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A STUDY

FOR

HYPERGOLIC VAPOR SENSOR DEVELOPMENT

FINAL REPORT - APRIL 8, 1977

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FOREWORD

This report was prepared for the National Aeronautics and Space Administration, Kennedy Space Center by Energetics Science, Incorporated under contract NAS 10-8982 during the period February 8, 1977 to April 6, 1977. The contract performance period was from June 8, 1976 to February 8, 1977 and was entitled "A Study For Hypergolic Vapor Sensor Development". The ESI Program Managers were Dr. K.F. Blurton and Dr. J.R. Stetter, the Principal Investigator was Dr. J.R. Stetter, and the NASA contract Technical Manager was Mr. William R. Helms, Senior Design Engineer, code DL-DED-3, NASA, Kennedy Space Center, Florida.

Acknowledgements for the success of the work performed under this contract must include the entire ESI staff but in particular Joseph C. Delfino, Howard W. Bay, and Sydney Krivin for engineering, design, and documentation of the prototype instruments which were constructed and Edgar R. Torres of our laboratory research staff for this conscientious and thorough experimentation. Further, this program could not have achieved its goals without the full support, cooperation, and encouragement of Energetics Science management, Mr. H.C. Lieb, Chairman and Mr. R.E. Lieb, President. Expert consultations with the NASA Technical Manager and the Naval Research Laboratory were invaluable during the conduct of this program.

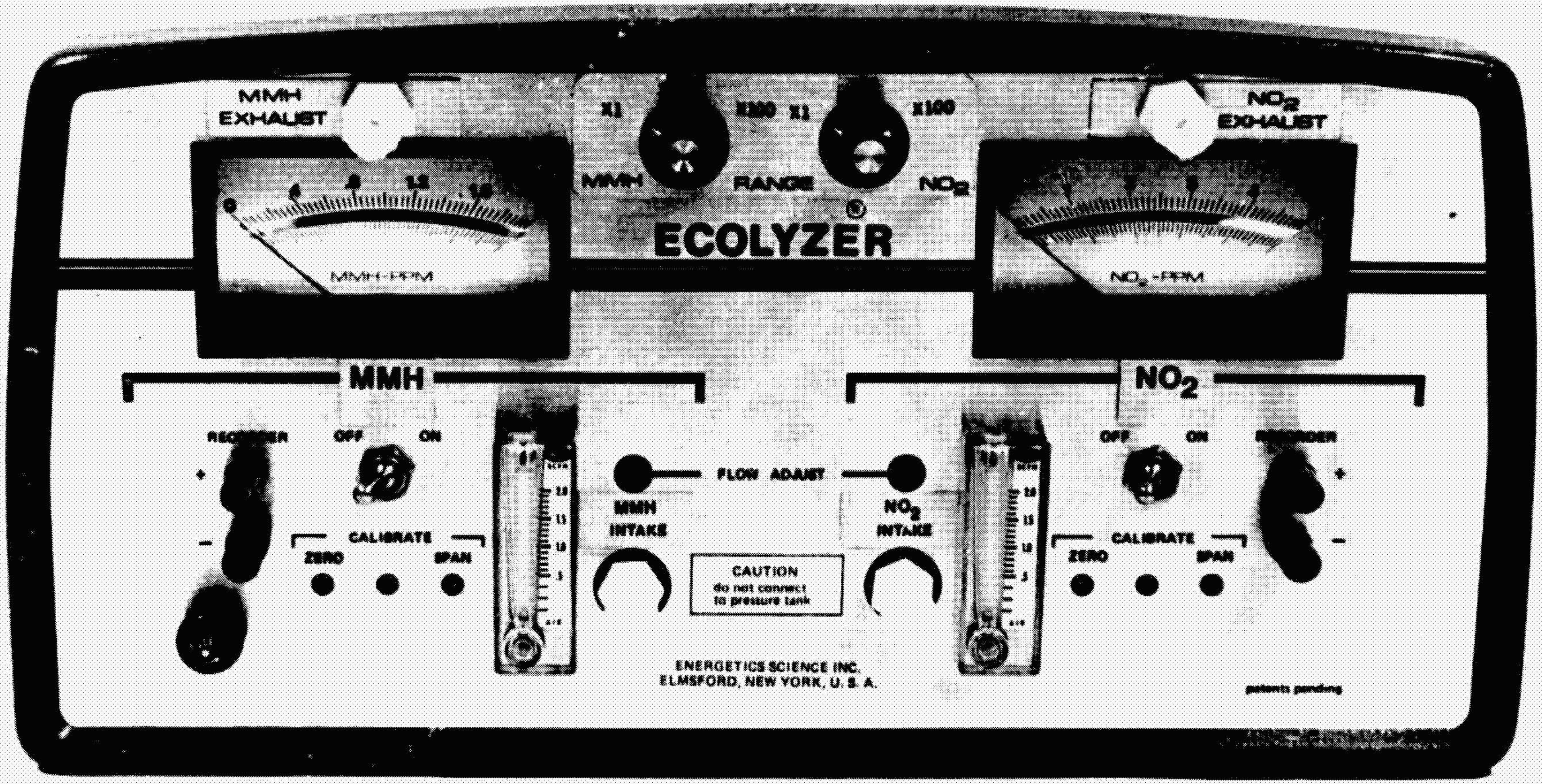
ABSTRACT

There has been recent research indicating the toxicity of NO_2 and hydrazines (H, MMH, and UDMH) toward humans. This has led to the need for fixed installation continuous measurement instruments providing a realtime monitoring capability for hydrazines and NO_2 at ppm and sub-ppm levels.

The objectives of this study were; a) to investigate the use of an electrochemical technique for MMH and NO_2 measurement, b) develop specific MMH and NO_2 electrochemical sensors, and c) to design and fabricate two engineering prototype instruments capable of continuous, specific, simultaneous and independent measurement of both MMH (H and UDMH) in the ranges 0-2, 0-20, and 0-200 ppm; and NO_2 in the ranges 0-5, 0-50, and 0-500 ppm.

During this program experimental techniques for preparation, handling, and analysis of hydrazines vapor mixtures at ppb and ppm levels were developed. Two approaches to NO_2 instrument design were evaluated including specific adsorption and specific electrochemical reduction. Two approaches to hydrazines monitoring were evaluated including catalytic conversion to NO with subsequent NO detection and direct specific electrochemical oxidation.

Finally two engineering prototype MMH/NO_2 monitors were designed and constructed as shown on page iii of this report. The instruments were characterized and delivered to NASA at the conclusion of this program.



ECOLYZER MODEL 7630
PROTOTYPE MMH/NO_2 ANALYZER

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I. INTRODUCTION

Future space programs at Kennedy Space Center involve the use of hydrazine, substituted hydrazines and nitrogen dioxide. Recent research indicates that the hydrazine compounds are carcinogenic and it is necessary, therefore, to monitor the concentration of these gases in the vicinity of the fueling, handling, and storage locations and wherever worker exposure may occur. There are no hydrazine monitors commercially available meeting KSC's requirement for a cost effective instrument which is accurate, reliable, and simple to operate and maintain.

