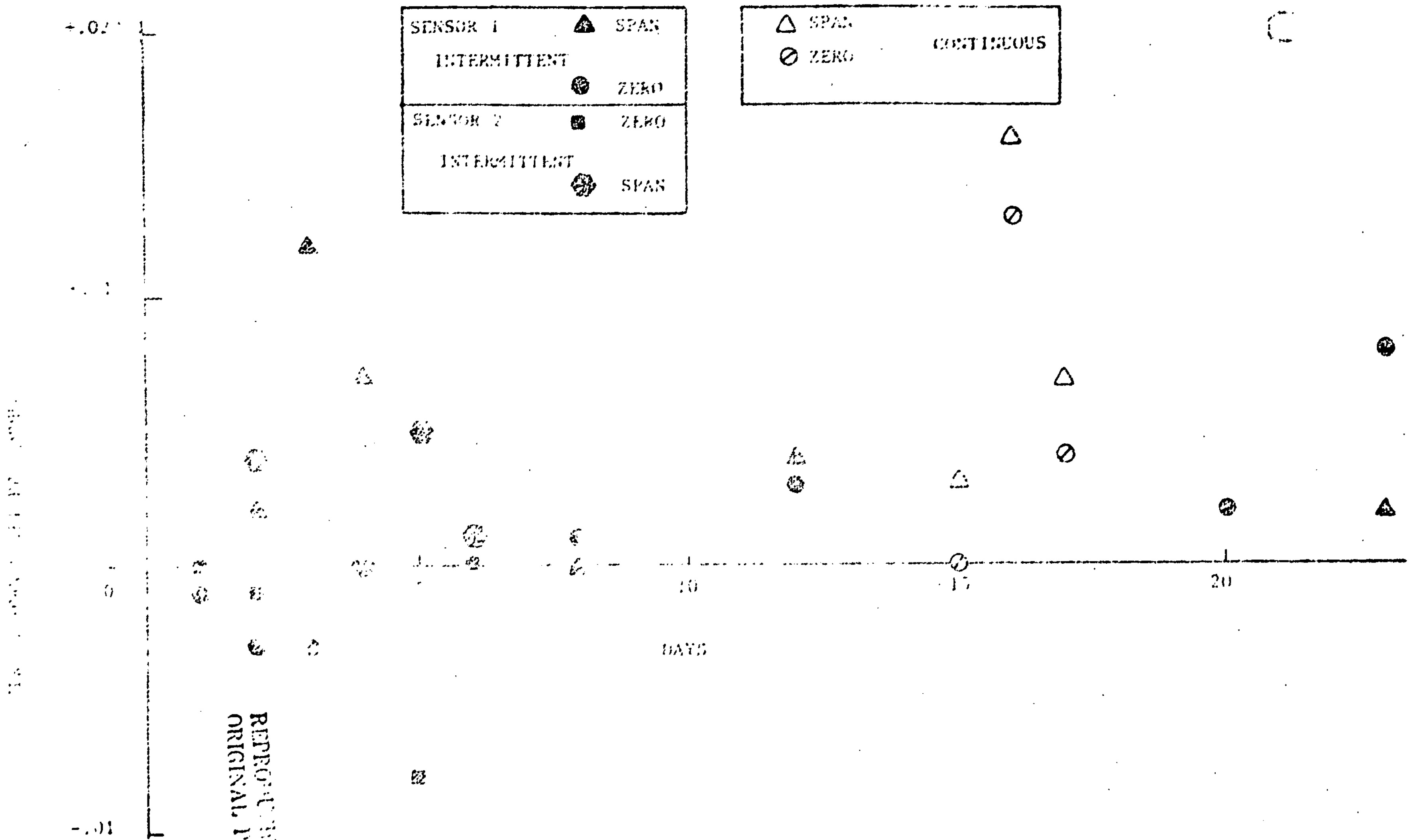
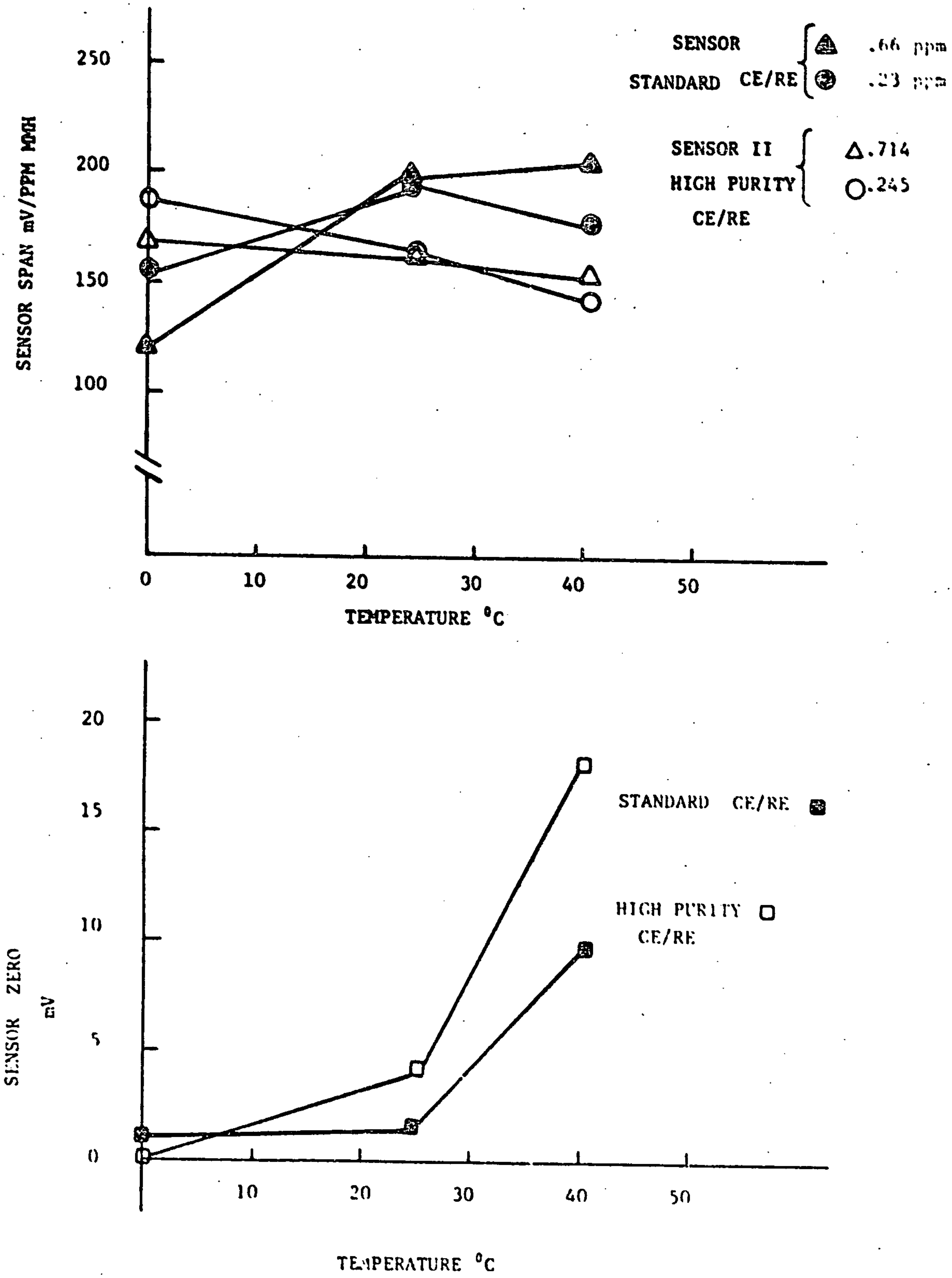


FIGURE 6 LONG TERM INSTRUMENT ZERO AND SPAN DRIFT MEASURED WITH FILTERED LABORATORY AIR

FIGURE 7 INSTRUMENT RESPONSE MAGNITUDE AND ZERO DRIFT AT VARIOUS TEMPERATURES



sults were obtained which appears later in the text.

II. Response Time

An observation made in the course of a linearity study was that the sensor's response was more rapid to changes of 100 to 200 ppb than from 0 to 200 ppb, (See Figure 8). This indicates that changes near TLV will be detected more rapidly than would be predicted by the response time specification since it is measured as a change from zero ppm MMH. Therefore, the ability of the unit to respond to changing problem conditions is better than the response time specification would indicate. The size of the electrode also found to affect the response time (Table XIV). Response time is found to decrease with the size of the electrode; however, the signal/concentration ratio (μA/ppm) also decreased with the decrease in the electrode size, therefore a compromise of the two factors must be weighed and an optimum electrode area of 1.0 cm^2 was chosen to use with this sensor.

The response time as indicated before is also dependent on the flowrate of gas through the sensor(Figure 5.) Two mechanisms can account for the response time characteristic; (1) different rates for the establishment of steady-state conditions in the electrochemical sensor and (2) losses of sample by adsorption and/or decomposition in the sampling system prior to analysis. Losses due to adsorption and decomposition can be minimized by use of an optimum flowrate and smallest sample system volume. However even with the optimum geometry employed in the ppb MMH sensor, response times are typically in the range of 10-210 seconds for 0.100 ppm samples. Further, hydrazine has been shown to be chemically active on certain materials, therefore an inert material, Teflon or polypropylene, is used in the construction of system components that come into contact with the analyte gas stream.

FIG. 8 RESPONSE TO CHANGING CONCENTRATION (MMH)

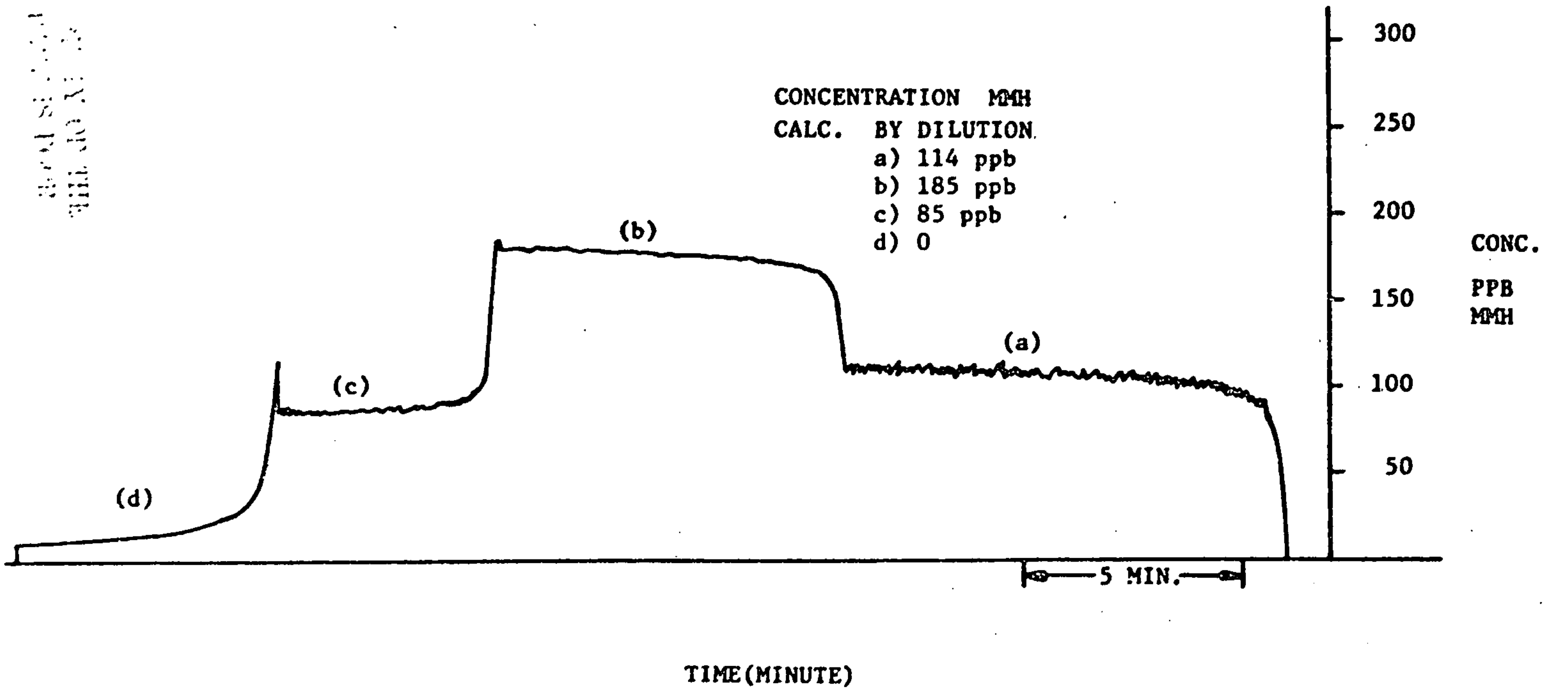


TABLE XIV

HYDRAZINE SENSOR RESPONSE MAGNITUDE AT VARIOUS FLOWRATES

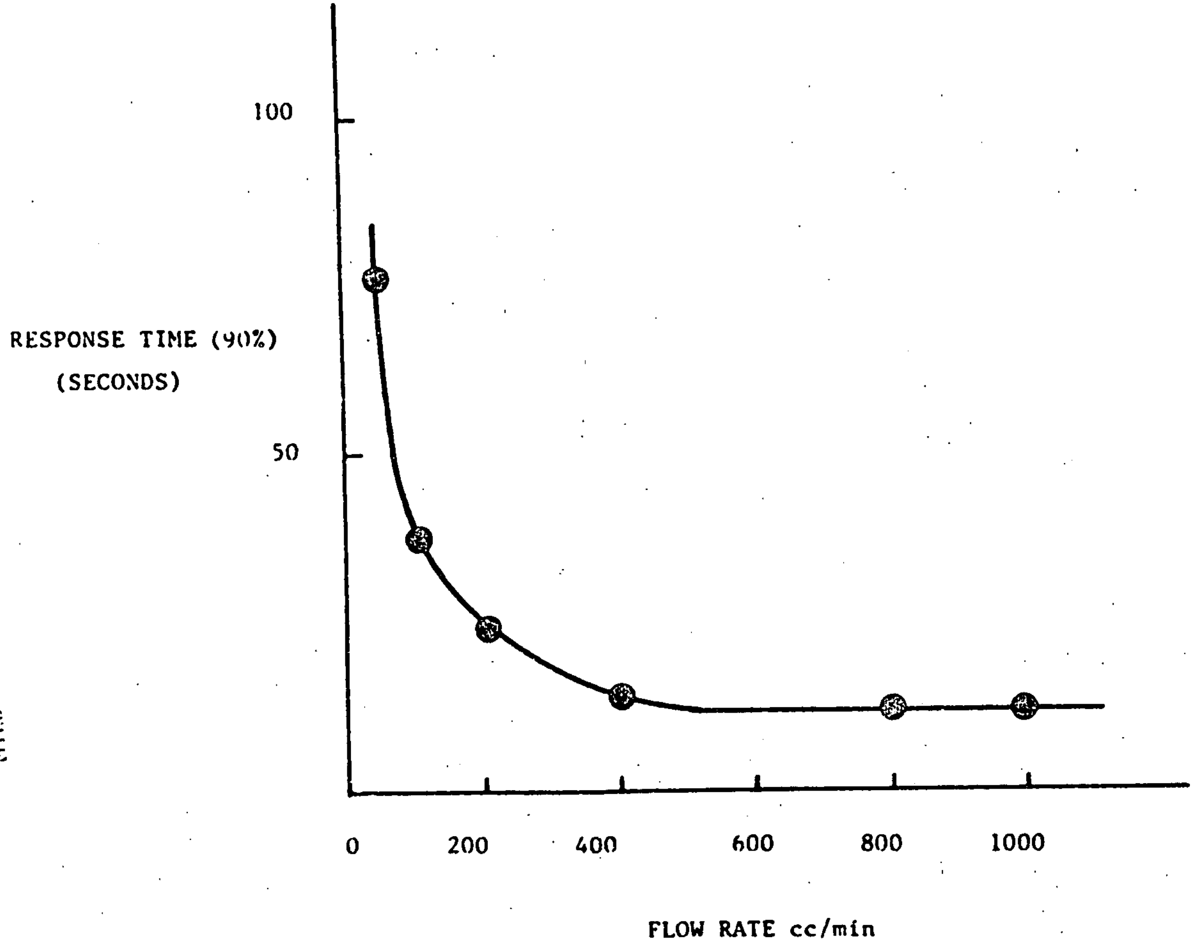
	ELECTRODE GEOMETRIC AREA	
FLOWRATE	0.50 cm^2	1.33 cm^2
(cc/min)	(μA/PPM)*	(μA/PPM)*
50	2.0	4.2
100	2.2	5.9
200	2.5	6.7
400	2.6	8.6
700	2.8	9.5
Response Time (90% Rise)	72 Sec.	105 Sec.

Electrode: High Purity Gold.

Electrolyte: 10% KOH, 2% Gel.

* Average of two separate measurements.

FIGURE 5 HYDRAZINE SENSOR RESPONSE TIME AT VARIOUS FLOWRATES



iii. Saturation

To determine the effects of saturating the analyzer with a high concentration of hydrazine, a spill was simulated by preparing a 70% N_2H_4/30% H_2O mixture in a closed vessel and drawing the vapors above the mixture into the intake of the instrument. The instrument became instantaneously saturated upon introduction of the sample and could not be used for further analysis of ppb levels of hydrazines for approximately two hours after removal of the sample. The characteristics of the instrument were the same after recovery as they were prior to its saturation, indicating that if the analyzer were exposed to a spill it could be reused with good reliability after a two hour recovery period.

The magnitude of the sensor response is dependent on the vapors concentration and the type of the vapor flow through the sensor chamber. The relative response of hydrazine, MMH and UDMH on ppb level instrument which has been calibrated with 0.288 ppm of MMH is summarized in (Table XVI).

E. ANALYSIS AND HANDLING OF HYPERGOLIC VAPORS

One of the most essential phases in the development of new technology is the development of a successful implementation scheme for the technology. In the case of the hypergolic vapors, the requirement is for laboratory calibration procedures, field functional testing and field calibration.

The calibration of the MMH analyzer requires the generation and analysis of H, MMH and UDMH vapor mixture and their analysis by a standard analytical technique. A dynamic dilution system has been described in a previous report (11) to generate vapor mixtures of hydrazine, monomethylhydrazine and unsymmetrical dimethylhydrazine. The dilution system and its operation are summarized in Appendix II.

However for ppb level hydrazines generation, the dynamic dilution system was found to be inadequate. To date the only reliable source of low level (ppb) hydrazines has been Kin-Tek's permeation tubes when used from their precision calibration system in an operating mode where the vapor passes directly into the analyzer.

TABLE XVI

THE RELATIVE INSTRUMENT RESPONSE RATIO FOR H, MMH, AND UDMH

GAS	CONC. (PPM)	SIGNAL (μA)	RATIO* (GAS:MMH)
MMH	.288	.288	1.0:1.0
H	.254	.269	.944:1.0
UDMH	.250	.108	2.315:1.0

* Ratio is defined to be the PPM of gas equivalent to the signal of 1 PPM MMH.

The permeation tube method of preparation of low concentrations of MMH was evaluated. Over seven days the device output concentration was between 1.2 and 1.8 ppm at 400 cc/min of N_2 and short term stability was much better as shown in (Table XVII). For comparison, gas emitted from the permeation tube at 60°C was collected for 2 hours into a midget impinger containing 25 ml of 0.10N H_2SO_4 and analyzed colorimetrically for MMH. Calculation of the emission rate in nanograms per minute yielded results in fair agreement with those specified by the tube manufacturer. Table XVIII shows the stability of the permeation tube over a two month period.

Utilizing the permeation tube with varied N_2 flows passing over the tube, different PPM concentrations of MMH were generated from the Kin-Tek's precision calibration system in an operating mode where the hydrazines proceeded directly into the analyzer. Five concentrations were prepared by using the thermostatted Kin-Tek permeation tube calibration system. The instrument was calibrated with a 115 ppb mixture and measurements were recorded with the more concentrated sample. Y (ppb MMH found) was fitted to the following least-squares line as a function of X (ppb MMH measured by the instrument):

$$Y = 101.9\ X + 3\ \text{ppb}$$

The standard deviation of the points from the line was only ± 2.5 ppb which includes the uncertainties in sample preparation. These results confirm the linearity of the instrument during low range MMH detection. Single point calibration is, therefore, possible without loss in accuracy (See Figure 9) in this range.

F. PROTOTYPE INSTRUMENT

With the optimum operation conditions, most sensitive sensors, and stable circuitry established, the prototype instrument was assembled. Its sensor exhibited a typical background current of 0.7 μA and a sensitivity to MMH of approximately 16 μA/ppm. This indicates a background signal equivalent to approximately 60 ppb.

TABLE XVII

SHORT TERM STABILITY OF THE PERMEATION TUBE

HOURS	400 cc/Min N_2 PPM READING ON MMH ECOLYZER SENSOR
0	---
1	1.83
2	1.87
3	1.88
4	1.88
5	1.88
10	1.89
14	1.91

TABLE XVIII

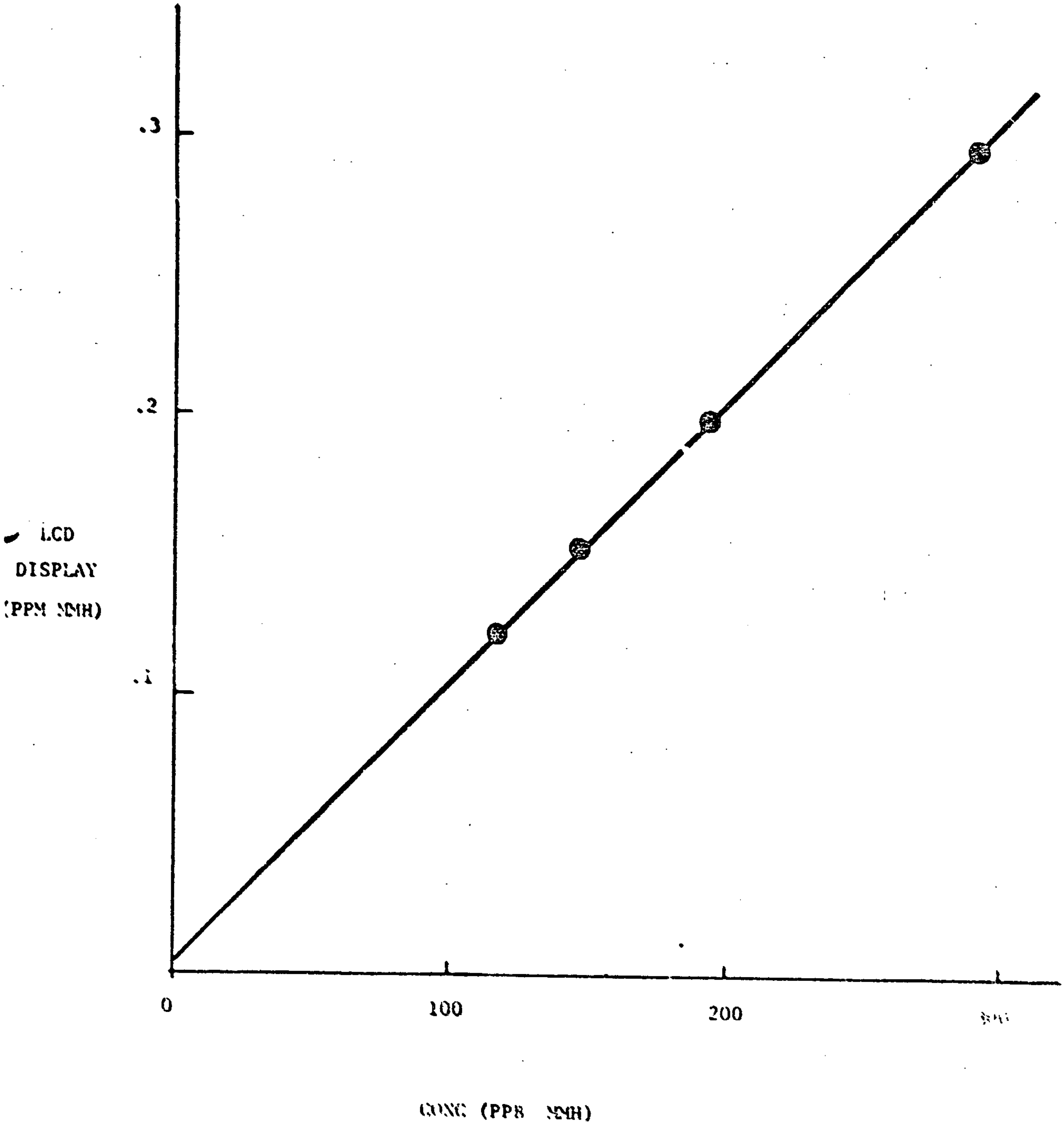
LONG TERM STABILITY OF THE PERMEATION TUBE

NO. OF DAYS	TEMPERATURE °C	[MMH] PPM	EMISSION RATE (ng/min.)
0	62	5.35	1,115
14	62	6.94	1,446
28	61	4.50	937.5
42	62	7.80	1,625
49	62	6.85	1,427
63	61	6.7	1,396

$$\text{Emission Rate (ng/min)} = \frac{\text{[MMH] PPM} \times 25{,}000}{\text{Minutes Collected}}$$

Rate as specified by manufacturer = 1,130 ng/min @ 60°C

FIGURE 9 LINEARITY OF THE MMH PPB LEVEL ANALYZER



The sensor, PEMH-0004, had a rise time of 35 seconds to 90% of signal and a decay time of 50 seconds to 90% of signal when tested at 350 ppb MMH and 400 cc min^{-1} of sample gas flow. A typical response is shown in (Figure 10) where the arrow indicates exposure of the sensor to the MMH/N$_2$ mixture and then exposure to room air. The initial signal from the sensor is nearly instantaneous while the attainment of steady-state occurs only after several minutes.

A picture of the resulting ppb level hydrazine analyzer is shown in Figure 11. By reference to Table XIX, the control functions of the instrument can be understood. The analyzer is contained in a durable metal case. All operating adjustments are mounted on the front face of the instrument. Two levels of controls to the left of the LCD display readout; the upper level contains switches for POWER and BATTERY TEST while the lower level contains FUNCTION TEST, DISPLAY ILLUMINATION and HORN ON/OFF switches. Directly above the HORN ON/OFF switch is a red ALARM LIGHT. Below the display readout are calibration adjustments for SPAN, ZERO and ALARM SET. To the right of the display readout is a multi-pin, DC powered, chart recorder connection jack. A receptacle below and to the right of the recorder jack accepts the plug from the battery charger to recharge the self-contained [illegible] power pack. At the extreme right of the front face are a two-position [illegible], the probe receptacle, and a flow indicator.

The flow adjustment and flowmeter are accessible through the bottom side of the analyzer. The left and right sides contain [illegible] the alarm horn and the exhaust outlet. The instrument was designed to [illegible] range 0-2 ppm MMH. Figure 12 illustrates how the instrument separates for service revealing the internal structure and layout. The major components from left to right contained in the top half are the Teflon sample inlet, outlet for recorder [illegible] readout, and the lower half contains from left [illegible] the sensor, [illegible], the rechargeable battery pack, pump and the audible alarm.

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FIGURE 10 MMH RESPONSE FOR PROTOTYPE TOXIC LEVEL MMH DETECTION INSTRUMENT

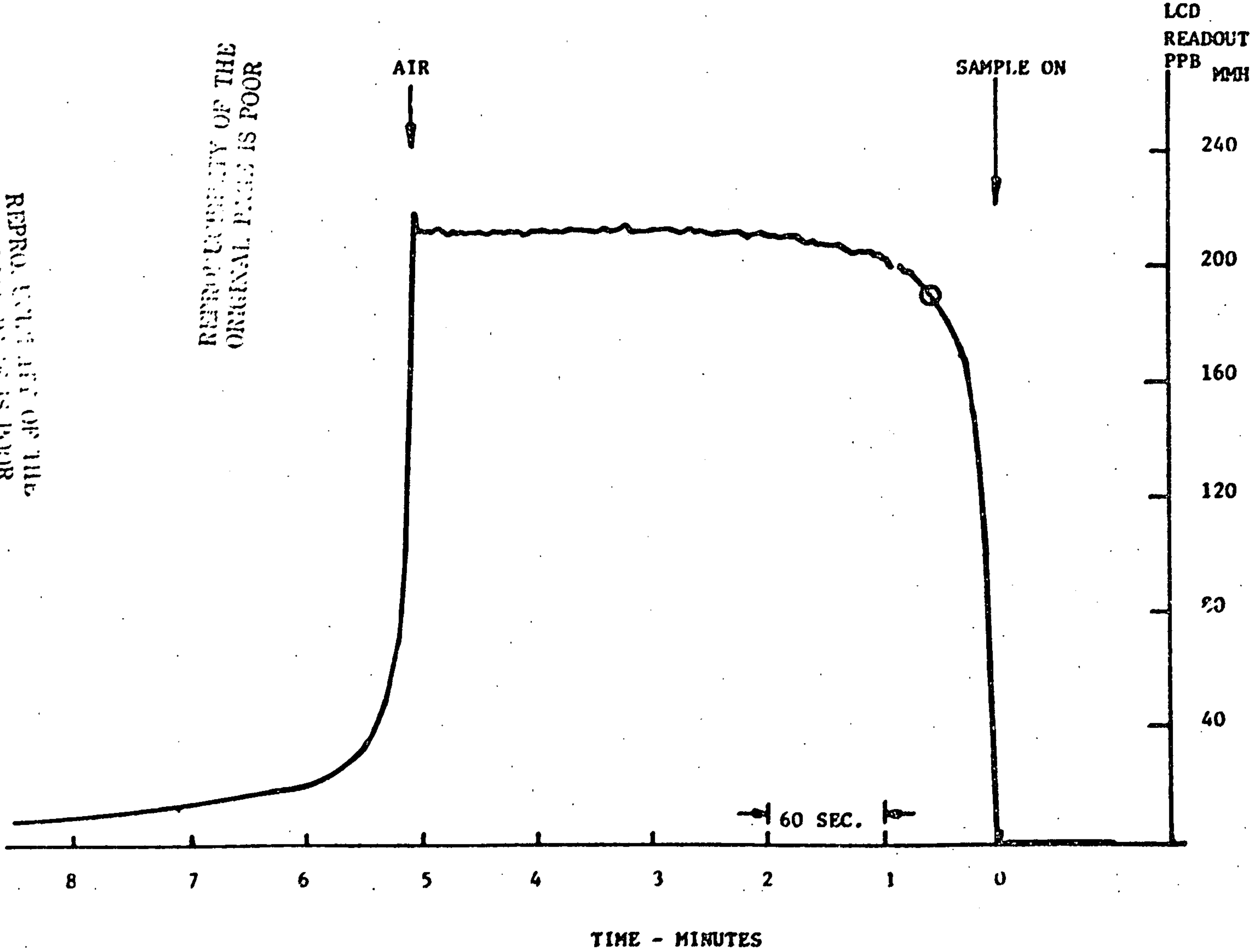


FIGURE 11 PROTOTYPE HYDRAZINE ANALYZER

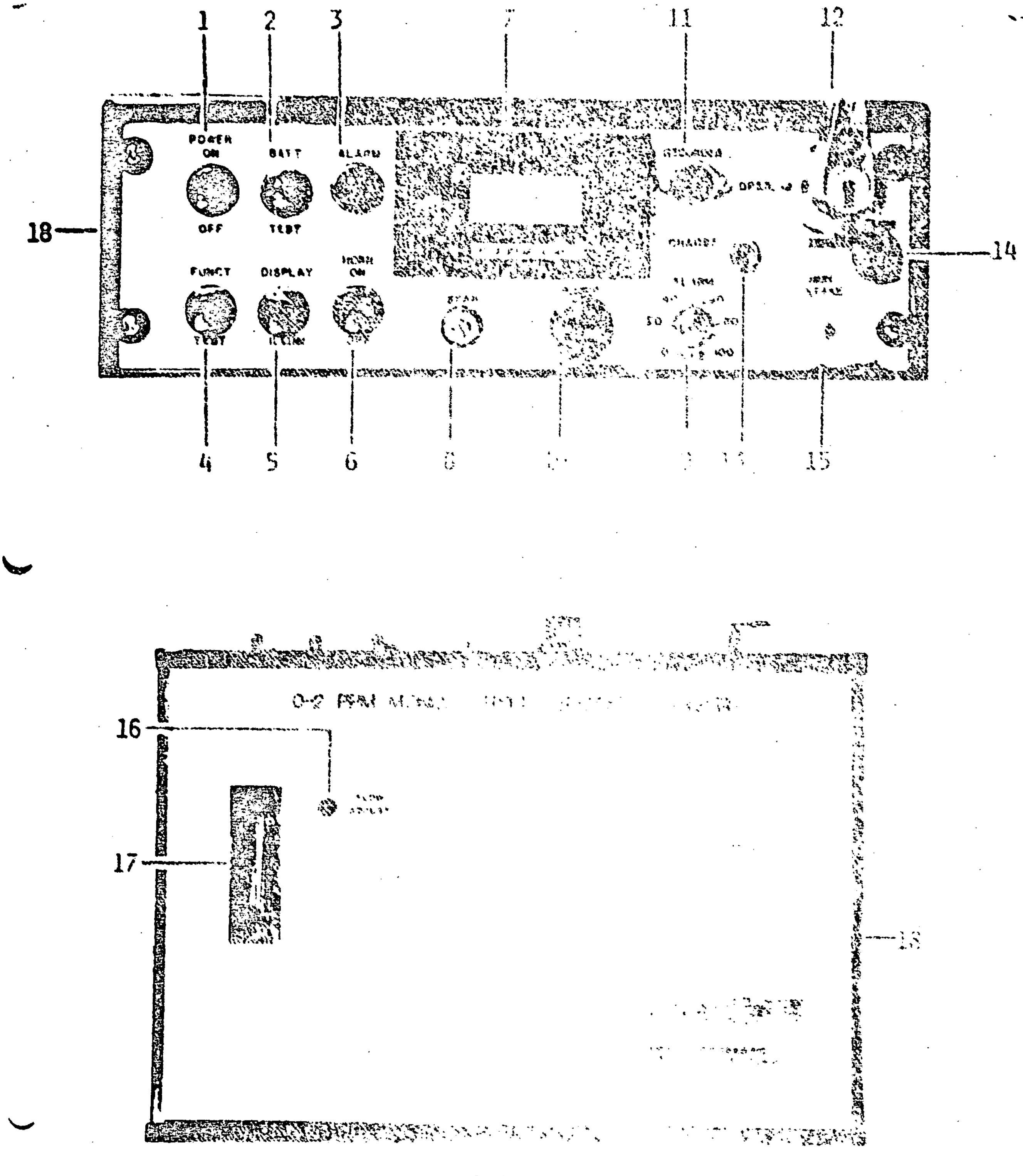


TABLE XIX

OPERATING CONTROLS AND INDICATORS OF THE PROTOTYPE HYDRAZINE ANALYZER

CONTROL OR INDICATOR	FUNCTION
1. Power	Turns pump on and off. Supplies power to all circuits except potentiostat.
2. Battery Tester	Checks battery condition on LCD readout.
3. Alarm Light	Illuminates when an alarm condition is reached.
4. Function Test	Checks electronic circuitry, alarm light, and horn.
5. Display Illumination	Brightens LCD readout for easier viewing in darkened areas.
6. Horn "ON/OFF" Switch	Used to silence or activate audible alarm.
7. Gas Level LCD Readout	Indicates the level of hydrazines in parts per million (ppm). (See note below).
8. Span Adjustment	Used to calibrate the detector with known concentration of hydrazines.
9. Alarm Set	Used to set the level at which the audible and visual alarms will activate.
10. Zero	Used for the precise setting of instrument zero.
11. Recorder Output Receptacle	Provides power and analog signal to strip chart recorder on 0-1 volt full scale output.
ZERO	Allows "ZERO" Air to pass through sensor to establish instrument zero.
12. Intake Valve OPER.	Allows for sampling ambient MMH and calibration.
13. Charging Receptacle	Used for receiving plug from charging unit.
14. Flow Indicator	Green marker pops up to show flow through sensor is activated.
15. MMH Intake	Couples with the probe to sample ambient air and remove particulates.
16. Flow Meter	Indicates flow past sensor.
17. Flow Adjustment	Regulates flow past sensor.
18. Case	Durable, impact resistant protective instrument housing.

NOTE: Since the instrument can analyze H, MMH, or UDMH, the LCD reading refers to the concentration of the gas for which it is calibrated.