Many approaches have been taken to measuring the nitrogen oxides in the atmosphere (1-3). One of the earlier techniques is chemiluminescence (4-7). However, this suffers from limitations such as: 1) the need to convert NO_2 to NO prior to analysis (3), 2) NO_2 is measured by difference introducing additional uncertainties (7), 3) the need to pre-filter other interfering nitrogenous compounds (e.g., NH_3) (8), 4) interference from water vapor and carbon dioxide (9), and 5) high power requirements which limit the ability to make the instrument truly portable (10).

Presently, the analysis of hydrazines in air is at best a difficult problem. A variety of techniques have been investigated including the earlier methods of colorimetry and sophisticated instrumental analyses involving chromatography, mass spectrometry, spectroscopy and electrochemistry (11, 12, 13). All of these methods except the electrochemical (11) lack either the simplicity, reliability, sensitivity, continuous measurement capability, or the cost-effectiveness necessary to meet present requirements. Within the scope of this program several of these techniques including colorimetry and gas chromatography were evaluated for potential application as a reference analytical method for the electrochemical analysis technique.

During this program a Hydrazines/NO_2 monitor was developed and tested in order to overcome these limitations and meet the needs of Kennedy Space Center. It was modeled after the 7000 Series NO/NO_2 ECOLYZER produced by Energetics Science, Inc. This technology (14, 15) is an electrochemical technique using a proprietary three electrode sensor and Teflon-bonded diffusion electrodes which offer significant advantages of improved accuracy, stability, selectivity, and reliability over other conventional electrochemical systems.

The following report describes the major technological findings of this study in detail and the development, design, fabrication, and laboratory testing of the two prototype hydrazines/NO_2 monitors which were capable of direct continuous measurement of hydrazines (H, MMH, and UDMH) at ppb levels. The application of the electrochemical technique for analysis and gas monitoring have resulted in a significant advance in the state of the art of analytical measuring techniques for hydrazine (H), monomethlyhydrazine (MMH), and 1,1-dimethylhydrazine (UDMH) vapors.

1) Program Goals

The overall objective of this study was to develop and test an engineering prototype hydrazines (H, MMH, and UDMH) sensor and subsequently to fabricate two instruments which contain both an hydrazines and a nitrogen dioxide sensor system. The instrument package will provide a reliable, sensitive, accurate, rapid, cost effective, and operationally simple method for the continuous and/or intermittant simultaneous and independent measurement of NO_2 and hydrazine vapors in air or a diluent gas.

The initial specific design goals are summarized in Table I. Item 9 was modified during contract performance and these instruments were designed to utilize AC source power only. Portable battery operated units are under development independently.

The following sections of this report detail the work performed from June 8, 1976 to February 8, 1977 and the characteristics of two engineering prototype instruments (ECOLYZER Model 7630 MMH/NO_2 Analyzers) constructed under NASA contract NAS 10-8982.

TABLE I

PROTOTYPE INSTRUMENT DESIGN GOALS

	Function	Design Goal
1.	Operating Principle	a) Electrochemical sensor for specific NO_2 analysis. b) Electrochemical sensor for specific hydrazine vapor analysis or quantitative catalytic conversion of hydrazines to NO with subsequent analysis using a specific NO electrochemical sensor.
2.	Specificity	NO_2 instrument does not respond to hydrazines and hydrazines section of the instrument does not respond to NO_2. Neither instrument responds to N_2, O_2, H_2, He, Ar, CO, CO_2, CH_4, or Freon.
3.	Sensitivity	Instrument ranges are: NO_2 - 0-5, 0-50, 0-500 ppm NO_2 N_2H_4 - 0-1, 0-10, 0-100 ppm H MMH - 0-2, 0-20, 0-200 ppm MMH UDMH - 0-5, 0-50, 0-500 ppm UDMH
4.	Accuracy	Instrument accuracy is: NO_2 - ±50% at 0.5 ppm NO_2 and ±5% at 500 ppm NO_2 H - ±50% at 0.1 ppm and ±5% at 100 ppm MMH - ±50% at 0.2 ppm and ±5% at 200 ppm UDMH - ±50% at 0.5 ppm and ±5% at 500 ppm
5.	Resolution	NO_2 - ± 50 ppb H - ± 10 ppb MMH - ± 20 ppb UDMH - ± 50 ppb
6.	Zero and Span drift	≤ ± 10% of full scale over 60 days
7.	Response Time	30 seconds to 90% of signal
8.	Stability	Performance of above specifications within: Temperature of 0-35°C Relative Humidity of 10-95% Pressures of 29-31 in. Hg

TABLE I (continued)

	Function	Design Goal
9.	Power Requirements	AC/DC operation 8 hours on batteries 16 hours recharge at 115 VAC 30 days continuous operation
10.	Output	Independent panel meters for NO_2 and hydrazines. Analog 0-5V recorder output schunted by 0.25 μf into > 100 KΩ Isolated output.
11.	Size and Weight	8" x 8" x 16" and < 20 lbs.

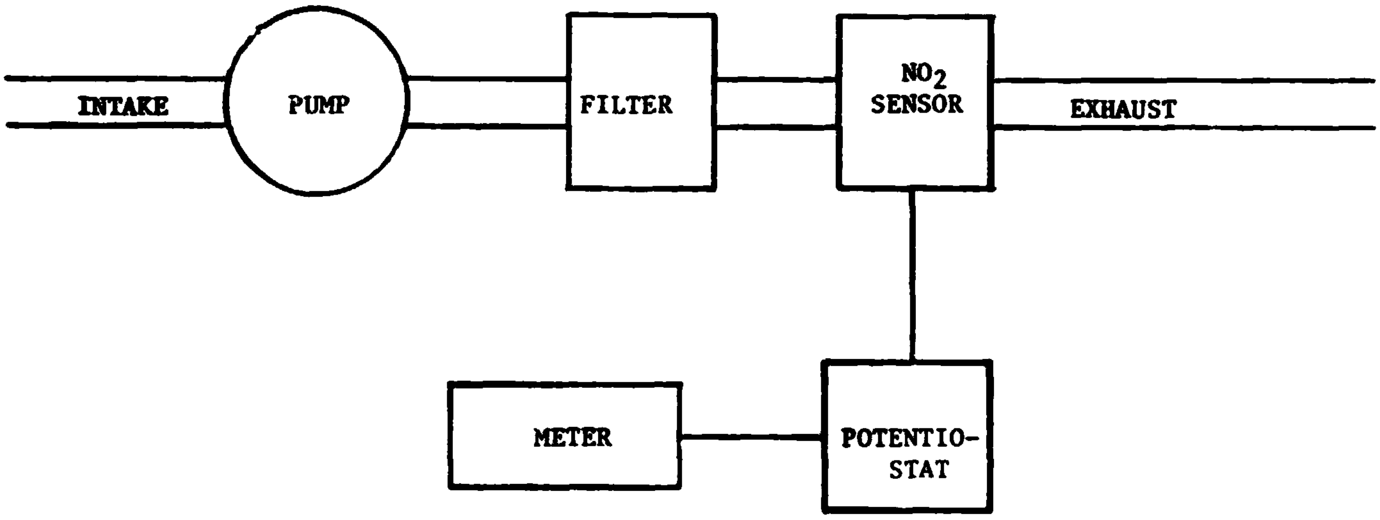
2) ECOLYZER Instrument Design

Successful completion of these design goals demand that a selective continuous electrochemical analysis scheme be developed for NO_2 and for hydrazines. The approaches to each analysis are now discussed.