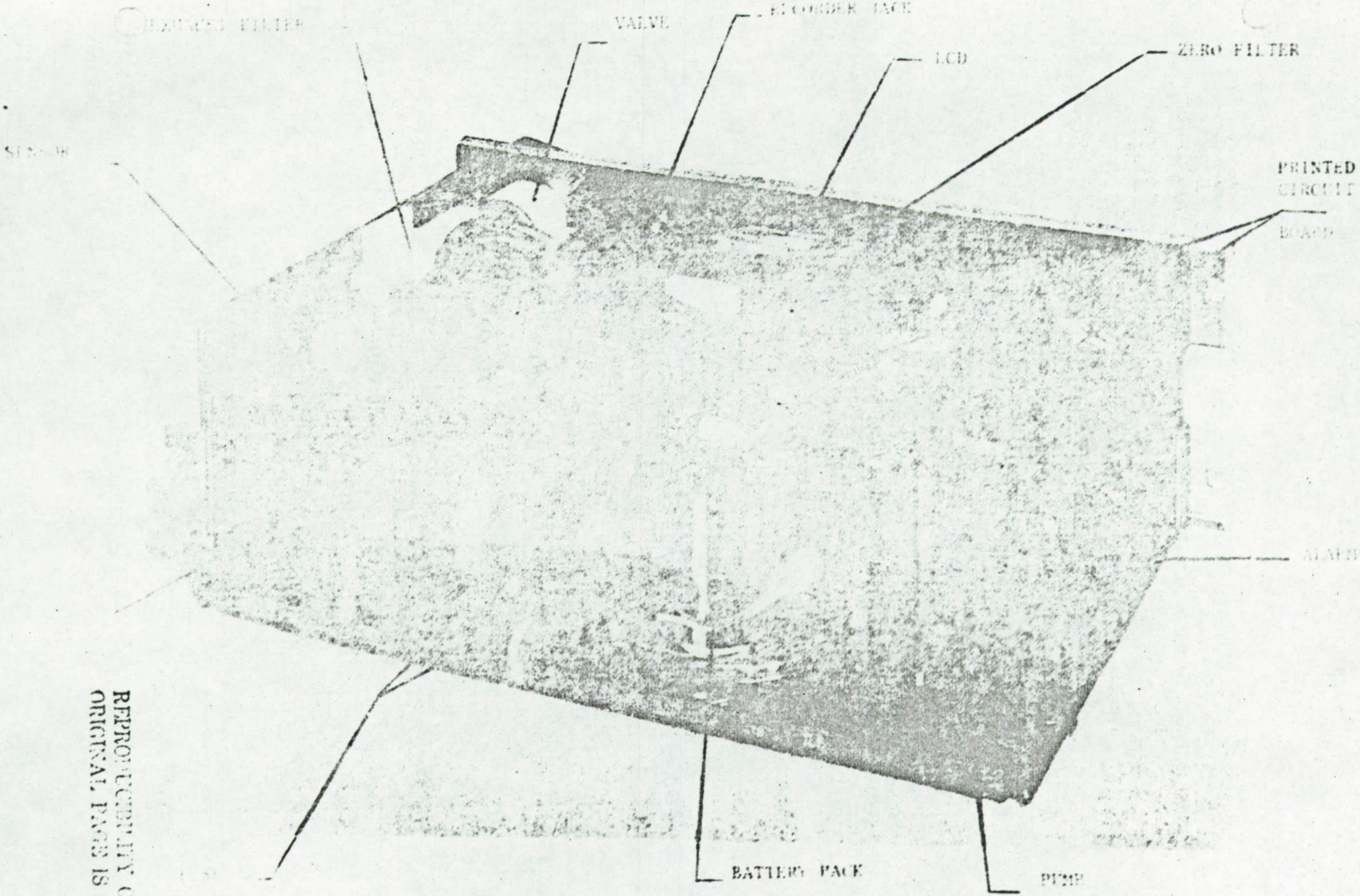


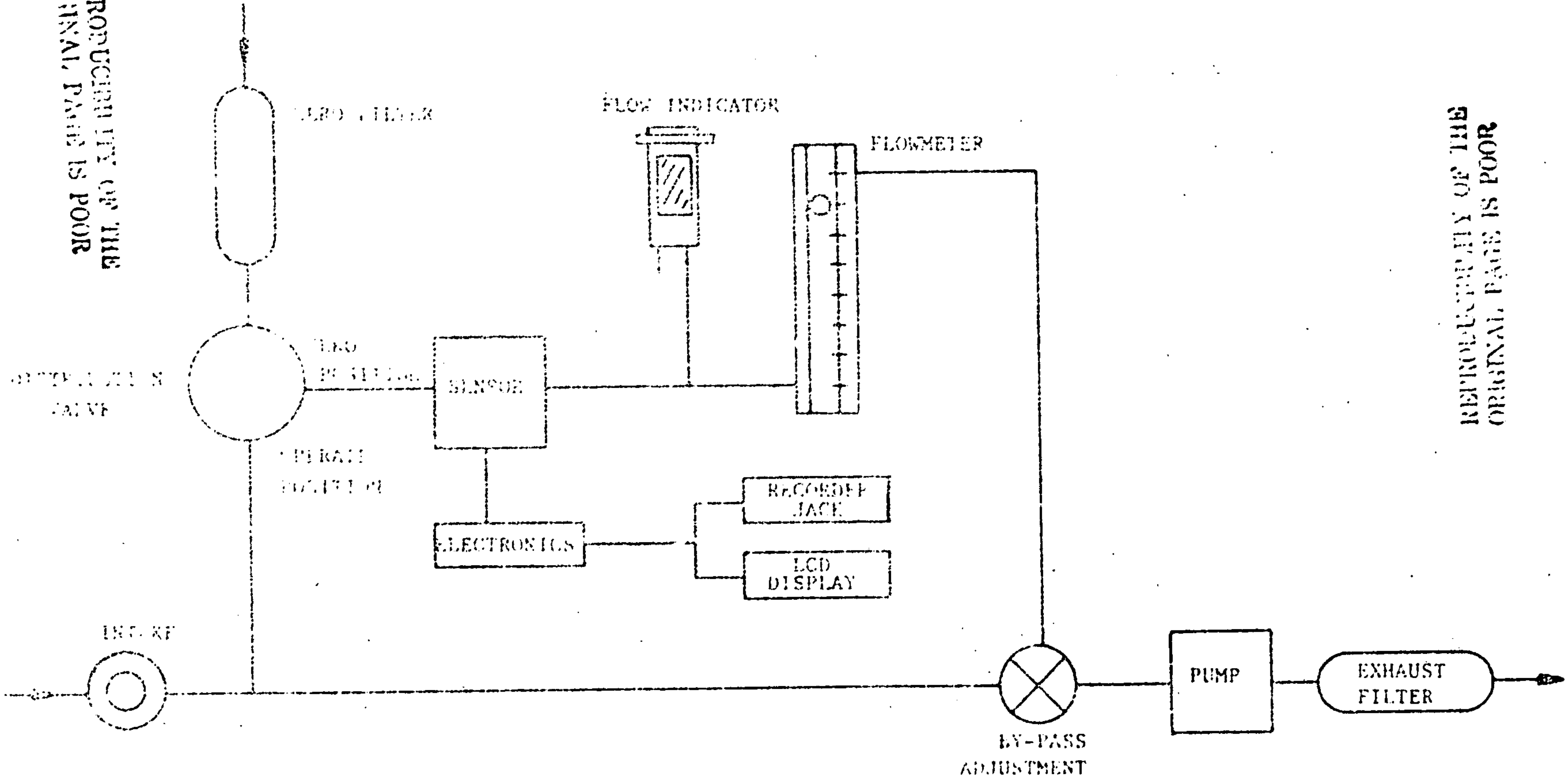
FIGURE 12 PROTOTYPE HYDRAZINE ANALYZER-INTERNAL LAY-OUT

The essential parts of the instrument are the electrochemical sensor (t[illegible] ducer), a pump, electronic control and amplifications circuitry and are illustrated schematically in Figure 13. The pump draws the sampled vapor mixture through intake and into the electrochemical sensor constant flowrate. The sensor then analyzes the vapor mixture producing an electric current which is proportional to the concentration of hydrazine in the vapor mixtures. That electrical current is [illegible] amplified and displayed on an LCD display showing the level in parts per million, a schematic electronic block diagram for the PPB level MMH detection is shown in Figure 14. A detailed description for the electronic circuit block diagram can be found in Appendix IV. Representative responses at room temperature are shown in Figure 10 for 250 ppb of MMH in N_2. The circles mark the 90% rise and decay points and these are within 50 seconds of vapor mixture exposure. The precision of these analyses was ± 1% (Figure 15) and both precision and response times were found to be improved at higher concentrations.

The instrument response was determined for several MMH concentrations and the results are shown in Figure 16. A linear least-square analysis of the data shown indicates that the instrument response is linear in MMH concentration within the experimental uncertainties in the measurements and yields a correlation coefficient of [illegible] for the 0-2 ppm range. The noise level on the instrument was less than 1 ppb MMH.

Studies of the effects of temperature upon the performance of the ECOLYZER instrument for hydrazine analysis were carried out in an environmental chamber. As observed previously (11) at temperature below 10°C, water vapor and hydrazine condensed in the instrument intake tubing and it was very difficult to obtain accurate and representative results. Special precautions were taken to utilize cal[illegible] dry gas mixtures and exclude room air from the environmental chamber and the ppb level analyzer. The results of these experiments are reported in Figure 7. T[illegible]

FIGURE 13 SCHEMATIC FLOW DIAGRAM FOR THE PROTOTYPE TOXIC LEVEL ANALYZER-MEASUREMENT PRINCIPLE



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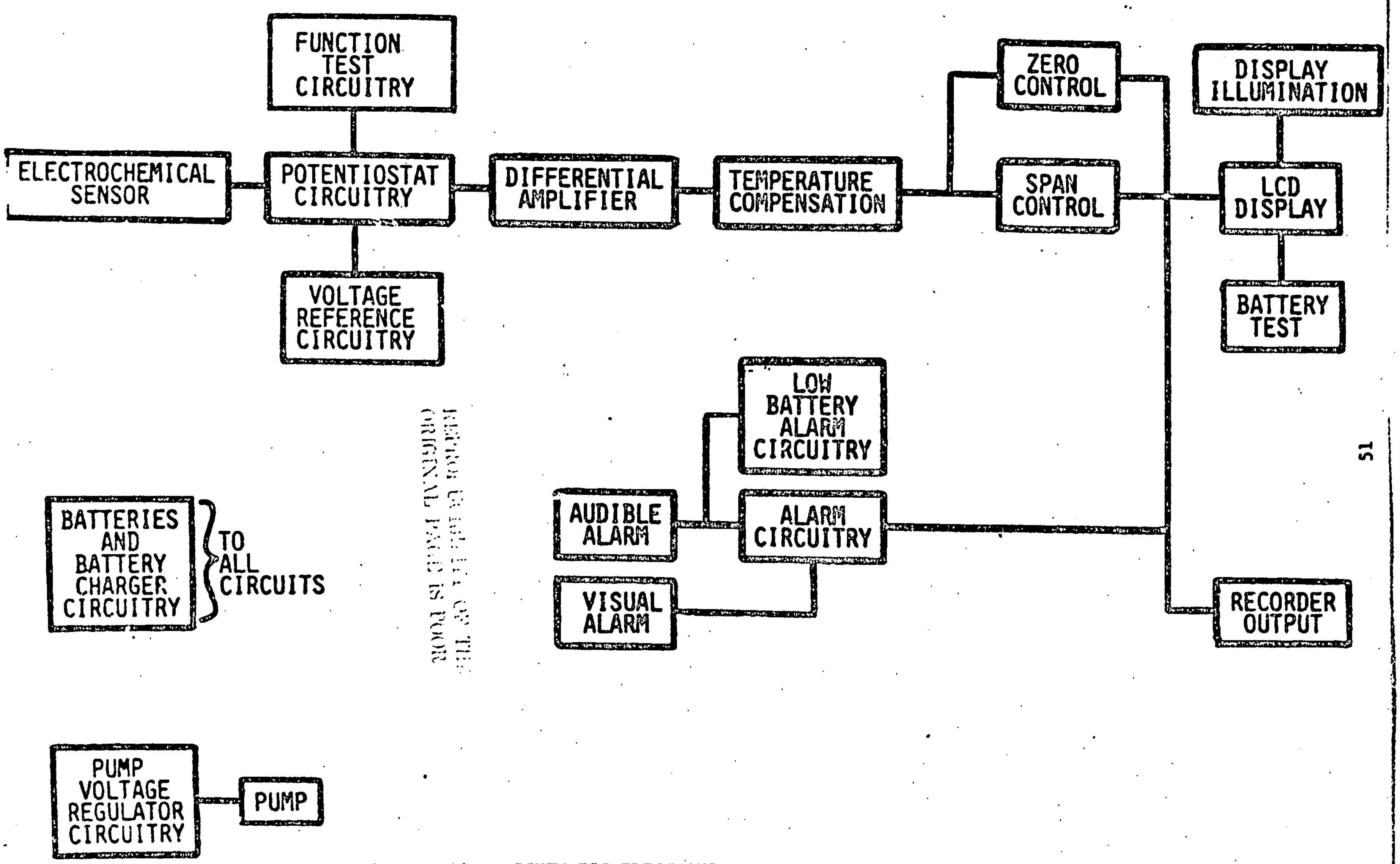