a) Selective NO_2 Analysis

A successful scheme for the continuous analysis of NO_2/air mixtures is part of ESI's present gas monitoring technology (14, 15) and it it illustrated in FIGURE 1. It consists of an air sampling pump, particulate filter, sensor specifically responsive to NO_2, potentiostatic control and amplification circuitry and readout device. This system was found to meet all specificity requirements (Table I, Function 2) except that of hydrazine interference.

FIGURE 1: SELECTIVE NO_2 ANALYSIS SCHEME



Two approaches were investigated to increase the selectivity of this method prior to final instrument design; 1) develop a selective NO_2 sensor and 2) develop a selective filter for removal of hydrazine prior to analysis in the NO_2 sensor. Clearly either method is suitable, however, the former is preferred since it has significant advantage over the use of consumable filters. Both procedures were evaluated during the test program.

b) Selective Hydrazines (H, MMH, and UDMH) Analysis

The planned approach to instrument development included the investigation of two schemes for hydrazines analysis and their evaluation for potential instrument design.

The first scheme illustrated in FIGURE 2A consists of flow controlled continuous sampling of the ambient, its particulate filtration and subsequent catalytic conversion of hydrazines in a catalytic reactor to NO, detection by a specific NO sensor and readout of the concentration of NO which is directly proportional to the concentration of input hydrazine.

The second analysis scheme illustrated in FIGURE 2B consists of direct electrochemical detection of hydrazines in a similar scheme to the NO_2 analysis (FIGURE 1). The sensor developed for this purpose is specific for hydrazine and linearly responsive to hydrazine concentration in the sampled gas mixture.

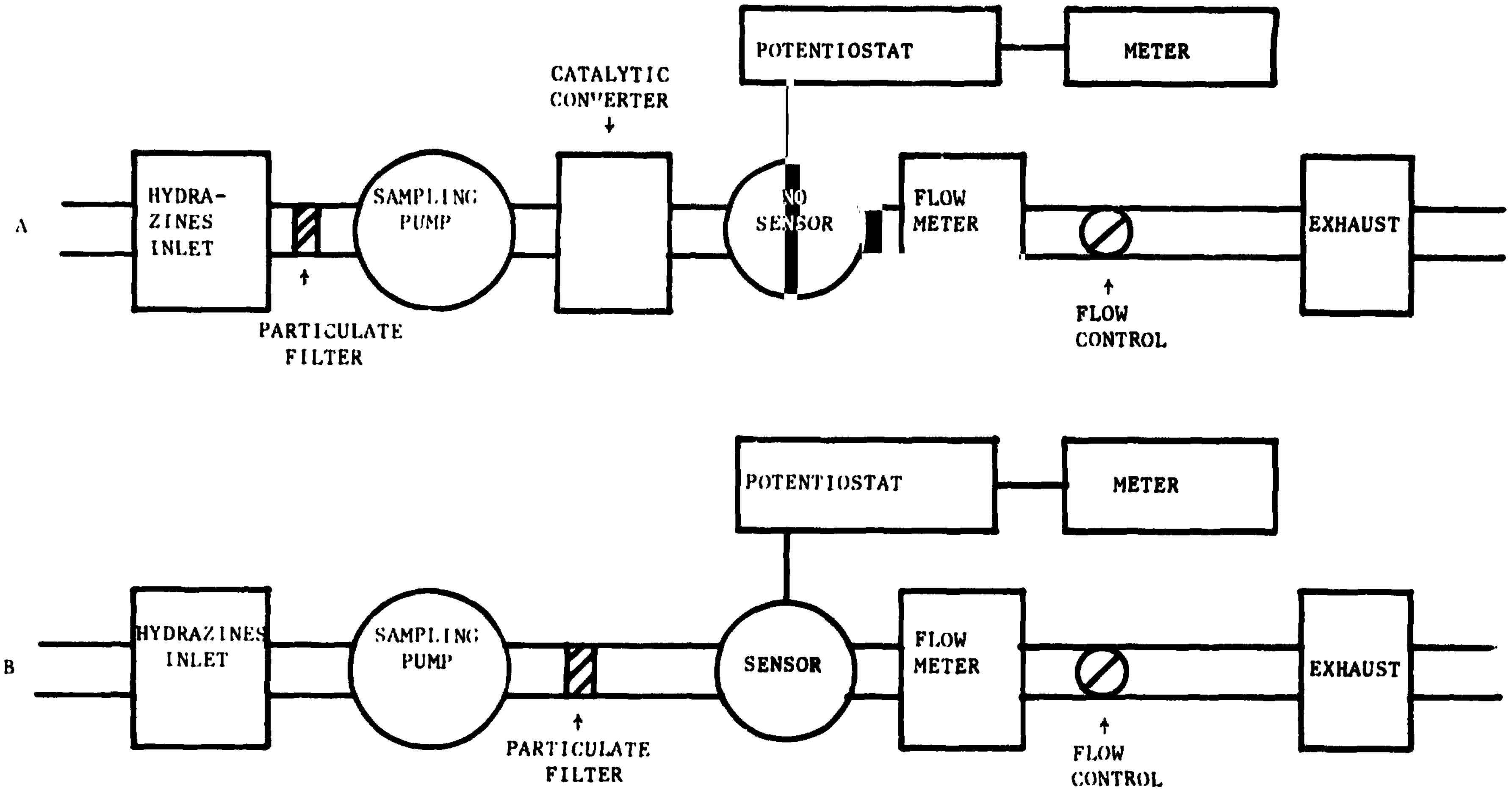


FIGURE 2 SELECTIVE HYDRAZINES ANALYSIS SCHEMES

A) DETECTION WITH PRIOR CONVERSION TO NO

B) DIRECT ELECTROCHEMICAL DETECTION

II. EXPERIMENTAL TECHNIQUES

1) Electrochemical Sensors and Test Procedures

A schematic diagram of the electrochemical sensor design is shown in (FIGURE 3). The three electrodes are all Teflon-bonded diffusion electrodes prepared by spraying a catalyst-Teflon dispersion onto a hydrophobic Telfon film. The catalyst materials were all purchased as high surface area powders and include Platinum, Gold, Palladium, Iridium, Ruthenium, Rhodium and Carbon. These electrodes were sealed to a polypropylene chamber which was subsequently filled with electrolyte. The aqueous electrolyte, either 28% H_2SO_4 or 23% KOH, was prepared from reagent grade materials and triply distilled water.