FIGURE 14 SCHEMATIC ELECTRONIC BLOCK DIAGRAM FOR THE LOW LEVEL MMH DETECTION

FIGURE 10 MMH RESPONSE FOR PROTOTYPE TOXIC LEVEL MMH DETECTION INSTRUMENT

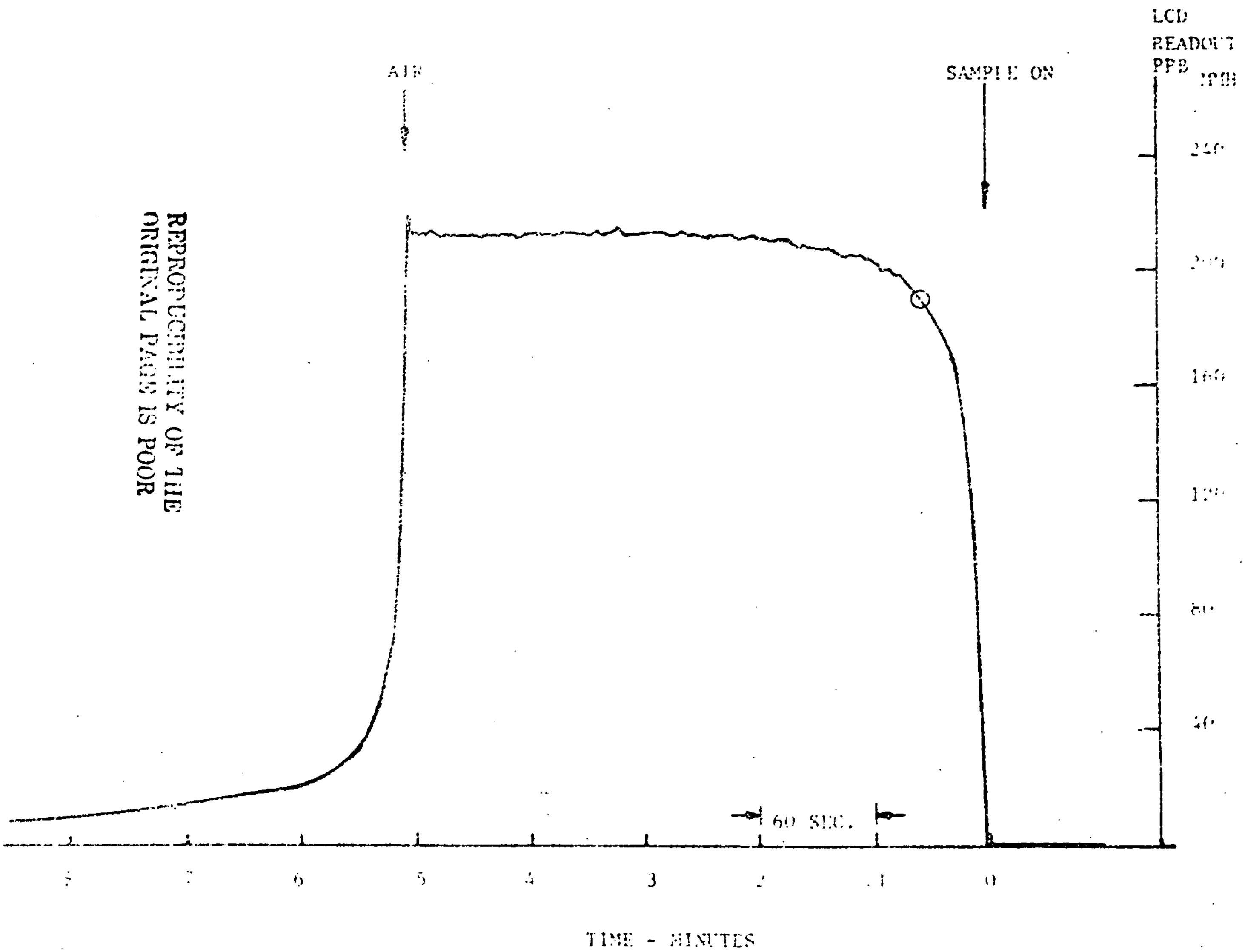


FIGURE 15 PRECISION STUDY OF THE PROTOTYPE TOXIC LEVEL MMH ANALYZER

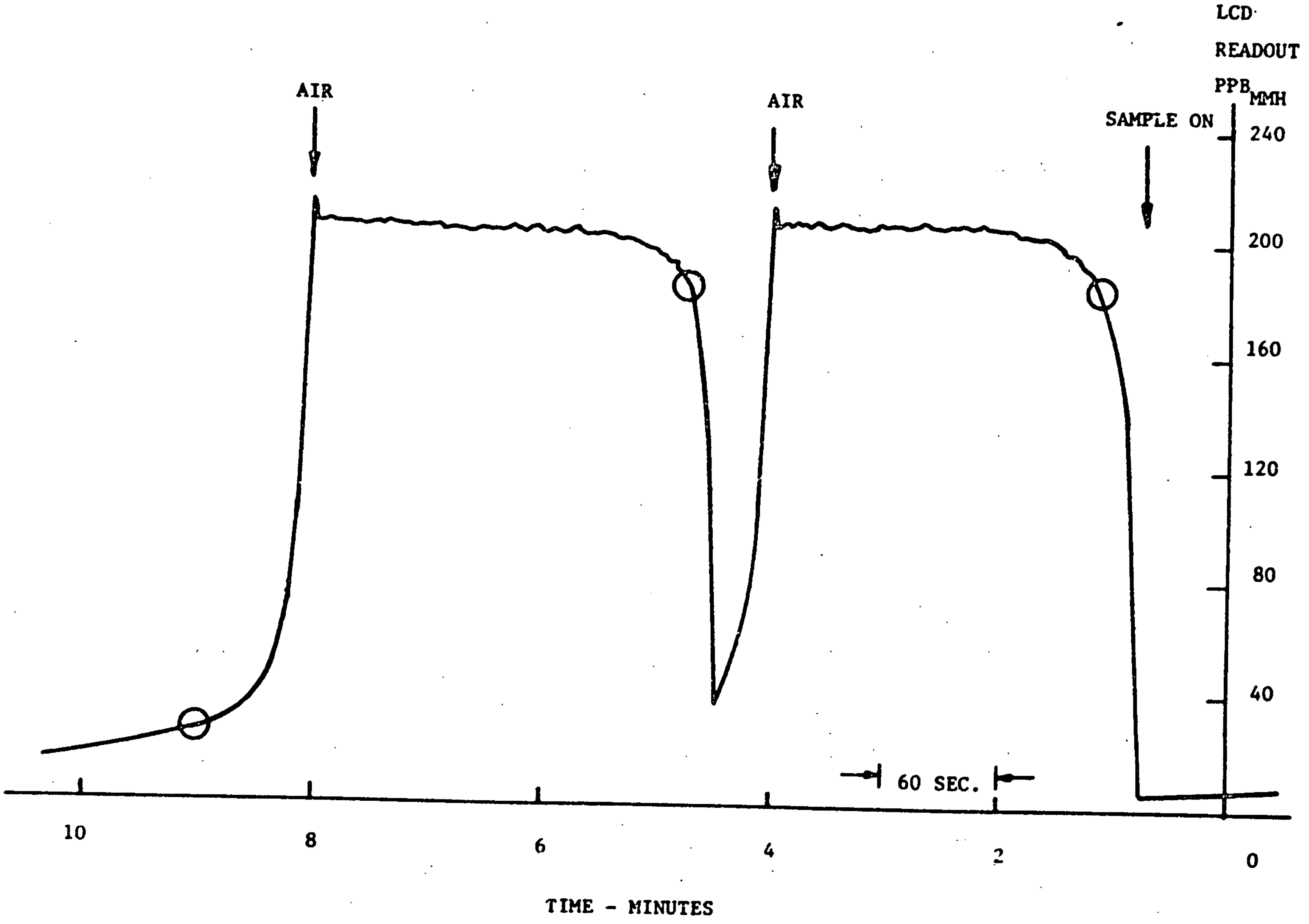


FIGURE 16 LINEARITY STUDY OF THE PROTOTYPE TOXIC LEVEL MMH ANALYZER

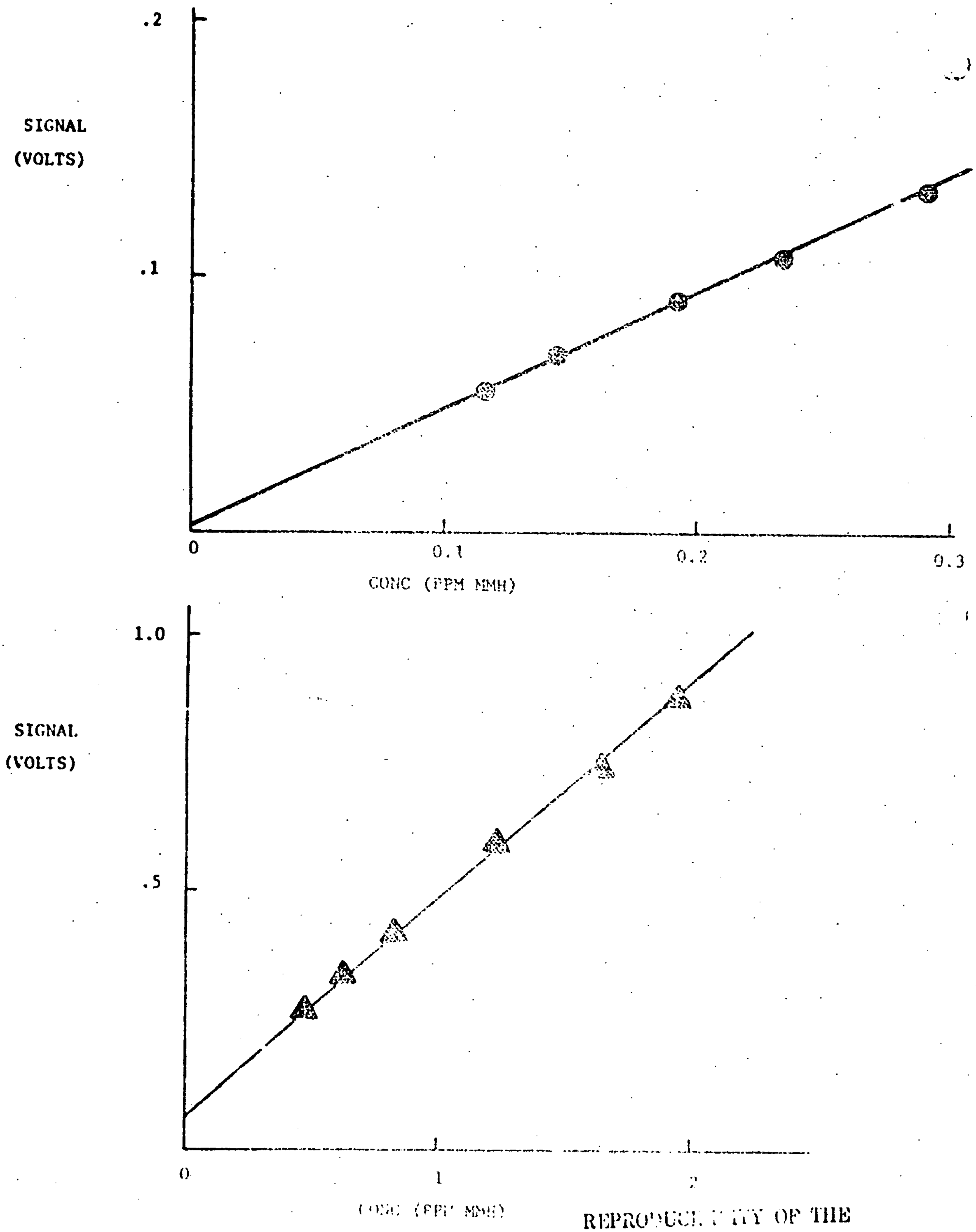
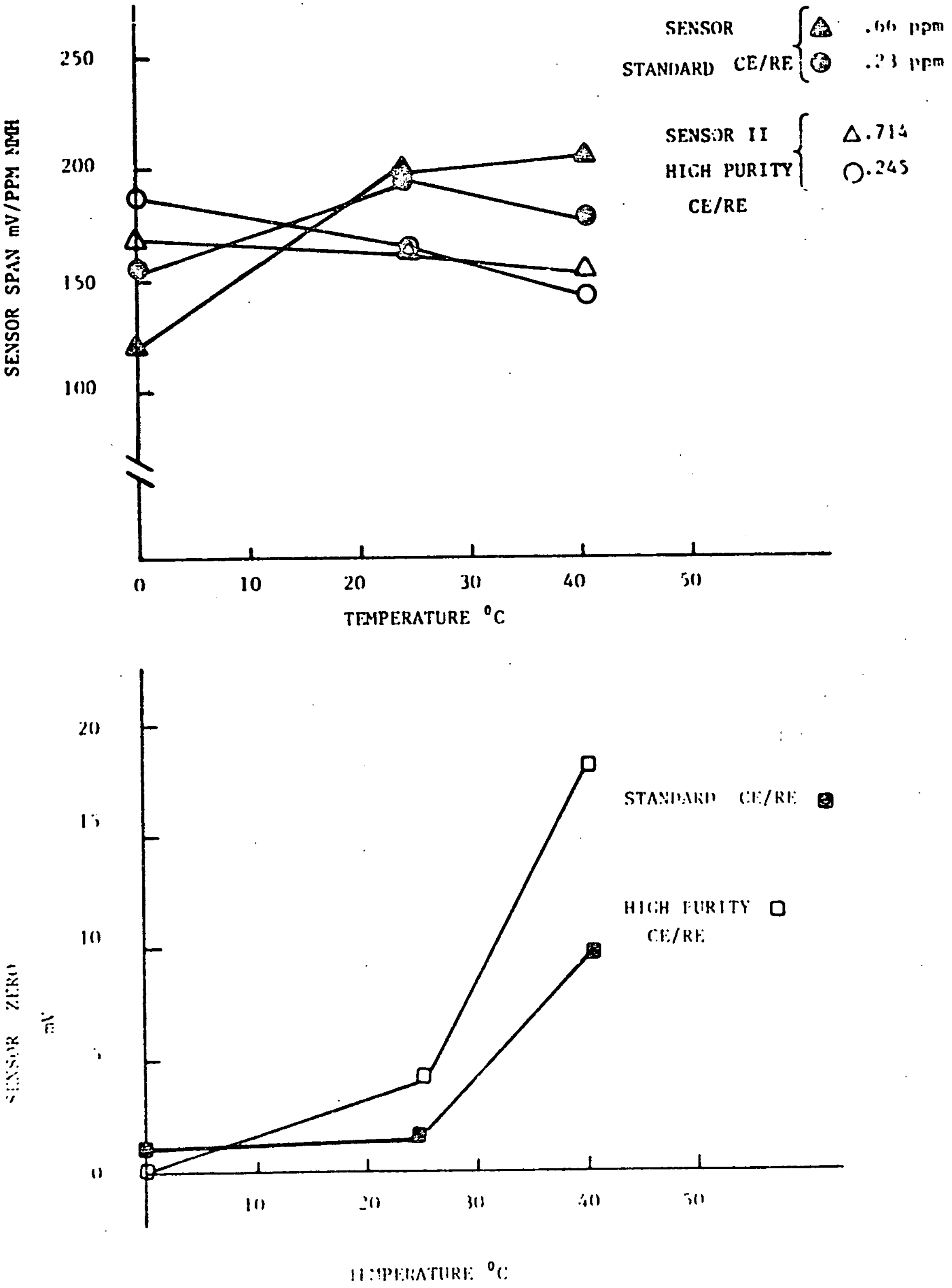


FIGURE 7 INSTRUMENT RESPONSE MAGNITUDE AND ZERO DRIFT AT VARIOUS TEMPERATURES



sor output (Figure 17) exhibits only slight variation from 0-20°C but shows a span variation of 25-35% over the temperature region of 20-40°C. More instrument testings and data has to be obtained before a proper temperature compensation can be incorporated into the instrument.

Instrument zero changes (Figure 18) of ± 100 ppb are observed using this instrument but this poses little problem since the instrument can easily be zeroed in the field immediately prior or subsequent to vapor measurements.

The zero and span drift measurements are complicated since there is a simultaneous time dependence for zero and span drift occurring along with the temperature measurements. The zero drift of an intermittently operated ppb analyzer was 4 ppb over a period of 7 days and the span drift was 5% over the same period. These drifts are necessarily included in the reported temperature measurements.

From the descriptive instrument data collected, the general instrument specifications are given in Table XX and XXI. By comparison with Table I and II (INTRODUCTION), we note that the design goals of the program except the response time have been achieved. It is also important to point out that the zero and span specification given in Table XXI are valid under typical ambient air temperature variations. At extreme temperature conditions zero and span deviations will be expected as no electronic temperature compensation has been incorporated in the instrument at this time.

In any field use, the selectivity to detect the toxic vapor of interest in the presence of other atmospheric constituents is absolutely essential for the instrument. The interferences due to selected pollutants for this specific hydrazine sensor are given in Table XXII. The major interference is found to be H_2S. The normal constituents of ambient air namely, N_2, O_2, CO and CO_2 are not reactive with this sensor and hence do not interfere with the vapor analysis.

FIGURE 17 PROTOTYPE TOXIC LEVEL ANALYZER SENSOR AND INSTRUMENT RESPONSE MAGNITUDE AT VARIOUS TEMPERATURE

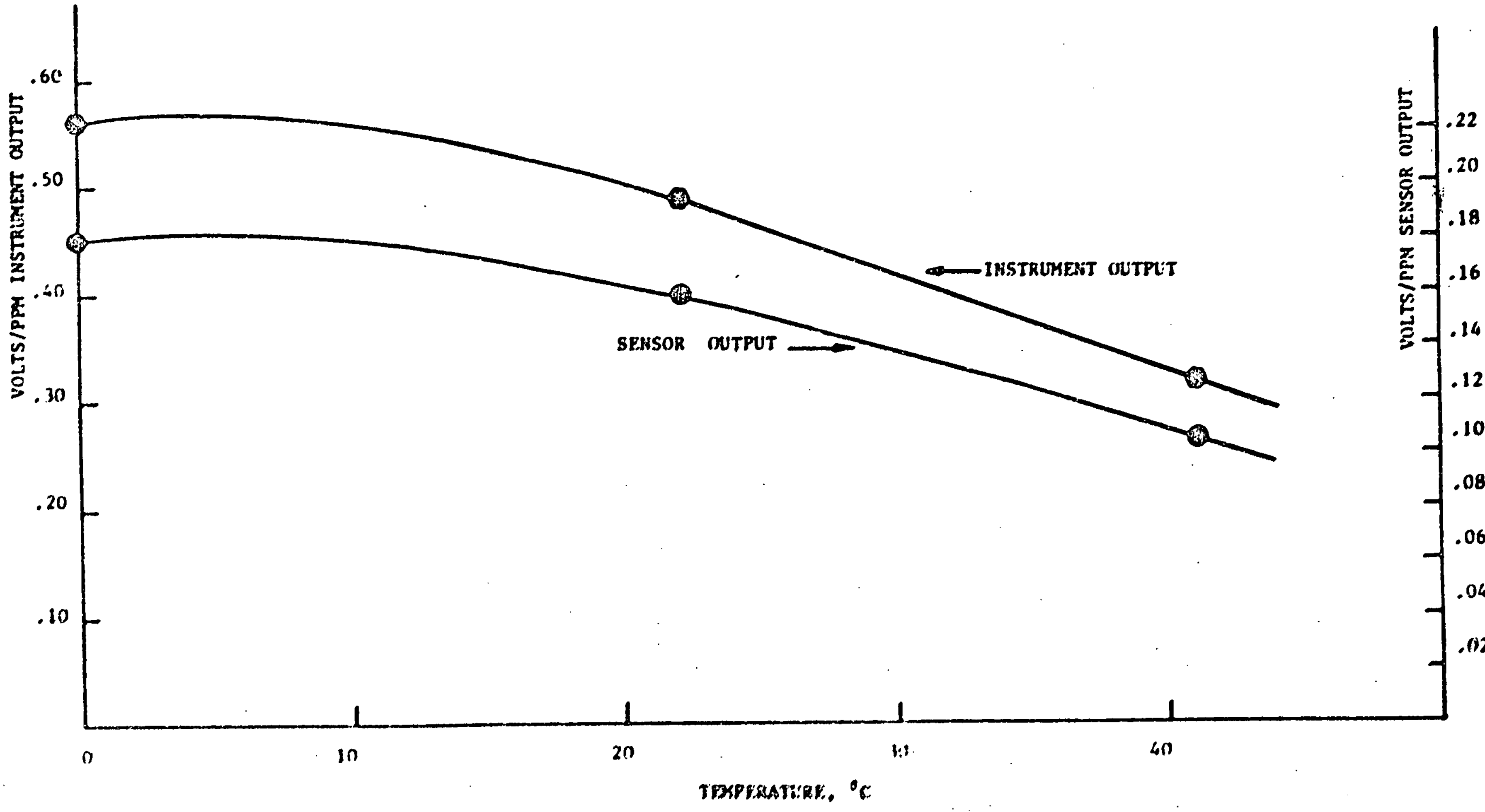


FIGURE [illegible] PROTOTYPE TOXIC LEVEL ANALYZER ZERO AT VARIOUS (NORMALIZED VS. ZERO OF OUTPUT @ 24°C) TEMPERATURE

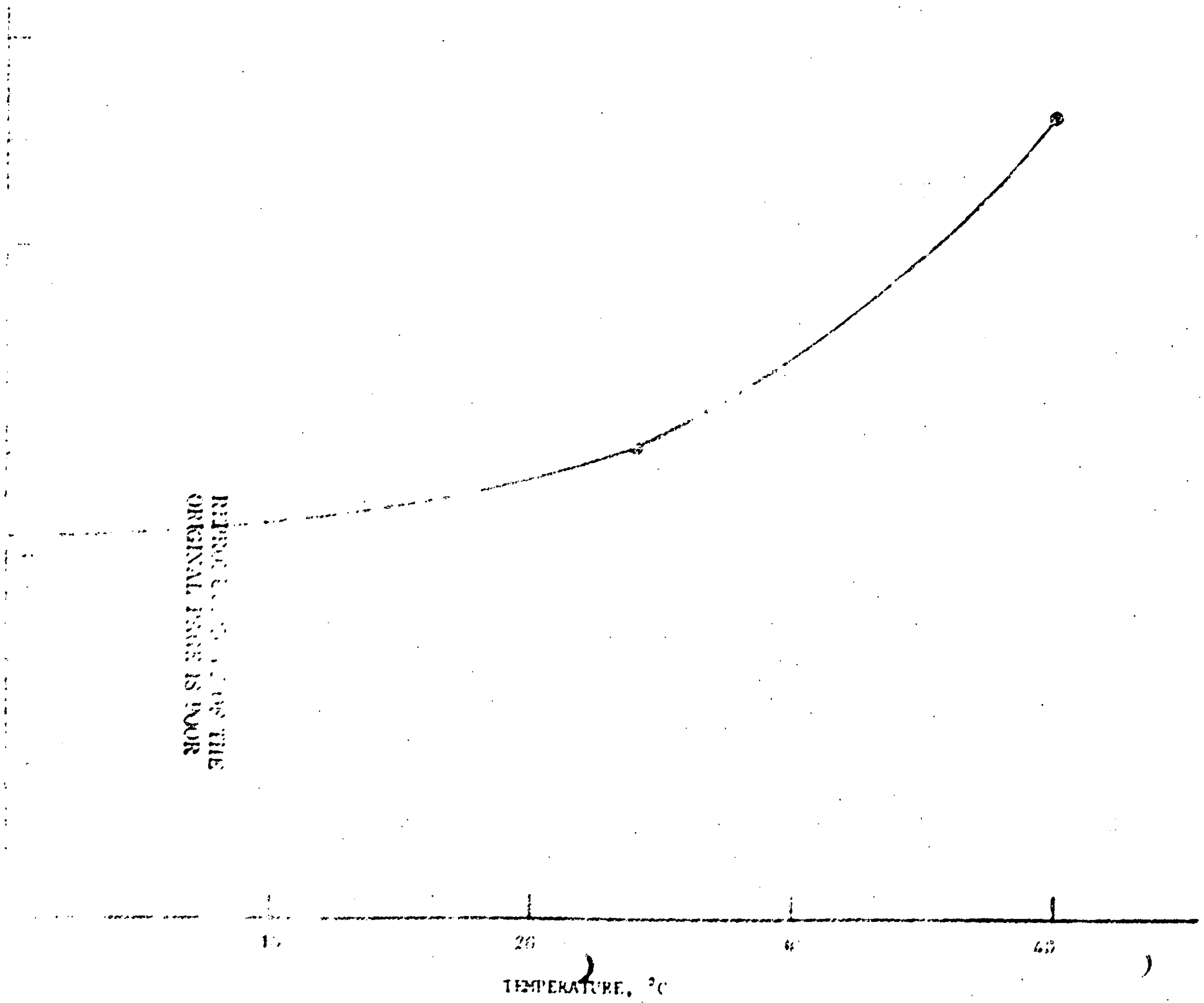


TABLE XX

PROTOTYPE TOXIC LEVEL INSTRUMENT DESIGN SPECIFICATIONS

	Description
INSTRUMENT TYPE:	Portable, Single Readout of MMH (H or UDMH) Vapor Concentration in air or diluent gas.
SPECIFICITY:	Sensor responds to all Hydrazine types (H, MMH and UDMH), but does not differentiate between them. The unit is calibrated for the particular gas of interest.
RANGE:	0-2 ppm with 1 ppb resolution.
SENSITIVITY:	Readable to ±1 ppb.
ALARM:	Audible horn and visible light, adjustable trigger level.
TEMPERATURE RANGE:	0-40° C
RELATIVE HUMIDITY:	10-95% RH (can operate at 0-100% RH but is designed for extensive service between 10 and 95% RH).
DIMENSIONS (Maximum):	21.cm 30.5 cm x 10 cm (8.27 in x 12.0 in. x 3.94 in.)
WEIGHT (includes case and strap):	5.0 kg (11 lbs. .4 oz.)
READOUT:	LCD DPM with 3½ digits. Recorder outputs provided.
CONSTRUCTION:	Ruggedized, hazard proofed, insensitive to changes in position.
POWER:	Battery, 8 hours continuous, with provision for recharge. For an hour total.
CURRENT DRAIN-NOMINAL:	OFF, 0.002 A; ON, 0.110 A: on (with full alarm 0.310 A).

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TABLE [illegible]

PROTOTYPE TOXIC LEVEL INSTRUMENT PERFORMANCE CHARACTERISTICS

	Description
RESPONSE TIME (to 90% of reading change at 0.1 ppm or above:	3-3.5 minutes. Virtually immediate response to 25% signal and 4 to 7 minutes to 99-100% signal.
ACCURACY (at 0.1 ppm or above):	± 10% (Dependent upon accuracy of calibration method and within precision of instrument).
PRECISION:	± 1% of reading (typically [illegible] at 200ppb MMH
ZERO DRIFT:	<1% F.S. per day (typically [illegible]
SPAN DRIFT:	<1% of reading per day (typically [illegible] PPB at 200ppb MMH)
NOISE:	<±1% F.S. (typically [illegible]
INTERFERENCES:	The following gases will give the interference ratio shown or greater:

Gas	Interference Ratio	
	Minimum	Typical
H_2S	1:1	[illegible]
[illegible]	[illegible]	[illegible]
NO_2	[illegible]	[illegible]
CO	[illegible]	[illegible]
[illegible]	[illegible]	Not Detected
[illegible]	[illegible]	Not detected
[illegible]	[illegible]	[illegible]
N_2, O_2, Ar, He,		
[illegible], CO_2, [illegible]		
[illegible]	[illegible]	[illegible]

TABLE I

DESIGN GOALS
PORTABLE HYPERGOLIC VAPOR DETECTION INSTRUMENT

	GOAL
INSTRUMENT TYPE:	Portable, Single Readout of Hydrazine Vapor Conc. in Air.
SPECIFICITY	Sensor responds to all Hydrazine types (H, MMH and UDMH), but need not differentiate between them.
RANGE:	0-2 PPM with 1 PPB resolution.
SENSITIVITY:	0.05 PPM minimum detectable conc. readable to ± 1 PPB.
TEMPERATURE RANGE:	0-40°C.
RELATIVE HUMIDITY:	10-95%.
DIMENSIONS (Maximum):	8" x 8" x 16".
WEIGHT:	< 12 lbs.
READOUT:	Digital, readable in sunlight 3 digit resolution. Also provide a recorder output.
CONSTRUCTION:	Ruggedized, hazard proofed, insensitive to changes in position.
POWER:	Battery, 8 hours continuous, with provision for 105-125V AC power/ recharge jack.
ALARM:	Audible alarm and light alarm, adjustable trigger level.

TABLE II

INSTRUMENT PERFORMANCE GOALS

	GOAL
RESPONSE TIME (to 90% of reading change at 0.1 PPM or above):	30 seconds
ACCURACY (at 0.1 PPM or above):	± 10%
PRECISION:	± 1% F.S.
ZERO DRIFT:	± 1% F.S. per day
SPAN DRIFT:	± 1% F.S. per day
NOISE:	± 1% F.S. per day
INTERFERENCES:	The following gases will give the interference ratio shown or greater:

<u>GAS</u>	<u>INTERFERENCE RATIO GOAL</u>
NH_3	100:1
NO_2	100:1
FREON	1,000:1
CO	1,000:1
N_2, O_2, H_2, Ar, He, CH_4 and CO_2	No Response

TABLE XXII

INTERFERENCE EQUIVALENTS OF SELECTED POLLUTANTS

GAS MIXTURES	READING DUE TO INTERFERENT ON MMH IN PPM	INTERFERENCE RATIO PPM INTERFERENT = PPM MMH
.288 ppm MMH	.288	1:1
46.3 ppm NO_2/Air	.008	5787
2931 ppm H_2	.002	1465500:1
1015 ppm CO/Air	.012	84583:1
50 ppm NH_3/N_2	<.019	2631>:1
46.6 ppm NO/N_2	-.004	-11650
21.5 ppm SO_2/N_2	-.004	-11650
902 ppm H_2S	.860	1.049:1
10^6 ppm N_2	-.004	-11650:1
1060 ppm CO_2/Air	0.00	0
1160 ppm Freon-12	.002	580000:1
Air	0.000	0
19.4 ppm C_2H_4/Air	0.000	0

In order to sample specific locations at a distance from the instrument intake, a remote sampling probe (Figure 19) developed and described in a previous report (11) was used and evaluated for the instrument. The response of the ppb level analyzer is shown in Figure 20 for 200 ppb MMH with the 5 foot Teflon probe attached to the instrument inlet. The response is the same magnitude as the instrument without the probe except a slightly longer time is required to achieve the steady-state signal. This means that calibration of the instrument without the probe, will not cause error in the field when sampling with a probe. However it is recommended to calibrate with the probe in place since this will also ensure proper probe performance. The activity of the MMH sensor for all the hydrazines i.e., H, MMH, and UDMH are measured. Results are summarized in Table XXIII. A knowledge of this activity will allow one to calibrate the instrument for either H, MMH, or UDMH and by introduction of an appropriate scale fraction obtaining an accurate measurement for each of these vapors. The ppb analyzer when calibrated for MMH will be calibrated for H by multiplying the observed MMH reading by 1.06, and will be calibrated for UDMH by multiplying the observed MMH readings by 0.37. These calibration factors are accurate to ± 10% at present and are appliable in the linear range of the instrument. However, long term drift and temperature characteristics of these analyses have not been completely verified. Continuing effects have been undertaken to refine the cross-calibration fraction in order to be able to certify for each instrument and allow accurate field measurements of all the hydrazines with only a single calibration.

Hydrazines (H, MMH, UDMH) had long been established to undergo oxidative decomposition in air (12,13,14,15). Recently, we have observed that the toxic level analyzer does not give the same response to MMH in Air and in N_2 in the sampling system. Independently NASA (16) had observed the same results. In order to verify

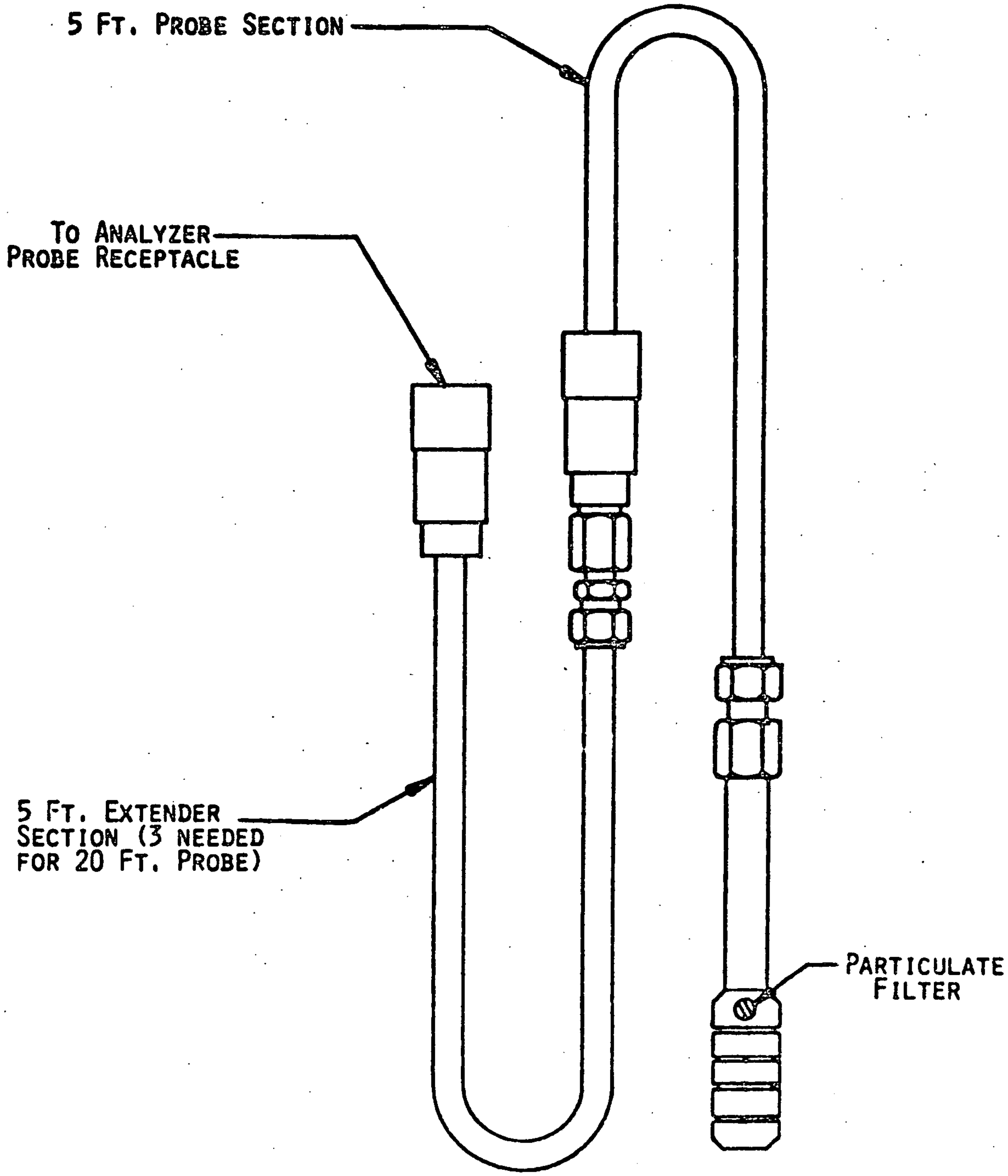


FIGURE 19
REMOTE SAMPLING PROBE ASSEMBLY

FIGURE 20 EFFECT OF REMOTE SAMPLING PROBE ON MMH RESPONSE

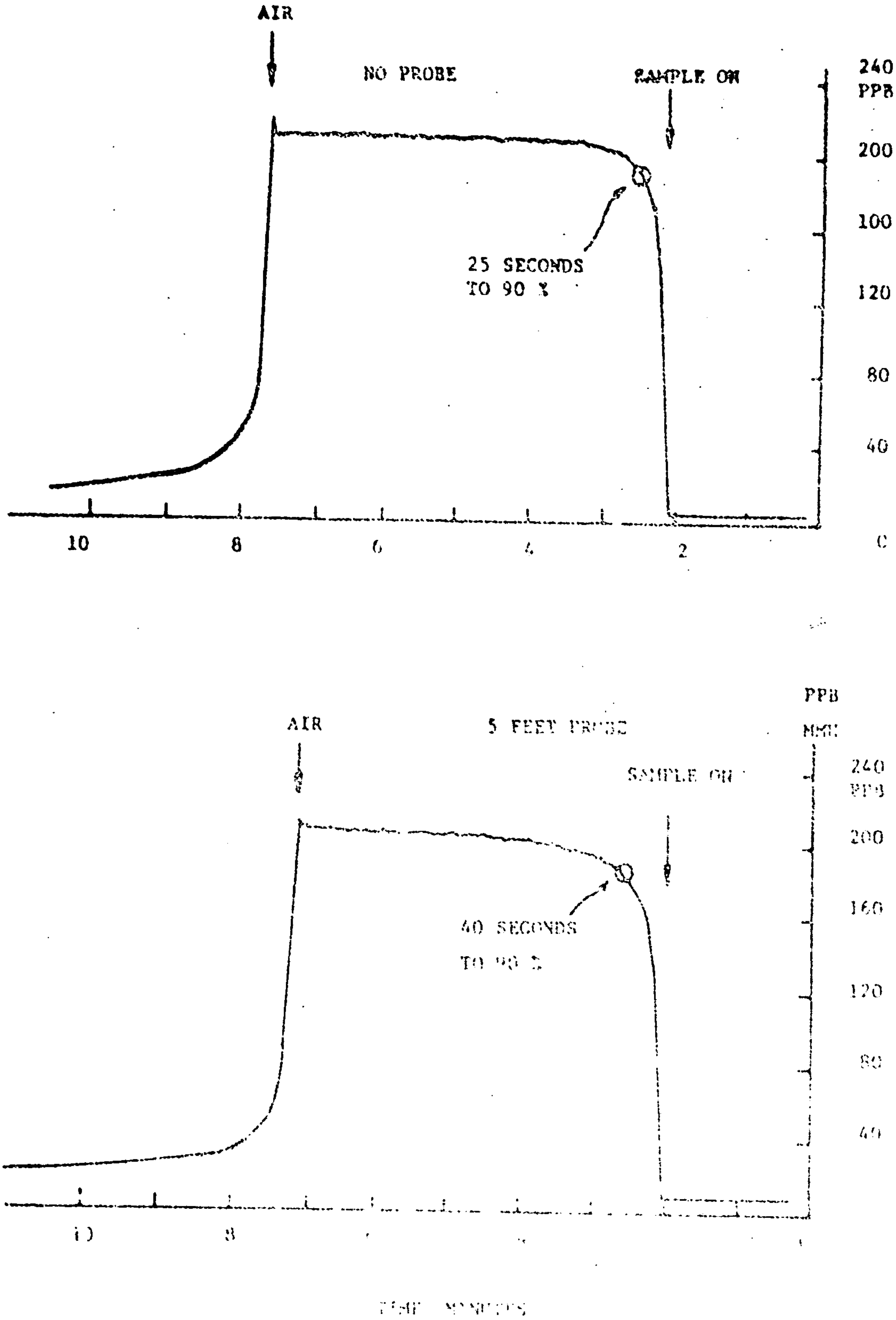


TABLE XXIII

THE PROTOTYPE TOXIC LEVEL ANALYZER RELATIVE RESPONSE RATIOS FOR H, MMH AND UDMH

GAS	CONC. (PPM)	SIGNAL μA/PPM	RATIO (GAS:MMH)*
MMH	.250	16	1:1
H	.254	17	0.94:1
UDMH	.250	6	2.7:1

* Ratio is defined to be the PPM of gas equivalent to the signal of 1 PPM of MMH.

that the difference in Air/N_2 reading is due to a sampling decomposition problem rather than an artifact due to the electrochemical sensing approach, the following experiments were undertaken. In one set of experiments, the MMH permeation device is allowed to equilibrate in air overnight, the MMH/Air mixture is then introduced into the electrochemical sensor directly from the permeation system. The experiment was then repeated with N_2 as the diluent gas. For comparison, colorimetric determination of the MMH concentration is also recorded. Results for this set of experiments are summarized in Table XXIV.

It can be seen that both colorimetric and electrochemical measurements give significantly lower MMH concentrations in air than in N_2. The large concentration difference observed in air can be attributed to the fact that a high temperature for the permeation device (60°C), long equilibration time with air and low concentration of MMH used all, maximized the decomposition process. To further support this hypothesis, another experiment was performed where the MMH stream in N_2 from the outlet of the permeation system was mixed with either air (20% oxygen) or N_2 through a Teflon T-joint before it entered the electrochemical sensor. At all concentrations studied, no difference was observed for the MMH concentration readout in air or in Nitrogen (Table XXV and Figure 21). These experiments clearly support the ideas that:

1) Significant oxidative decomposition had occurred in the permeation device at the experimental conditions if air was used as the diluent gas.

2) Colorimetric methods for detection of MMH lack specificity and are generally not sensitive to concentrations < .25 ppm.

3) The electrochemical sensor is selective towards MMH, and only MMH, whether in N_2 or Air, and not its air decomposition products.

TABLE XXIV

COMPARISON OF ELECTROCHEMICAL AND COLORIMETRIC METHOD FOR THE DETERMINATION OF HYDRAZINES IN AIR AND IN NITROGEN

CONC. (PPM MMH)	CONC. ANALYZED LCD READOUT	
	COLORIMETRIC	ELECTROCHEMICAL
.288 (AIR)	.0575	.0235
.288 (N_2)	.288	.288
SIGNAL MMH (AIR) / SIGNAL MMH (N_2)	0.2:1	0.08:1

TABLE XXV

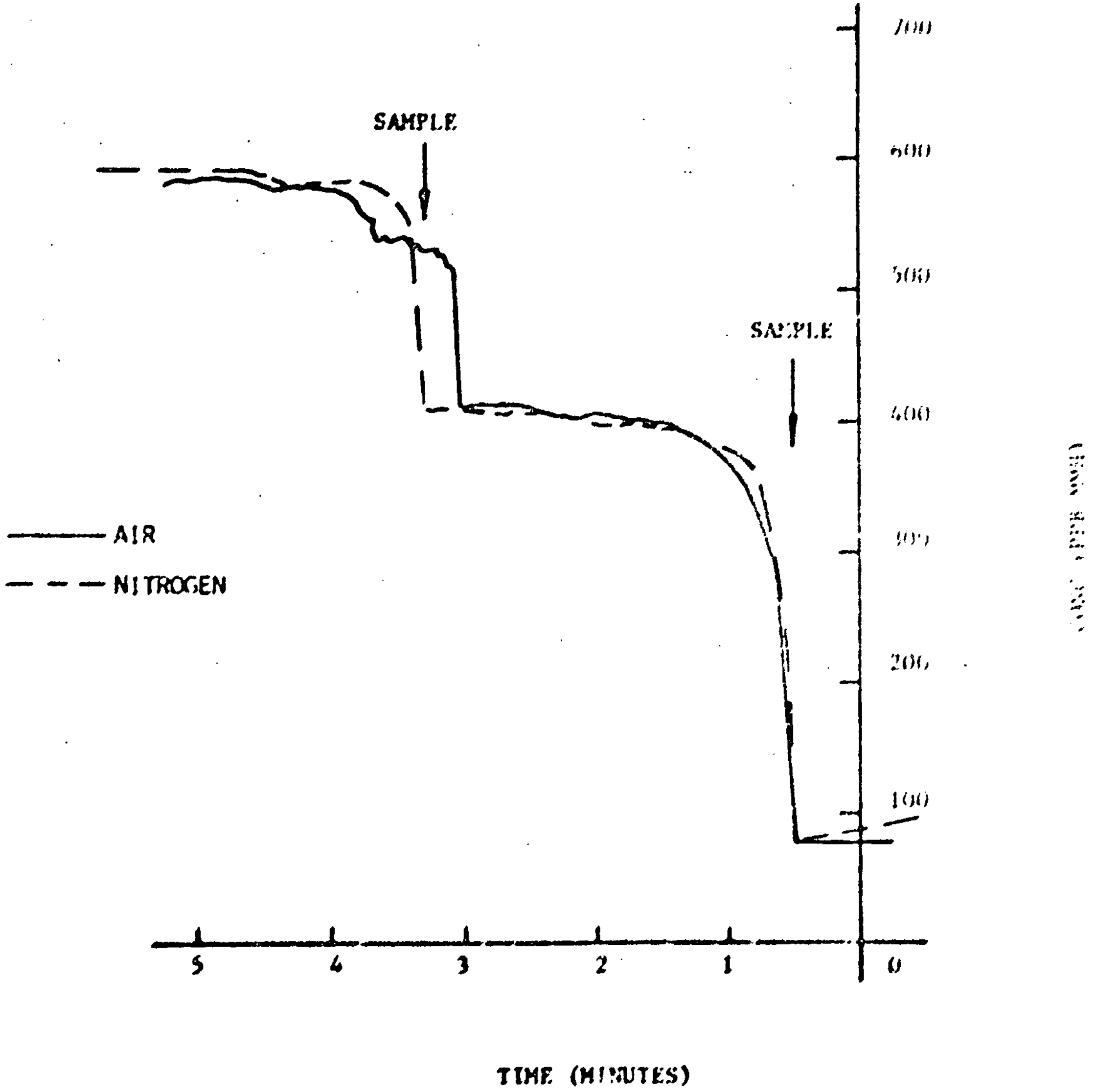
COMPARISON OF THE PROTOTYPE TOXIC LEVEL ANALYZER RESPONSE TO MMH IN AIR AND IN NITROGEN

CONC. MMH (PPM) (FROM PERMEATION) DEVICE	LCD READOUT (PPM MMH)		MMH MMH
	AIR	N_2	(AIR)/(N_2)
.309	.320	.320	1:1
.447	.468	.464	1.008:1
.577	.572	.55	1.04:1
.665	.620	.632	.99:1

Permeation flowrate: 0.5 ℓ/min.

Air or N_2 flowrate: 1.8 ℓ/min. → 3.9 ℓ/min.

FIGURE 21 COMPARISON OF THE PROTOTYPE TOXIC LEVEL ANALYZER RESPONSE TO MMH IN AIR AND IN NITROGEN



4) Reliable calibration of the MMH prototype instrument should be done using hydrazines/in nitrogen mixtures

CONCLUSIONS AND RECOMMENDATIONS

A prototype electrochemical instrument capable of PPB level hypergolic vapor sensing has been developed, designed, fabricated and tested. Accessory hardware and supporting technology has been developed. The instruments complete system (Figure 22) consists of a 5 foot all Teflon sampling probe, a battery recharger, a DC powered recorder and the prototype toxic level analyzer. This instrument is capable of reliable measurement of H, MMH, UDMH at 0-2 ppm concentrations with ± 1 ppb resolution provided that the instrument is being calibrated with the gas of interest and in the absence of interferences from the other gases during measurements. Except the response time requirement, which requires further development, the prototype meets this program's required design goals (Table XXVI, XXVII).