The gold and platinum leads from the sensor electrodes were attached to a potentiostat capable of variable bias (FIGURE 4). The reference electrode was Pt/air and even though it was not thermodynamically reversible it was stable to ±0.01V at approximately 1.0 ±.030V in acid electrolyte vs. the normal hydrogen electrode.

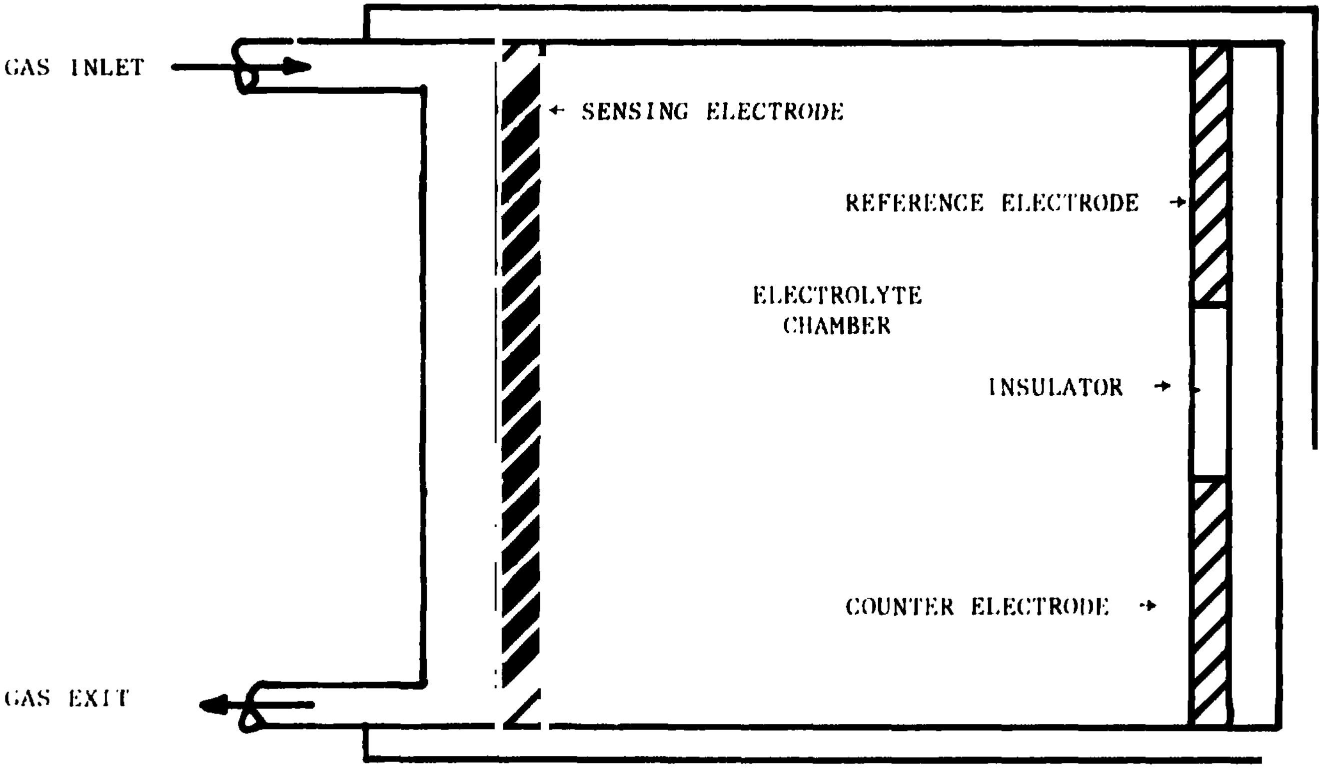


FIGURE 3 SCHEMATIC OF ELECTROCHEMICAL SENSORS

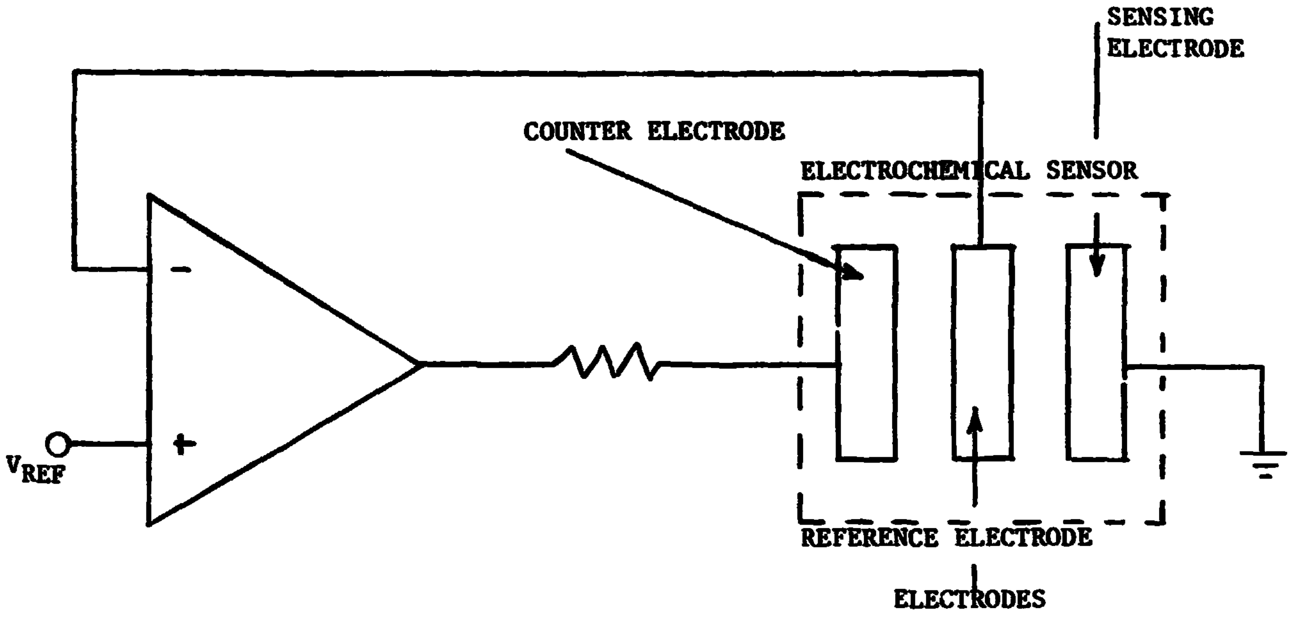


FIGURE 4 POTENTIOSTAT AND SENSOR ELECTRODES

During sensor evaluation, gas mixtures were passed over the back (gas) side of the sensing electrode at constant flow rate, typically 700 cc/minute, and the current produced by electrochemical reaction in the sensor flowing between the sensing and counter electrodes was monitored.