The electrochemical technique has been established to be a continuous portable analytical method for determination of trace level hypergolic vapors in air or any diluent gas. Its high degree of [illegible] on the [illegible] monitoring of these vapors [illegible] procedures for the toxic level [illegible] 9402 NASA, Kennedy Space Center, [illegible] from the manufacturer.

The prototype toxic [illegible] capable of performing [illegible] this instrument does not [illegible] is a useful state-of-the-art [illegible] electrochemical detector [illegible]

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FIGURE 22 PROTOTYPE TOXIC LEVEL ANALYZER

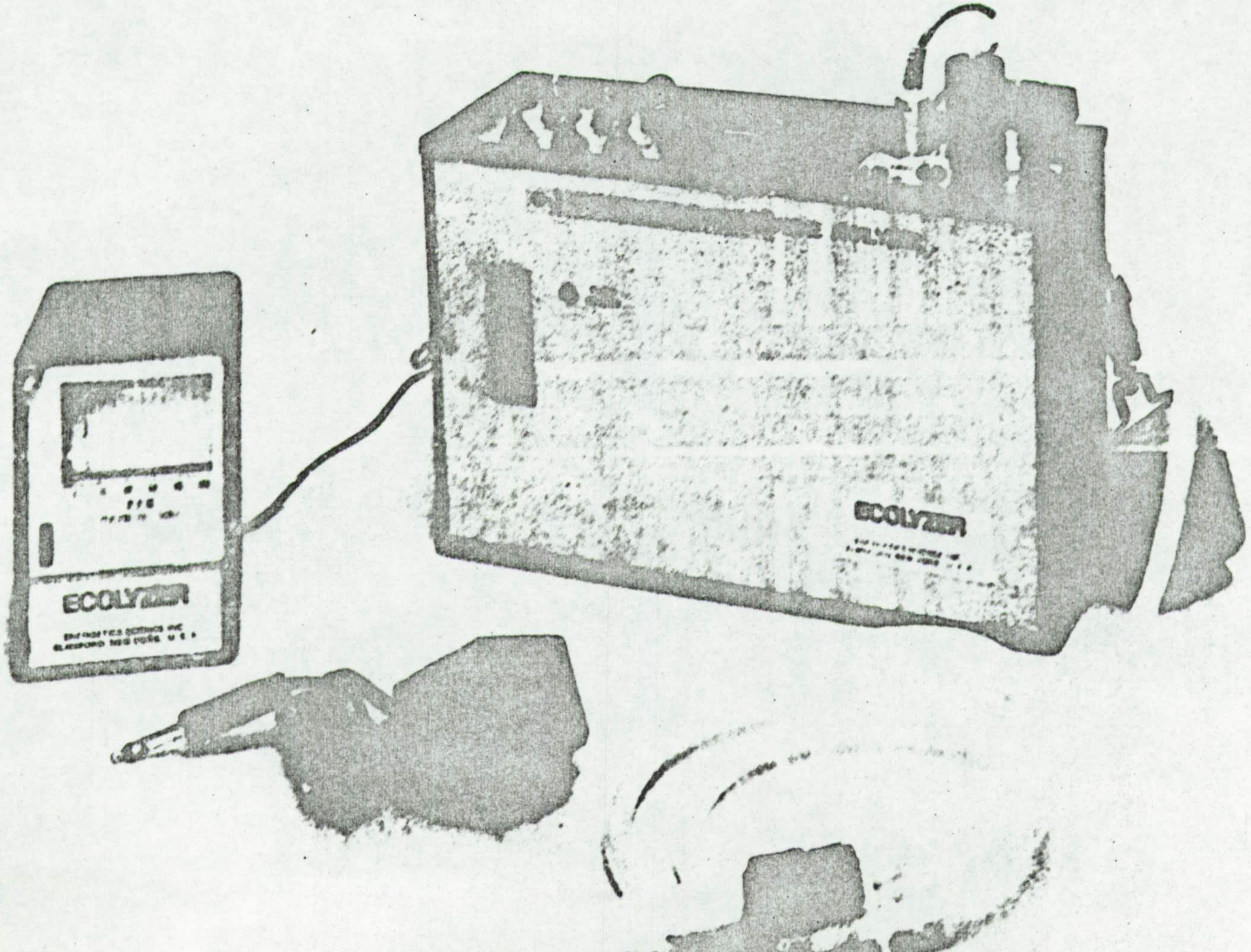

TABLE XXVI

DESIGN GOALS
PORTABLE HYPERGOLIC VAPOR DETECTION SENSORS

	GOAL	SPECIFICATION
INSTRUMENT TYPE:	Portable, Single Readout of Hydrazines Vapor Conc. in Air.	Accomplished
SPECIFICITY:	Sensor responds to all Hydrazine types (H, MMH and UDMH), but need not differentiate between them.	Accomplished The unit is calibrated for the particular hydrazine of interest.
RANGE:	0-2 PPM with 1 PPB resolution.	Accomplished
SENSITIVITY:	0.05 PPM minimum detectable conc. readable to ± 1 PPB.	Accomplished
TEMPERATURE RANGE:	0-40°C	Accomplished
RELATIVE HUMIDITY:	10-95%	Accomplished
DIMENSIONS (Maximum):	8" x 8" x 16"	Accomplished 8.27 x 3.94 x 12.0"
WEIGHT:	< 12 lbs.	Accomplished 11 lbs. 4 oz.
READOUT:	Digital, readable in sunlight 3 digit resolution. Also provide a recorder output.	Accomplished
CONSTRUCTION:	Ruggedized, hazard proofed, insensitive to changes in position.	Accomplished
POWER:	Battery, 8 hours continuous, with provision for 105-125V AC power/recharge jack.	Accomplished
ALARM:	Audible alarm and light alarm, adjustable trigger level.	Accomplished

TABLE XXVII

INSTRUMENT PERFORMANCE GOALS

	GOAL	SPECIFICATION
RESPONSE TIME (to 90% of reading change at 0.1 PPM or above):	30 seconds	1-3.5 minutes Virtually immediate response to 25% signal and 4-7 minutes to 99-100% signal.
ACCURACY (at 0.1 PPM or above):	± 10%	Accomplished (Dependent upon accuracy of calibration method and within precision of instrument.
PRECISION:	± 1% F.S.	Accomplished.
ZERO DRIFT:	< 1% F.S. per day	Accomplished.
SPAN DRIFT:	< 1% F.S. per day	Accomplished.
NOISE:	± 1% F.S. per day	Accomplished.

INTERFERENCES:

The following gases will give the interference ratio shown or greater:

GAS	INTERFERENCE RATIO GOAL	MINIMUM	TYPICAL
NH_3	100:1	150:1	1,000:1
NO_2	100:1	150:1	1,000:1
FREON	1,000:1	NOT DETECTED	NOT DETECTED
CO	1,000:1	3,000:1	75,000:1
NO		5,000:1	NOT DETECTED
SO_2		200:1	NOT DETECTED
H_2		500:1	NOT DETECTED
N_2, O_2, Ar, He, CH_4, CO_2, FREON-12	NO RESPONSE	NOT DETECTED	NOT DETECTED
H_2S		1:1	1:1

Present limitations of the sensing technique are specificity, response time, sensor lifetime, and expanded detection ranges. These characteristics can be improved by further sensor developments, and more field testings along with improvements in accuracy, environmental stability, sensitivity and attitude insensitivity.

The permeation tube method of preparation of low concentration of hydrazines was evaluated and its reliability was established by comparison with both colorimetric and electrochemical methods. The electrochemical method is further established to be more selective than the colorimetric method towards MMH detection. Calibration of the prototype toxic level analyzer is thus recommended to be done with hydrazine mixtures in nitrogen, as oxidative decomposition of hydrazine has been shown to occur in the presence of air. The prototype instrument also shows no difference in response to commercial hydrazines or air force grade propellant hydrazines. Future applications of electrochemical sensing technology will be made in the development of analytical instrumentation, dosimeters and safety monitors for hypergolic vapors.

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APPENDIX I
OPERATION OF PERMEATION TUBE CALIBRATION SYSTEM

A permeation tube calibration system is necessary for continuous generation of hydrazines vapor mixtures between 0.010 PPM and 5.000 PPM. The preparation of accurate and precise low concentration vapor blends using sealed permeation tubes requires accurate control of the absolute temperature of the permeation tube, precise control and accurate measurement of the diluent flowrate and careful selection of materials in contact with the low concentration blend. Figure 1 is a flow schematic of a Model 670 Kin-Tek Precision Calibration System used for this purpose.

The system operates by maintaining a constant temperature at which a permeation tube emitts a known weight of the vapor at a constant rate into a diluent stream of 99.9998% N_2. N_2 was most frequently used as the diluent since hydrazines vapors were found to be more stable in N_2 than Air. A controlled flow of the diluent gas passes through a preheating chamber which is used to warm the gas to the same temperature at which the tube is thermostatted. It then passes through the permeation tube glass chamber where it picks up and mixes with the vapor. The blended vapor then exits the system and is connected directly to the analyzer via a manifold which allows venting of excess calibration gas through a scrubber - See Figure 2.

To set up the calibration system, the diluent gas source at 25 psi (in the case of N_2, a gas tank) is connected to the intake of the calibration system marked Diluent In and the flow is set to a point where the float of the 1 to 5 liter/min. flowmeter is raised just above zero. The temperature of the system is set to 60°C and allowed to warm-up for 1 hour. A 10 cm. H, MMH, or UDMH permeation tube which has been certified at 60°C is inserted into the system and allowed to equilibrate overnight.

The diluent flowrate is then adjusted to some rate equal to or greater than 2.0 liters/min. and the vapor mixture is ready to be sampled.

The concentration of the vapor can be determined by knowing the emission rate of the tube at 60°C and the flowrate of the diluent. The equation giving the ppm vapor concentration by volume is:

$$C = \frac{P \times K}{F} \times 10^6 \text{ ppm}$$

C = concentration of vapor leaving the system in PPM (volume).

P = emission rate of permeation tube in grams/minute.

K = unit conversion factor peculiar to the particular permeant vapor (24.45/mol wt. of permeant).

F = diluent flowrate measured in liter/minute at 25°C and 1 atm.

(For example using 10 cm. MMH tube at 60°C whose certified rate = 1,086 ng/min. and N_2 diluent flowrate of 2.5 liters/minute.

$$[\text{MMH}] = \frac{1086 \times 10^{-9} \text{ gm./min.} \times 0.531 \text{ liters/gm.}}{2.5 \text{ liters/min.}} \times 10^6 \text{ ppm}$$

$$= 0.231 \text{ ppm}$$

Concentration can be changed by altering flowrate, varying temperature, or using varied quantities and/or lengths of permeation tubes.

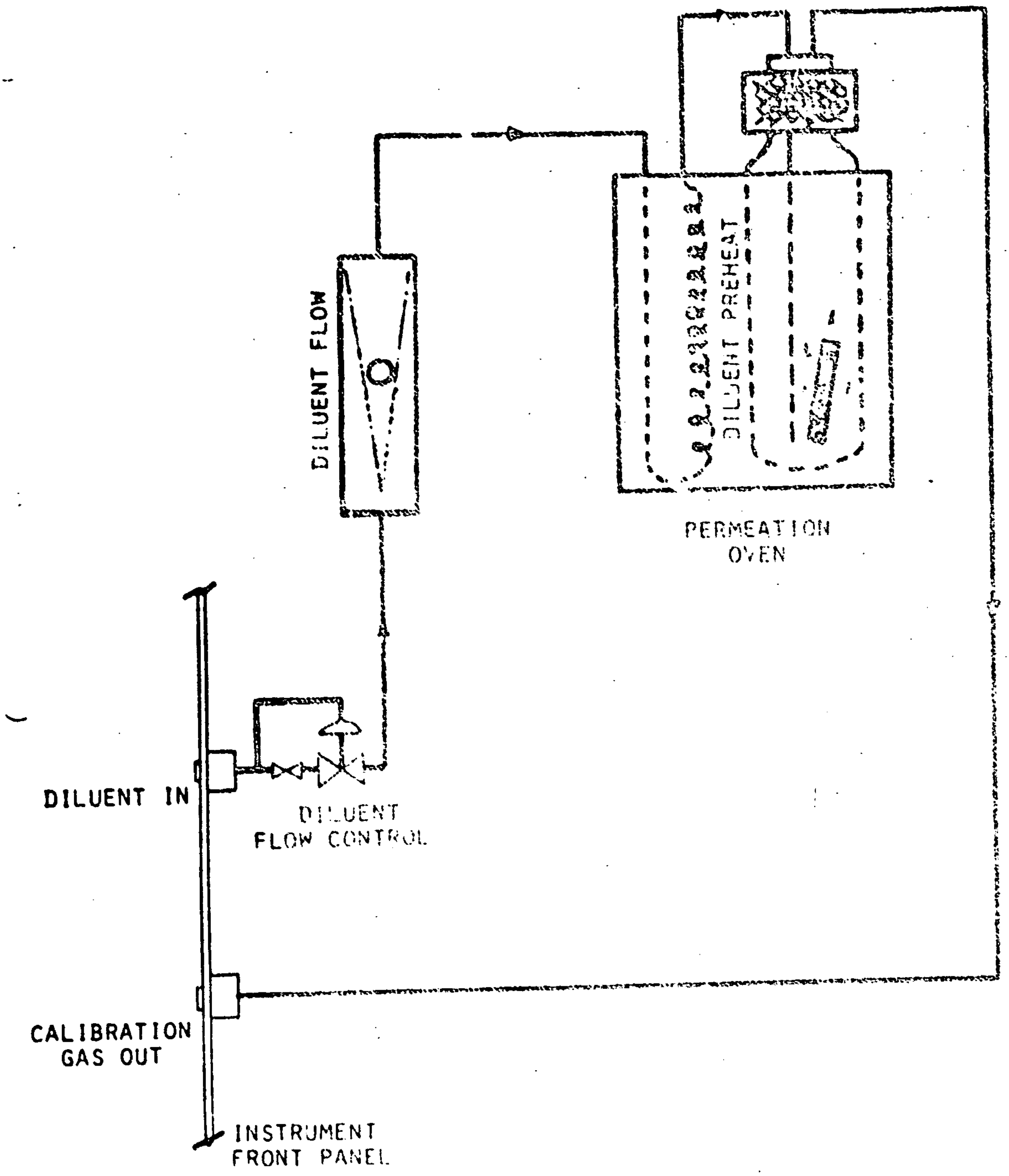

FIGURE 1

FLOW SCHEMATIC - MODEL 6[illegible]
KIN-TEK PRECISION CALIBRATION SYSTEM

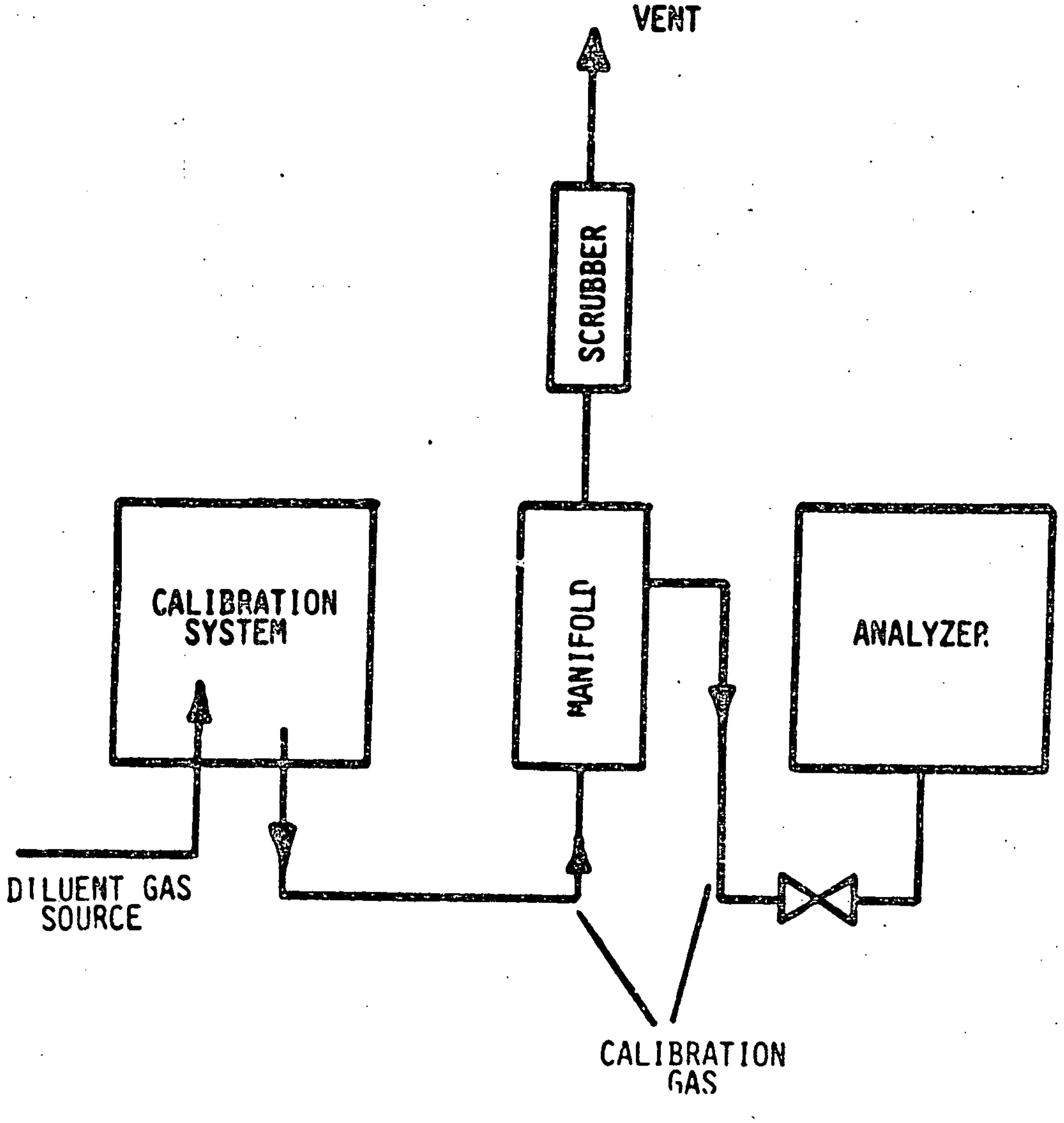

FIGURE 2

SYSTEM FOR CALIBRATING HYDRAZINES ANALYZER

APPENDIX II

OPERATION OF THE HYDRAZINES DILUTION APPARATUS

A. The Hydrazine Dilution Apparatus is used to make hydrazines vapor mixtures of $<$ 1 ppm to $>$ 100 ppm in a continuous manner. The dilution apparatus is shown in FIGURE I-A-1, which is contained in a large fume hood, since the hydrazines are of a toxic and dangerous nature. Also, any bottles or vials of neat hydrazines are kept in the hood.

The apparatus operates by supplying a uniform low flow of liquid Hydrazine, MMH, or UDMH contained in a 10 μℓ Hamilton syringe with a Sage Model 355 syringe pump through a septum sealed port into a custom fabricated glass mixing apparatus through which a diluent gas flows. 99.998% N_2 was most frequently used as a diluent since hydrazines vapors were found to be more stable in N_2 than air. A controlled flow of the diluent gas passes through a pre-conditioning chamber, which may be used to warm the gas stream when relatively high concentrations ($>$ 50 ppm) of Hydrazines are desired. It then passes the syringe needle, picking up the vapor and into a 1 liter bulb which mixes the vapor and diluent gas. The vapor mixture then may be divided by two teflon glass valves and the sampling stream passes a 603 Matheson flowmeter. The vapor mixtures may either be collected in Teflon bags for remote sampling or be used directly from the sample exit stream.

To set up the dilution system, the diluent gas source at 40 PSI (in the case of N_2, a gas tank) is connected to a manifold which supplies the diluent to the glass mixing apparatus. The diluent is adjusted to the desired sample flow (using the sample flowmeter with the vent valve closed) by using the appropriate valve on the manifold. A 10 μℓ syringe is filled with neat MMH, Hydrazine or UDMH from a Teflon valve cap vial containing the proper liquid, moving the plunger up and down several times to wet and remove bubbles from the syringe. [illegible] is injected into the septum port in the glass mixing apparatus, and placed on the syringe pump and secured with the clamp. The syringe pump carriage is [illegible] the pump and the syringe pump is put on a high speed until the carriage is just pushing the syringe plunger. The pump is then adjusted to some lower delivery rate (for example settings 60% flow X $\frac{1}{1000}$). After allowing 15 minutes for the system to reach steady state, the vapor mixture is ready to be sampled.

The theoretical concentration of the vapor can be found by knowing the delivery rate of the liquid and the flowrate of the diluent. The equation giving the ppm vapor concentration by volume is:

$$[\mathrm{MMH,\ H,\ or\ UDMH}] = \frac{AD \times 24450 \frac{\mathrm{ml}}{\mathrm{mole}} \times 10^6 \ \mathrm{ppm}}{MF}$$

where: A = the delivery rate Hydrazines liquid ($\frac{\mathrm{ml}}{\mathrm{min}}$).

D = the density of the liquid (g/ml).

M = the molecular weignt of the liquid ($\frac{\mathrm{g}}{\mathrm{mole}}$).

F = the flowrate of the diluent (ml/min).

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Since the syringe pump delivery 0.024 ml/min for a 10 μℓ syringe at pump setting 100% Flow X 1, A is given by:

$$A = 0.024 \ \mathrm{ml/min} \ \frac{BC}{100\%} \tag{2}$$

where B = % Flow

C = X1, X $\frac{1}{10}$, X $\frac{1}{100}$, or X $\frac{1}{1000}$.

Substituting equation (2) into (1) gives:

$$[\mathrm{MMH,\ H,\ or\ UDMH}] = \frac{0.024 \ \mathrm{ml/min} \ BCD \times 24450 \ \mathrm{ml/mole} \times 10^6 \ \mathrm{ppm}}{M \ F \ 100\%} \tag{3}$$

(For example MMH at pump settings 60% X $\frac{1}{1000}$ and diluent flow of 700 ml/min yields

$$[\mathrm{MMH}] = \frac{0.024 \ \mathrm{ml/min} \times 0.866 \ \mathrm{g/ml} \times 60\% \times \frac{1}{1000} \times 24,450 \ \mathrm{ml/mole} \times 10^6 \ \mathrm{ppm}}{\times 46 \ \mathrm{g/mole} \times 100\% \times 700 \ \mathrm{ml/min}} = 9.4 \ \mathrm{ppm}$$

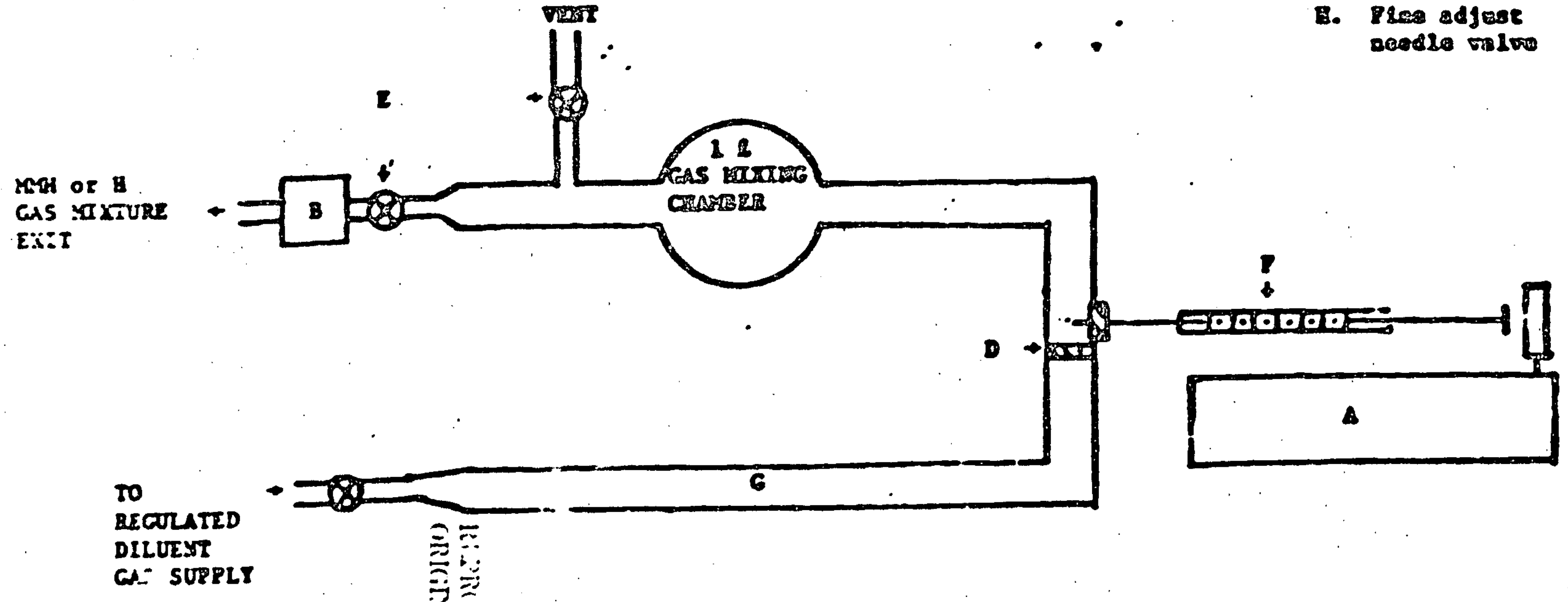
Bag samples are collected by disconnecting the sample stream from the flowmeter and connecting a Teflon bag to the sample stream. The bag is left on until it is 95% full. The bag is then removed and its valve is closed. The sample stream is replaced on the flowmeter. The bag may then be calibrated colorimetrically or electrochemically and used for remote sampling.

For direct sampling the sample stream is connected to a 500 ml plastic bottle with a sample exit and a vent. A portion of the sample stream is then drawn for testing.

FIGURE I-A-1

LEGEND

- A. Sage Model 355 Syringe Pump
- B. 0-2000 cc/min Flowmeter
- C. Septum Sealed Port
- D. Porous Glass Frit
- E. Flow control Teflon/glass valves
- F. Syringe
- G. Diluent Pre-conditioning
- H. Fine adjust needle valve



APPENDIX III-A

DETERMINATION OF GASEOUS MONOMETHYLHYDRAZINE

A. Preparation of PDMAB Dye Solution

1) MIX:

    1.6 g. dimethylaminobenzaldehyde
    15 ml concentrated HCl
    200 ml Methanol

2) Store the dye solution in an amber bottle in a dark place. Shelf life two weeks.

B. MMH Stock Solution, 100 ppm

1) Carefully weigh 0.156 g. of MMH. H_2SO_4 salt on an analytical balance.

2) Completely transfer the MMH . H_2SO_4 to a 500 ml volumetric flask containing about 100 ml 0.1 N H_2SO_4. Shake the flask, dissolving the MMH. H_2SO_4. Fill to the mark with 0.1 N H_2SO_4.

C. Use of the Spectronic 20 Colorimeter

1) With the instrument off, ensure that the "blue" phototube, number CE-A59RX (gray internals), for wavelengths less then 650 nm is installed.

2) Turn the instrument on by rotating the Power - Zero control clockwise and allow the instrument to warm up at least 30 minutes before use.

D. Sampling

1) Pipet 25 ml of 0.1N H_2SO_4 into a midget impinger with a bubbler attachment.

2) Connect the inlet of the impinger to a female fitting to allow easy bag sampling. Connect the outlet to a flowmeter and the flowmeter to a valve and the valve to a pump with tygon tubing (See Figure III-A-1).

3) Turn the pump on and adjust the flowrate between 700 and 200 cc/min with the valve. NOTE the flowrate.

4) Calculate the time needed to collect the desired volume of MMH/N_2 or MMH/Air by the equation:

$$\text{Collection time (Minutes)} = \frac{\text{Volume}}{\text{F.R. (cc/min)}}.$$

Connect the bag sample or other source of MMH vapor to the impinger inlet and start stopwatch.

5) After collecting for the desired time, remove bag or other source of MMH, stop stopwatch and turn off pump.

6) Collect 106 liters at 0.1 ppm MMH, 10.6 liters at 1 ppm MMH, and 1.06 liters at 10 ppm MMH. This volume needs to be determined by trial and error for unknown vapor samples.

E. Analysis

1) Turn on the Spectronic 20 and allow it to warm up.

2) Prepare a blank by pipeting 5 ml of 0.1N H_2SO_4 to one of the test tube cells supplies with the colorimeter.

3) Pipet 5 ml of the sample solution in the impinger to a colorimeter test tube.

4) Pipet 2 ml of the PDMAB dye solution to each of the test tubes.

5) Stop per the test tubes and allow to stand for 30 minutes.

6) After 30 minutes, read the %T as follows:

   a) Set the Spectronic 20 wavelength dial at 457 nm and adjust the zero control so that the meter reads 0%T with the cell holder empty and the cover closed.

   b) Ensure that there are no bubbles in the blank sample and wipe the outside of the cell clean with a tissue. Open the cell holder cover and insert the test tube cell, aligning the mark on the cell with the line on the holder.

   c) Close the cover and adjust the LIGHT control until the meter reads 100%T.

   d) Remove the blank and save for future use.

   e) Ensure that the sample cell contains no bubbles and wipe the outside clean with a tissue. Insert the cell in the holder, aligning the mark on the cell with the mark on the holder.

   f) Close the cover and read %T. NOTE the results.

   g) Repeat, steps b,c,d,e, and f three times and take average %T value.

7) Remove sample from colorimeter. If additional samples have been prepared for measurement, repeat steps 6b through 6g for each sample.

8) Convert the average %T of the sample to A (absorbance) by the formula:

$$A = \log \left(\frac{100}{\%T} \right)$$

9) Obtain the MMH value from the calibration curve.

F. Calculation

The concentration of gaseous MMH in N_2 or air is found by the equation:

$$\text{ppm MMH} = A\,\frac{13.3}{V}$$

A = ppm MMH in the solution sample.

V = volume MMH/N_2 or MMH/Air collected in cc?

G. Calibration Curve

1) Prepare a 10 ppm MMH standard solution by pipeting 10 ml of the stock solution to a 100 ml volumetric flask and diluting to the mark with 0.1N H_2SO_4. Repeat for standard solutions of 8,5,2 and 1 ppm MMH by pipeting 8,5,2, and 1 ml respectively instead of 10 ml.

2) Follow steps E1 through E8 in the analysis using the standard solutions as samples. Plot A, absorbance, vs. ppm MMH on graph paper. Draw the best straight line through the points and extrapolate to 0 ppm.

3) A separate curve shall be prepared for each colorimeter. A new curve, shall be prepared if it is necessary to change the colorimeter lamp or phototube.

4) Standard samples should be run periodically (i.e., one with each days calibrations) to check the accuracy of the calibration curve.

NOTE: This procedure may be modified to fit the individual operators needs.

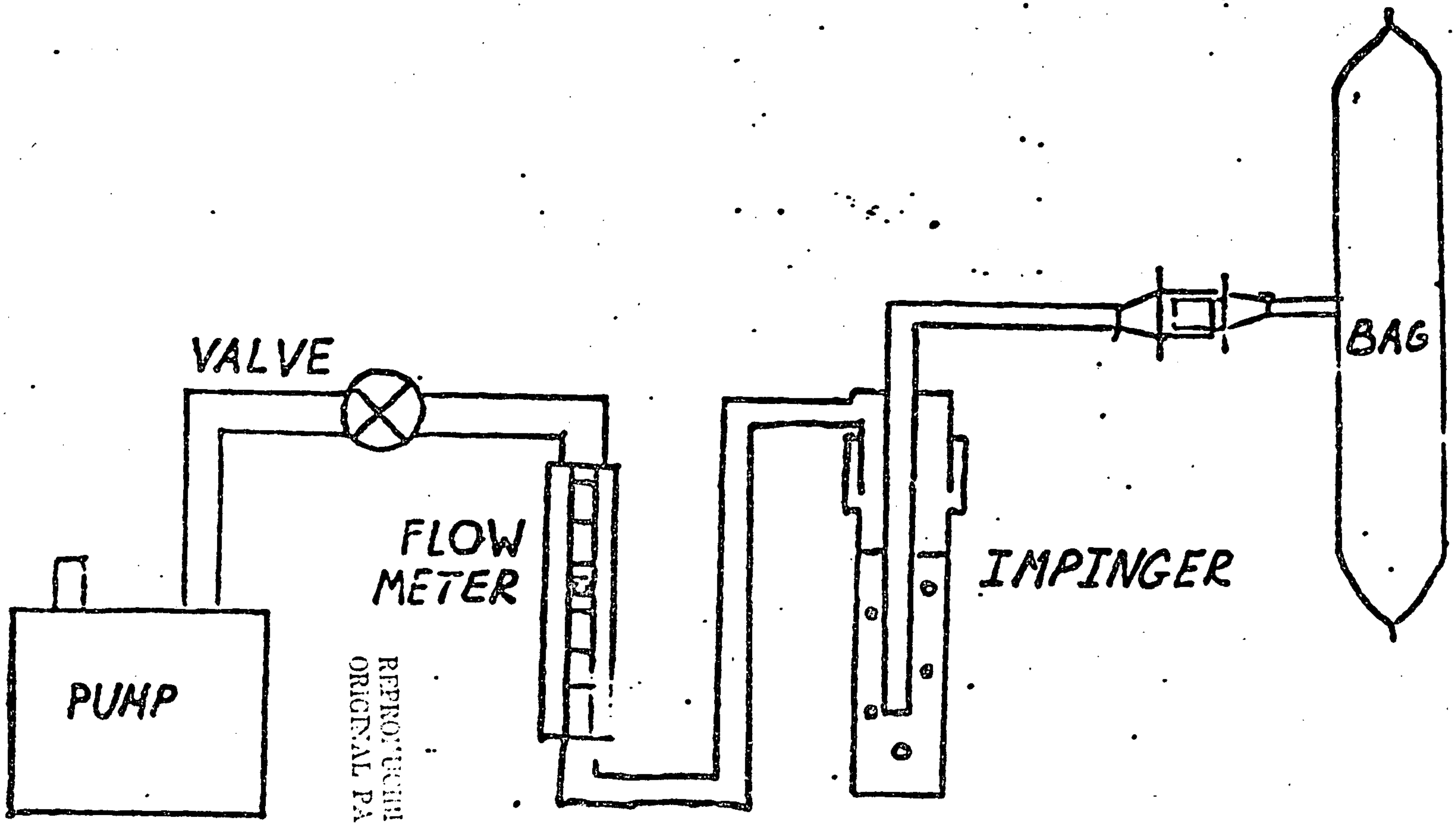


FIGURE III-A-1

APPENDIX III-B

DETERMINATION OF GASEOUS HYDRAZINE

A. Preparation of PDMAB Dye Solution

1) Refer to Section A in the Determination of Monomethylhydrazine Appendix II-A.

B. N_2H_4 Stock Solution, 100 ppm

1) Carefully weigh 0.152 g. of $N_2H_4 \cdot (HCl)_2$ salt on an analytical balance.

2) Completely transfer the $N_2H_4 \cdot (HCl)_2$ to a 500 ml volumetric flask containing about 100 ml 0.1N HCl_2. Shake the flask, dissolving the $N_2H_4 \cdot (HCl)_2$. Fill to the mark with 0.1N HCl.

C. Use of the Spectronic 20 Colorimeter

1) Refer to Section C in the Determination of Monomethylhydrazine; Appendix II-A.

D. Sampling

1) Pipet 25 ml of 0.1N HCl into a midget impinger with a bubbler attachment.

2) Refer to Sections D 2-5 in the Determination of Monomethylhydrazine, Appendix II-A.

3) As a guide, collect 19 liters at 0.1 ppm H, 1.9 liters at 1 ppm H, and 0.2 liters at 10 ppm H.

E. Analysis

1) Turn on the Spectronic 20 and allow it to warm up.

2) Prepare a blank by pipeting 25 ml of 0.1N HCl into a small vial.

3) Transfer the entire impinger sample to a small vial.

4) Pipet 1.25 ml of the PDMAB dye solution to each of the vials.

5) Cap the vials and allow to stand for 20 minutes.

6) After 20 minutes, read the %T as follows:

   a) Set the Spectronic 20 wavelength dial at 457 nm and adjust the zero control so that the meter reads 0%T with the cell holder empty and the cover closed.

   b) Rinse a test tube cell twice with the blank and fill halfway with the blank. Wipe the outside of the cell clean with a tissue. Open the cell holder cover and insert the test tube cell, aligning the mark on the cell with the line on the holder.

c) Close the cover and adjust the LIGHT control until the meter reads 100%T.

d) Remove the blank and save for future use.

e) Rinse a cell twice with the sample and fill halfway with the sample. Wipe the outside clean with tissue. Inser the cell in the holder, aligning the mark on the cell with the mark on the holder.

f) Close the cover and read %T. NOTE the result.

g) Repeat, steps b,c,d,e, and f three times and take average %T value.

7) Remove sample from colorimeter. If additional samples have been prepared for measurement, repeat steps 6b through 6g for each sample.

8) Convert the average %T of the sample to A (absorbance) by the formula:

$$A = \log \left(\frac{100}{\%T} \right)$$

9) Obtain the N_2H_4 value from the calibration curve.

F. Calculation

The concentration of gaseous N_2H_4 in N_2 or air is found by the equation:

$$\text{ppm } N_2H_4 = A \ \frac{19.1}{V}$$

A = ppm N_2H_4 in the solution sample.

V = volume N_2H_4/N_2 or N_2H_4/Air collected in cc?

G. Calibration Curve

1) Prepare a 10 ppm N_2H_4 standard solution by pipeting 10 ml of the stock solution to a 100 ml volumetric flask and diluting to the mark with 0.1N HCl. Repeat for standard solutions of 8,5,2, and 1 ppm N_2H_4 by pipeting 8,5,2, and 1 ml respectively instead of 10 ml.

2) Follow steps E1 through E8 in the analysis using the standard solutions as samples. Plot A, absorbance, vs. ppm N_2H_4 on graph paper. Draw the best straight line through the points and extrapolate to 0 ppm.

3) A separate cover shall be prepared for each colorimeter. A new curve, shall be prepared it if is necessary to change the colorimeter lamp or phototube.

4) Check calibration often by analyzing a standard sample.

APPENDIX III-C

DETERMINATION OF GASEOUS UNSYMMETRICAL DIMETHYLHYDRAZINE

A. Preparation of Buffer Solution

1) MIX: 9.6 g Citric Acid
15.7 g Na_2HPO_4
2 liters distilled water.