The sensors currents were all measured by monitoring the voltage drop across a precision resistor (typically 1K) in series with the sensing electrode and displaying this voltage on a strip chart recorder. Background currents were measured for the sensor in a "static" condition (no gas flow through the sensor) and in a dynamic or "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 were obtained by filling gas sample bags with the desired mixture and, by using an air sampling pump, drawing this gas into the sensor at flow rates 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.

2) Catalyst Studies

To evaluate the potential of the catalytic conversion scheme for hydrazine analysis instrumentation a series of catalysts were prepared which are listed in Table II along with the technique used for their preparation.

A portable catalytic reactor (16) illustrated in FIGURE 5 was used to evaluate the conversion technique. It consists of several layers of selected insulation to minimize heat loss and allow battery operation at elevated temperatures and temperature control and measurement circuitry (FIGURE 6) to facilitate operation over a wide range of temperatures. The reaction chamber is a quartz tube wound with a nichrome heater wire with temperature control and indication provided by a calibrated chromel-constantan thermocouple positioned in the insulation near the center of the heated zone.

The rate of the catalytic reaction is temperature dependent and therefore, the reactor tube temperature profile was studied. A temperature gradient of only 20°C was found across the reactor (with the

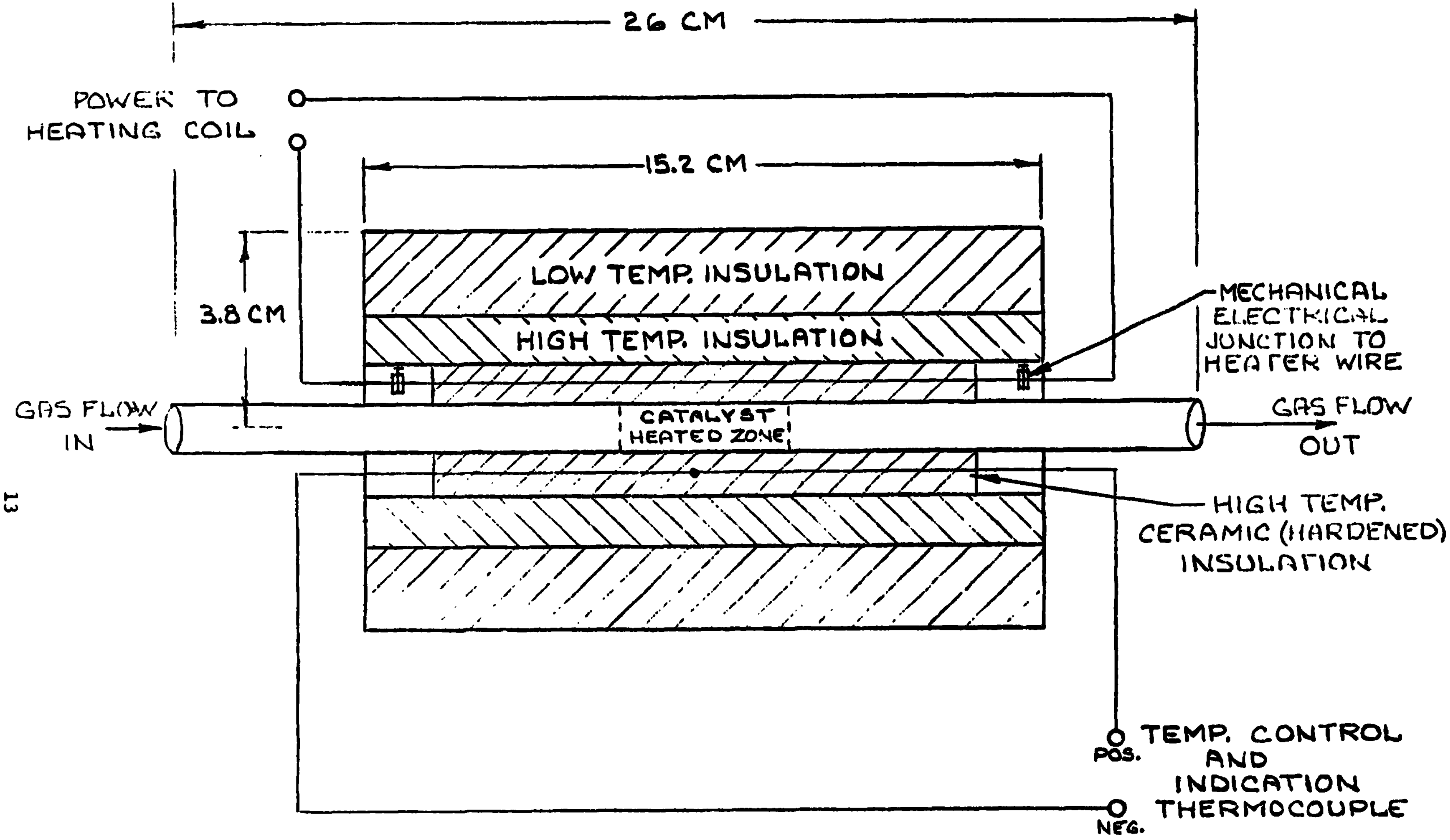


FIGURE 5 SCHEMATIC OF HIGH TEMPERATURE REACTOR

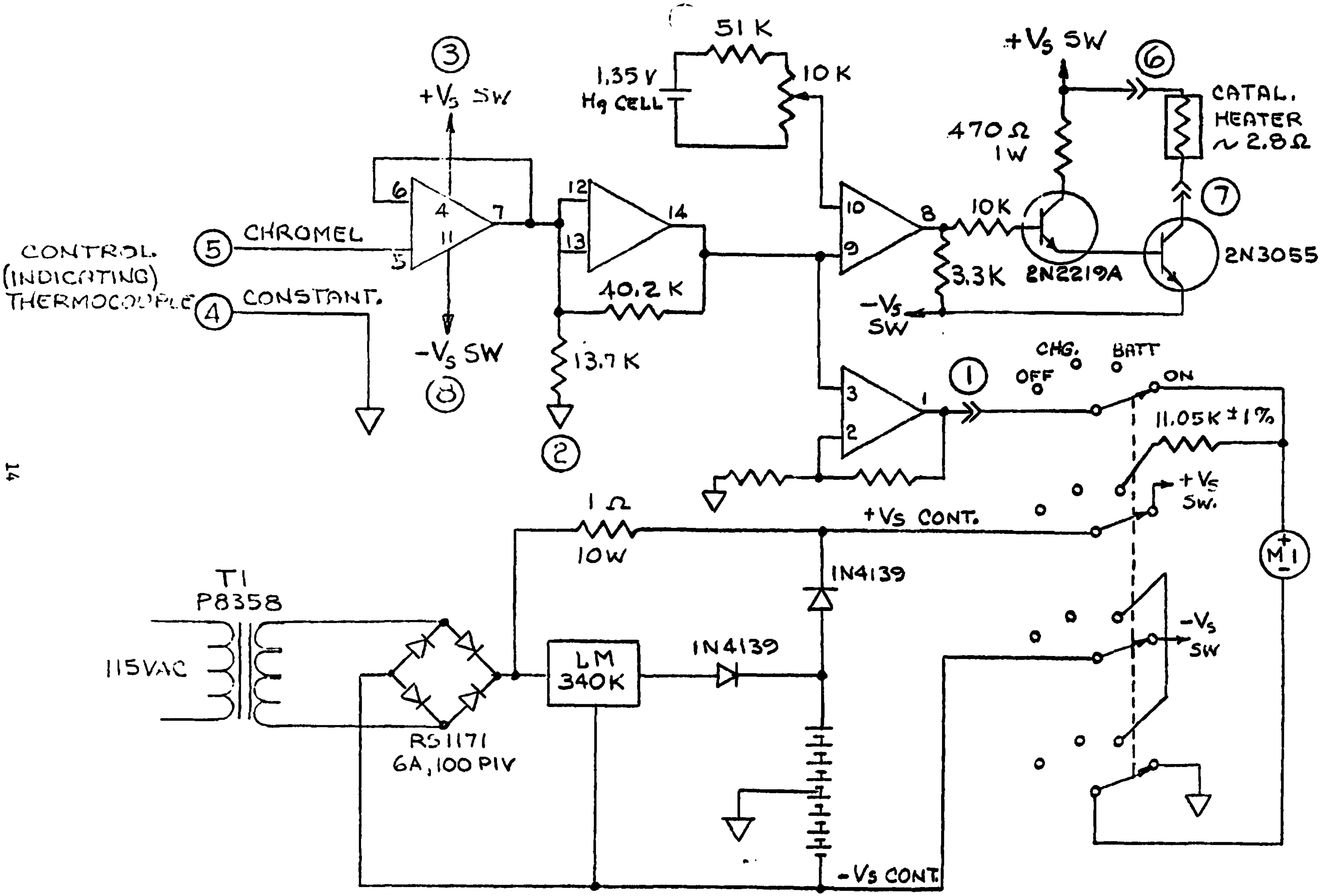


FIGURE 6 TEMPERATURE CONTROL CIRCUITRY FOR HIGH TEMPERATURE REACTOR

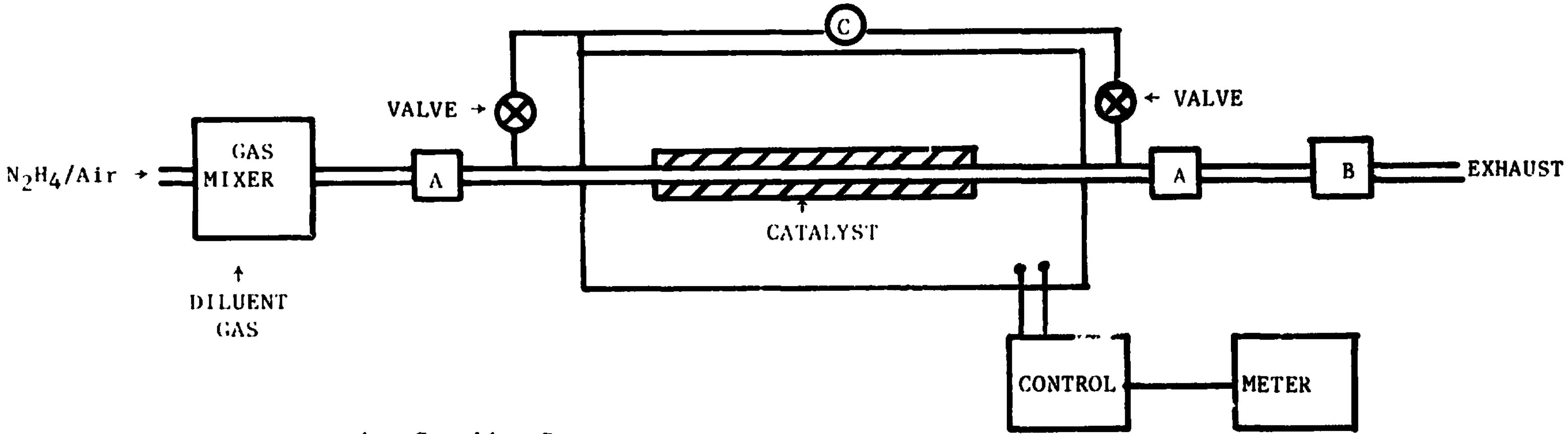
temperature and center of the tube being 710°C). Since this gradient was constant to within ±2°C, it is well within the temperature control required for high temperature catalytic reactions.

During a experimental evaluation a catalyst charge was placed into the reactor system shown in FIGURE 7 . A typical catalyst charge was 25 mg and it was positioned in the center of the heated reactor zone.

TABLE II

CATALYSTS FOR HYDRAZINE CONVERSION STUDIES

CATALYST	METHOD OF PREPARATION
Pt wire	Used as supplied - 30 mil wire
10% Pt on Al_2O_3	Evaporation of Chloroplatinic acid solution with subsequent reduction in H_2 at 300°C.
2% Ru on Asbestos (2%)	Physical mixture of Ru black and Asbestos
0.01% Pd on Copper	$PdCl_2$ solution evaporated to dryness on high surface area Cu prepared by decomposition of a carbonate precipitate.
Iridium Black	High Surface Area-Englehard Chem. Co.
CuO	Commercial (Harshaw) Preparation
Zinc-Chromium Oxide	Prepared by precipitation of carbonates from a nitrate solution with subsequent decomposition of the carbonate by roasting in air.
Cobalt-Nickel Oxide (Spinel)	
Ga doped ZnO	
Li doped NiO	



A. Sampling Ports

B. Flowmeter

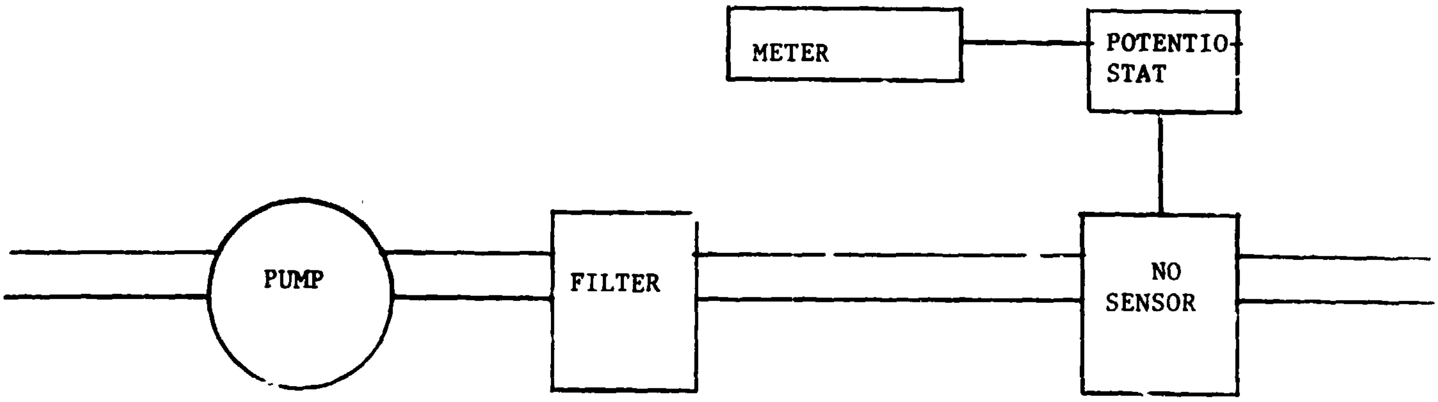
C. Pressure Guage

FIGURE 7 APPARATUS FOR CATALYST EVALUATION

The pressure drop across the reactor was monitored only periodically to be sure it was within the range for practical instrument design and during sampling was isolated from the system. The syringe sampling ports at A (FIGURE 7) could be used to withdraw samples during an experiment for analysis of reactant or product gases. The gas mixtures were attached to the reactor using a sampling bag and drawn through the heated reactor at constant flow rate. The gas mixture could easily be changed using a manifold arrangement from hydrazine vapors to zero air to room air to various gas (NH_3, NO_2, NO) mixtures by changing the sample bag or inlet gas mixer concentration.

During evaluation of hydrazine conversion to NO, the exit stream was sampled continuously using the selective scheme for NO analysis illustrated in FIGURE 8 . In this scheme a triethanolamine/firebrick filter is used to remove any NO_2 or N_2H_4 prior to NO analysis in an ECOLYZER NO Analyzer. In this manner the practical utility of the portable catalytic reactor for hydrazines to NO conversion was evalud along with its practical interface with a NO analyzer.

FIGURE 8 SELECTIVE NO ANALYSIS SCHEME



Either method is feasible for instrument design the former being dependent upon gas phase oxidation catalyst development while the latter depends upon electrochemical sensor development. Both techniques were evaluated during the scope of this program.

3) Preparation of Gas Mixtures

Wherever possible commercially available standard gas mixtures were obtained. For NO/N_2, NO_2/air, H_2/air, CO/air, CO_2/air, NH_3/N_2, and C_2H_4/N_2 samples, mixtures were obtained at various ppm level concentrations while CH_4, N_2, O_2, Ar, and He were obtained as pure gases.

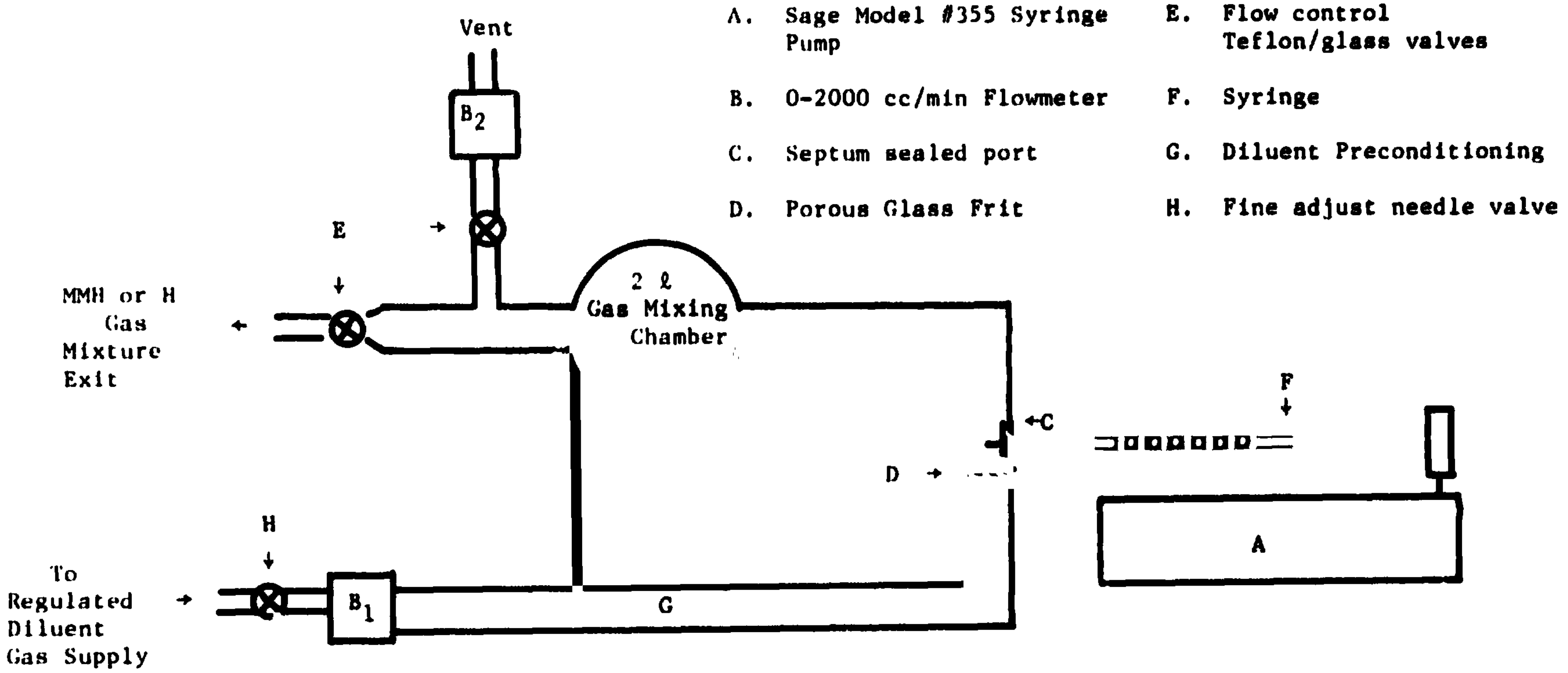
To obtain mixtures of gases at intermediate concentrations and for linearity studies a dynamic dilution scheme was used. It consisted of the pure gas or gas mixture and the diluent gas being continuously blended through two calibrated flowmeters (± 1%). This allowed dilution mixtures over approximately one order of magnitude to be prepared to approximately ±2%.