2) Adjust the pH to 5.4 (with a pH meter)? with citric acid?

B. UDMH Stock Solution

1) Fill a 500 ml volumetric flask with buffer solution to the line.

2) Transfer (63 x (purity of UDMH)) μℓ of neat UDMH with a 100 μℓ syringe to the flask. Shake the flask.

C. Use of the Spectronic 20 Colorimeter

1) Refer to Section C in the Determination of Monomethylhydrazine Appendix II-A.

D. Sampling

1) Pipet 25 ml of buffer solution into a midget impinger with a bubbler attachment.

2) Refer to Sections D 2-5 in the Determination of Monomethylhydrazine, Appendix II-A, however the flowrate through the impinger should be between 200 and 400 cc/min.

3) As a guide, collect 33 liters at 0.1 ppm UDMH, 33 liters at 1.0 ppm UDMH, and 0.33 liters at 10 ppm UDMH.

E. Analysis

1) Turn on the Spectronic 20 and allow it to warm up.

2) Prepare a 0.1% TPF solution by transfering 0.1 g of trisodiumpentacyanoaminoferrate into 10 ml volumetric flask and filling to the mark with distilled water.

3) Prepare a blank by pipeting 7 ml of the buffer solution to one of the test tube cells supplied with the colorimeter.

4) Pipet 7 ml of the sample solution in the impinger to a colorimeter test tube.

5) Pipet 1 ml of the TPF solution to each of the test tubes.

6) Stop the test tubes and allow to stand for 20 minutes.

7) After 30 minutes, read the %T as follows:

a) Set the Spectronic 20 wavelength dial at 500 nm and adjust the zero control so that the meter reads 0%T with the cell holder empty and the cover closed.

b) Ensure that there are no bubbles in the blank sample and wipe the outside of the cell clean with a tissue. Open the cell holder cover and insert the test tube cell, aligning the mark on the cell with the line on the holder.

c) Close the cover and adjust the LIGHT control until the meter reads 100%T.

d) Remove the blans and save for future use.

e) Ensure that the sample cell contains no bubbles and wipe the outside clean with a tissue. Insert the cell in the holder, aligning the mark on the cell with the mark on the holder.

f) Close the cover and read %T. NOTE the results.

g) Repeat, steps b,c,d,e, and f three times and take average %T value.

8) Remove sample from colorimeter. If additional samples have been prepared for measurement, repeat steps 6b through 6g for each sample.

9) Convert the average %T of the sample to A (absorbance) by the formula:

$$A = \log \left(\frac{100}{\%T}\right)$$

10) Obtain the UDMH value from the calibration curve.

11) NOTE: UDMH impinger sample should be analyzed within an hour of collection.

F. Calculation

The concentration of gaseous UDMH in N_2 or air is found by the equation:

$$\text{ppm UDMH} = A \frac{9.55}{V}$$

A = ppm UDMH in the solution sample.

V = volume UDMH/N_2 or UDMH/Air collected in cc?

Calibration Curve

1) Prepare a 10 ppm standard solution by pipeting 10 ml of the stock solution to a 100 ml volumetric flask and diluting to the mark with 0.1N H_2SO_4. Repeat for standard solutions of 8,5,2 and 1 ppm MMH by pipeting 8,5,2, and 1 ml respectively instead of 10 ml.

2) Follow steps E1 through E8 in the analysis using the standard solutions as samples. Plot A, absorbance, vs. ppm MMH on graph paper. Draw a curve through the points and extrapolate to 0 ppm.

3) A separate curve shall be prepared for each colorimeter. A new curve, should be prepared if it is necessary to change the colorimeter lamp or phototube.

Drawing CSC-852 is the electronic circuitry that describes the prototype toxic level analyzer's electronic components and design.

The following sections describe the function for each of the components in the circuitry.

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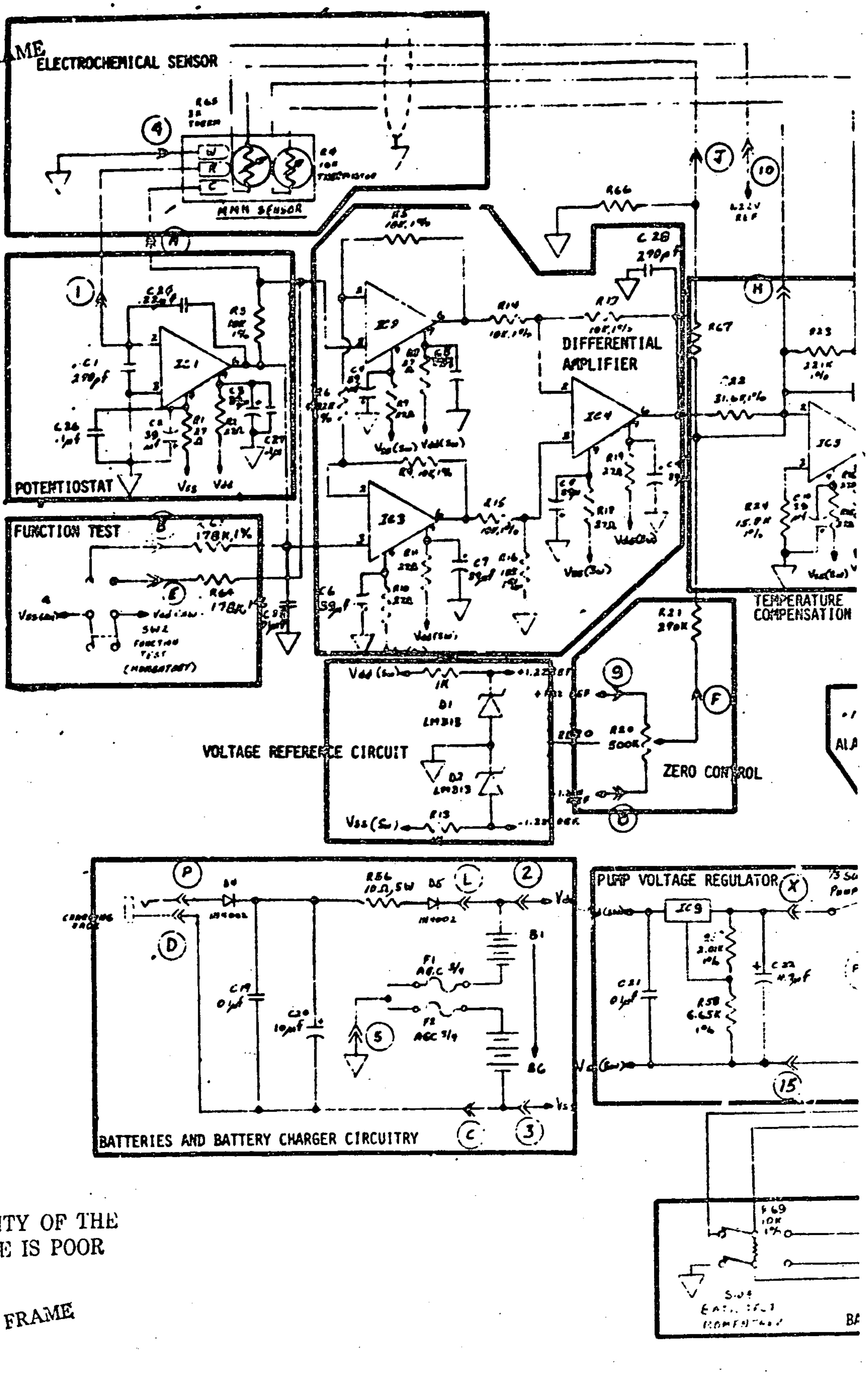
FOLDOUT FRAME



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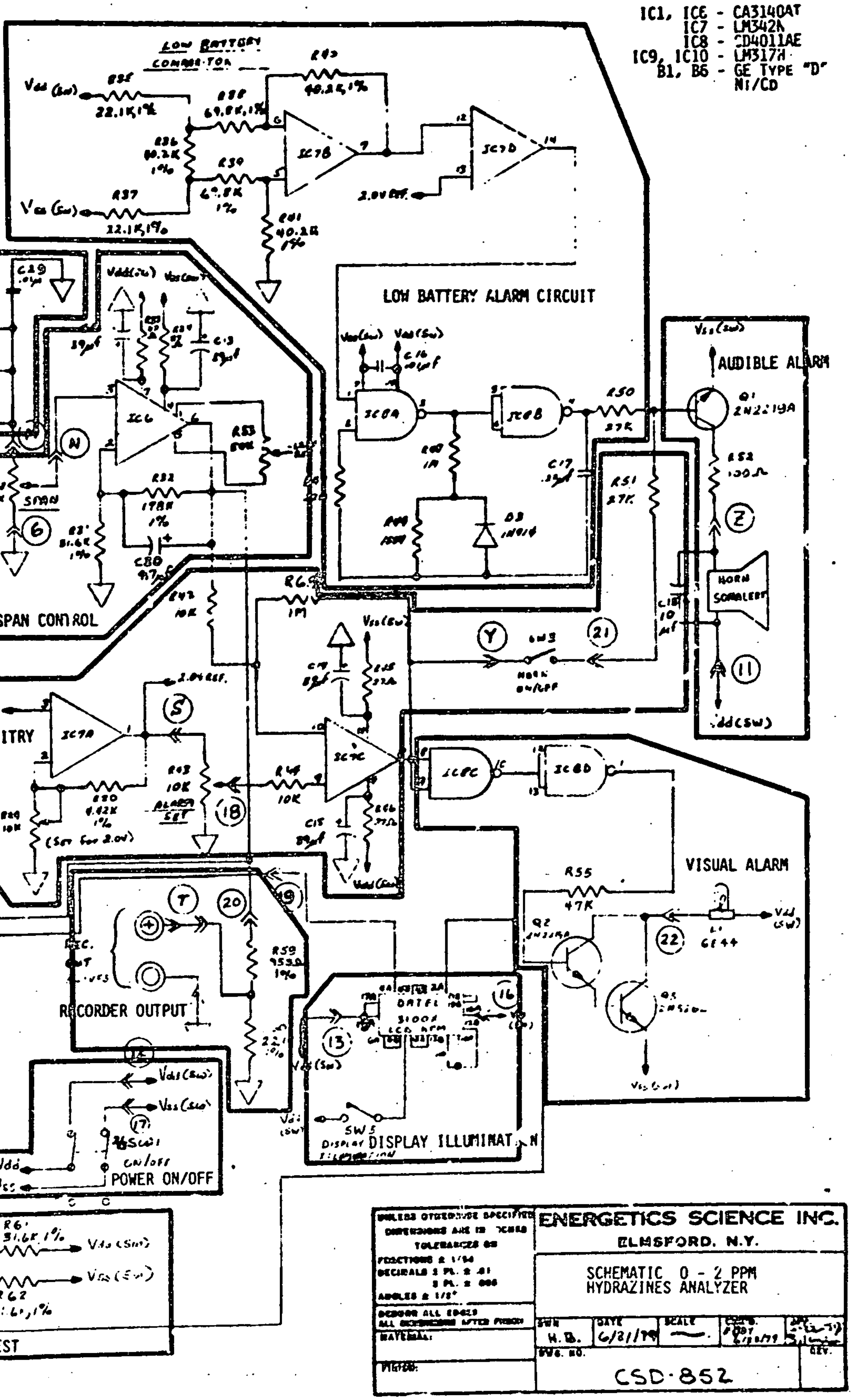
FOLDOUT FRAME

2 FOLDOUT FRAME

IC1, IC6 - CA3140AT
IC7 - LM342A
IC8 - CD4011AE
IC9, IC10 - LM317H
B1, B6 - GE TYPE "D" NI/CD



UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES
TOLERANCES ON
FRACTIONS ± 1/64
DECIMALS 2 PL. ± .01
3 PL. ± .005
ANGLES ± 1/2°
DEBURR ALL EDGES
ALL DIMENSIONS AFTER FINISH
MATERIAL:
FINISH:

ENERGETICS SCIENCE INC.
ELMSFORD, N.Y.

SCHEMATIC 0 - 2 PPM
HYDRAZINES ANALYZER

DWN H.B.
DATE 6/21/79
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APPENDIX IV

ELECTRONIC CIRCUIT DESCRIPTION

Potential Circuit

The potentiostat's function is to maintain a constant potential difference (Erw) between the working and reference electrodes of the sensor. Operational amplifier IC-1 performs this task. The potential Erw between the reference and working electrode is kept exactly equal, the voltage at the positive input (pin 3) of IC-1. Variations in the resistance of the electrolyte have no effect on Erw. Moreover any change in the electrochemical potential of the counter electrode is also compensated.

When gas is oxidized at the working electrode, the potentiostat provides the power to sustain the reaction. The output of IC-1 (pin 6) will swing negative and the necessary current goes through R3 to the sensor. This current, which is proportional to the gas concentration, causes a voltage drop across R3. This voltage drop is applied to the differential amplifier.

Differential Amplifier

IC-2, IC-3 and IC-4 constitute the differential amplifier. The use of three Op Amps results in a "classic" instrumentation amplifier. This configuration results in high input impedance, low offset and drift, low nonlinearity, stable gain and low effective output impedance. The gain of this section is 5.97. The output of the differential amplifier (IC-4, pin 6) is applied to the temperature compensation amplifying circuit.

Temperature Compensation Circuit

This circuit is configured as a summing amplifier with temperature dependent gain. At 25°C the gain is unity. To compensate for variations in the electrochemical reaction rate of the sensor a thermistor (R4) is placed in the feedback loop of IC-5. The sensor typically has a positive temperature coefficient while the thermistor has a negative temperature coefficient. The feedback resistance of IC-5 (R4, R23, R27) is scaled to counteract the sensors characteristics. Since the gain is varied there is no dependence on gas concentration. Should zero temperature compensation be required, provisions have been made to use thermistor R65 and resistors R66 and R67. The background current of the sensor nulled out by the zero control R20. However, the background current is temperature dependent resistor, current is added or subtracted from the summing junction of IC-5 thereby compensating for variations in sensor background current with temperature.

Voltage Reference Circuit

Various reference voltages are required throughout the instrument electronics. Diodes D1 and D2 provide the basis for the reference voltages. They are temperature compensated, low voltage reference diodes employing a band gas technique to insure stability. The nominal voltage of these devices is 1.20 V.

Zero Control

The zero adjust potentiometer (R20) is connected to the ± 1.20 reference voltages. The center tap voltage permits current to pass through R21 and into the summing junction of IC-5. This technique allows the instrument to be zeroed.

Span Control

The output of the temperature compensation circuit (IC-5, pin 6) is applied to the span control potentiometer (R28). Amplifier IC-6 is a voltage follower with gain. In this case the gain is 6.6. Potentiometer R53 is used as a zero offset adjust. In practice, the span control potentiometer is rotated counter-clockwise so that the center tap is at ground potential. R53 is now adjusted until the LCD display reads .000. Capacitor C30 is used to prevent IC-6 from oscillating. The output of this circuit is applied to various circuits through resistor R42. These circuits include the LCD display, alarm comparitor and recorder output.

Alarm Circuitry

IC7-A is used as a voltage follower with variable gain. The 1.20V reference voltage is applied to the non-inverting input of IC7-A. In practice, R29 is adjusted so that the output of IC7-A (pin 1) reads 2.00V. This 2.00V signal is applied to the alarm set control (R43). Since 2.00V represents the full scale of the instrument, rotating the alarm set control will provide comparitor IC7-C with an input ranging between zero and 100% full scale. The other input to IC7-C is the analog signal representing the parts per million of the gas being detected. As long as the analog signal input is less than the alarm set voltage, the output of IC7-C will remain low. When the analog voltage input exceeds the alarm set voltage, the output of IC7-C will be switched high.

Visual Alarm

When the output of comparitor IC7-C goes high, NAND gate IC8-D also goes high providing current to the base of Q2. Transistors Q2 and Q3 are arranged in a Darlington configuration to provide sufficient current to illuminate the GE44 lamp. This lamp will remain illuminated until the analog signal falls below the alarm set level.

Audible Alarm

When the output of comparitor IC7-C goes high the audible alarm is activated through the Horn ON/OFF switch (SW-3). Transistor Q1 is used to ensure that sufficient current is available to drive the audible alarm. The audible alarm will be silenced if the analog signal falls below the alarm set level or if the Horn ON/OFF switch (SW-3) is placed in the OFF position.

LCD Display

The LCD display is a modified DATEL Model 3100X digital panel meter. It has a full scale reading of 1.999. In positive over-range the display ready 1. with the remainder of the display blank. In negative over-range the display shows -1. with the remainder of the display blank. Positive over-range occurs when the analog voltage input exceeds 1.999V. Negative over-range occurs when the analog voltages is less than -1.999V. The DATEL 3100X is modified by the addition of two lamps (GE-1784) to provide illumination in low light environments. Putting the display illumination switch SW-5 in the ON position will turn on these lamps to provide viewing in dark areas. Lamp life is rated at 1000 hrs.

Recorder Output

The recorder output provides both analog signal and power to run a portable recorder. The analog signal is 0-1V representing 2 ppm. The recorder output circuit is designed to utilize the 1000 ohm recorder impedance. When connected to the ECOLYZER, the recorder impedance is in parallel with R60. This parallel combination is in series with R59 and together act as a voltage divider, halving the 2V full scale signal of the instrument.

NOTE: If a high input impedance voltmeter is used, a 1000 ohm, 1% resistor must be placed across its input.

Power ON/OFF

In order to ensure minimum warm-up time, the sensor is always kept under potentiostatic control. However, to minimize battery drain, power to the remainder of the instrument is turned off. The power ON/OFF switch performs this function. The power ON/OFF switch also is used to turn on the pump.

Battery Test

Battery test switch SW4 samples both positive and negative battery supplies and displays the sampled voltage on the LCD display. Resistors R61, R69 and R62 are used as voltage dropping resistors. The voltage drop across R69 is displayed on the LCD meter. Any voltage above 1.000V shows good batteries; any reading below 1.000V indicates that the batteries require recharge. Readings below 1.000V will occur when the Ni/Cd batteries reach an individual voltage of 1.22V.

Low Battery Alarm Circuit

IC7-B samples part of the battery voltage appearing across R36. The output of IC7-B is the input to comparitor IC7-D. As long as this output is above 2V the batteries do not require recharge. Below 2V the comparitor output goes low turning on an oscillator comprised of NAND gates IC8-A and IC8-B. The oscillator frequency is approximately 0.3Hz. Use of diode D3 causes the wave form to be asymmetric. The oscillator output is applied to the base of Q1 which energizes the audible alarm in a series of "beeps".

NOTE: An alarm caused by a high gas concentration will override the low battery circuit and the alarm will sound continuously.

Function Test

The function test enables the user to check the instruments electronics except for the potentiostat circuit. By depressing function test switch SW2, a current is fed across R3. The additional voltage drop is sensed by the differential amplifier and is applied throughout the various circuits to the panel meter. This injected voltage should cause audio and visual alarms to energize (depending on the positions of the Span control and Alarm Set control).

Batteries and Battery Charger Circuitry

The instrument is powered by six "D" size nickel cadmium rechargeable batteries each having a capacity of 4 Ampere-hours. Charging is accomplished by connecting the charger to the charging jack. Resistor R56 controls the charging current and diode D4 prevents damage due to an accidental shorting of the charging jack. Charging time is overnight (16 hrs).

Pump Voltage Regulator

This circuit employs a LM317M voltage regulator (IC-9) to provide a constant voltage to the pump regardless of load. It will supply sufficient current for the starting torque and will adjust for varying load conditions and battery voltage. The voltage is regulated at 4.3V.

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