For ppm level dilution of pure gases such as 1000 ppm CH_4/N_2, the preparation used included collection of a specified amount of diluent (e.g. 5 liters of N_2) in a sample bag of vinyl, nylon or Teflon (dependent upon the mixture constituent reactivities) and syringe injection (using a Hamilton gas-tight syringe) of the pure gas during diluent collection. In this manner 5.00 cc of pure CH_4 could be syringe injected into 5000 cc of pure N_2 while it was being collected from a 1000 cc/min N_2 stream and this resulted in a 1000 ppm CH_4/N_2 mixture in the sample collection bag.

4) Preparation of Hydrazines (H, MMH, and UDMH) Vapor Mixtures

Hydrazine vapors in air or nitrogen diluent pose a special problem in both preparation and handling. The nature and surface area of construction materials which are in contact with the vapors have a severe effect upon mixture stability. Further, the toxic and hazardous nature of these substances require special precautions to be observed during their use.

The hydrazines dilution apparatus is shown in FIGURE 9 and it was placed inside a large fume hood with a roof exhaust. It consists of a Sage Model 355 syringe pump (A) capable of delivering low flow rates of the liquid (neat) hydrazines contained in a Hamilton syringe (F) and injecting them through a septum-sealed port (C) into a controlled flow (H) diluent gas stream. The system was all glass except for the TFE valve stems (E) and the section G was used to prewarm the diluent such that complete vaporization of the hydrazine was accomplished at the syringe needle tip. This temperature was varied between ambient and 80°C and was utilized to supply heat to the hydrazine liquid without causing any decomposition or degradation. By adjusting the flow rate of diluent and hydrazine liquid a variety of mixtures from < 1 ppm to > 100 ppm could be synthesized in a continuous fashion. These streams were fed directly into a sensor or test apparatus (both valves at E adjusted to a desired level) or collected in a Teflon sample bag (vent closed) for remote mixture sampling.



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 Preconditioning
H. Fine adjust needle valve

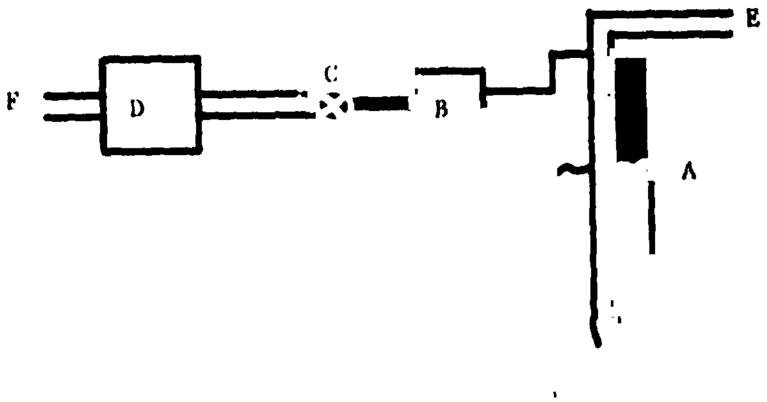
FIGURE 9 HYDRAZINE DILUTION APPARATUS

5) Analysis of Gases and Hydrazines (H, MMH, and UDMH) Vapor Mixtures

For the gas mixtures obtained commercially and gas mixtures prepared by dynamic dilution, the stated and calculated concentrations were taken as correct and wherever possibly the mixtures were analyzed by comparison to standard mixtures (e.g. CO). However, for hydrazine vapors, the special problems of mixture preparation and handling necessitated the development of precise procedures for vapor mixture analysis. Indeed, in order to calibrate the hydrazine analyzer it is necessary to accurately know the hydrazine concentration.

Three techniques for analysis and two sampling procedures were evaluated for hydrazines. The first sampling procedure involves collection of an airborn mixture of hydrazines on sulfuric acid impregnated silica gel and elution with triply distilled water to obtain an aqueous hydrazine sample for further analysis (17). The second sampling method involves direct collection of hydrazine vapor by trapping it in a midget impinger apparatus as shown in FIGURE 10. Here the sample is collected in aqueous acid solution using 0.1N HCl for N_2H_4 vapors and 0.1N H_2SO_4 for MMH vapors.

Analysis of these aqueous mixtures was performed using three methods. First, the aqueous sample was derivatized using 2-furaldehyde and the derivative hydrazone and azine products (18) analyzed chromatographically using a Varian Model 2800 Gas Chromatograph. The chromatograph was equipped with 3 ft., 2 mm i.d., silanized glass silicone OV-7 column and a flame ionization detector. Second, aqueous



A. Midget Impinger

B. 0-1000 cc min $^{-1}$ Flowmeter

C. Flow Control Valve

D. Air Sampling Pump

E. Inlet for Gas Sample

F. Vent or trap for gas exit

FIGURE 10 VAPOR COLLECTION APPARATUS

samples of H and MMH were reacted with 2,4-pentanedione (19) obtaining the derivatives 3,5-dimethylpyrazole and 1,3,5-trimethylpyrazole, respectively. These derivatives were again analyzed chromatographically using the silicone OV-7 column at 130°C, a 30 cc/min UHP N_2 carrier gas with a flame ionization detector. Third, the colorimetric analysis consisting of reaction of hydrazine and monomethlyhydrazine with p-dimethylaminobenzaldehyde to form a dye was evaluated. Several modifications of this technique have been reported (20) and we have adopted essentially the ASTM procedure given in Appendix I using HCl solutions only during hydrazine analyses and only H_2SO_4 solutions during MMH analyses. All colorimetry was performed with a Bausch and Lomb Spectronic 20 at 457 nm after 20 minutes of reaction of the derivative. Standard solutions of the aqueous hydrazines were prepared from neat H, neat MMH, hydrazine dihydrochloride and monomethylhydrazine sulfate, using both gravimetric and volumetric dilution techniques.

III. DISCUSSION

1) Hydrazine Analyses

a) Stability Considerations

In order to effectively calibrate our hydrazine vapor mixture preparation apparatus and to detail our instrument sensor performance it was necessary to know (absolutely) the hydrazine concentration. One of the major problems associated with any vapor mixture is sample losses associated with sorption interactions with apparatus walls. In addition for hydrazines, stability problems occur when they are in the presence of oxidants or in contact with catalytic surfaces, especially metals, which can promote molecular decomposition reactions.

During the program, H and MMH mixtures were prepared using both air and nitrogen as a diluent gas. However, it became evident that the hydrazine was decomposing during the time necessary to collect the sample in the sample bag.

Gas mixtures were continuously prepared in the syringe pump system using first air then nitrogen and once again air as the diluent. The mixture was then alternately passed directly into an electrochemical sensor (using a gold catalyst with alkaline electrolyte) and collected in a mylar sample bag (polyester coated aluminum). The sample bag was then analyzed by the same electrochemical sensor under identical conditions except that the vapor sample, due to collection in a bag, is 4-7 minutes old. The results are shown in Table III where these sensor signals are compared and it is clear that concentrations using nitrogen as a diluent are higher than those using air as a diluent (comparison

TABLE III

STABILITY OF H AND MMH VAPOR MIXTURES

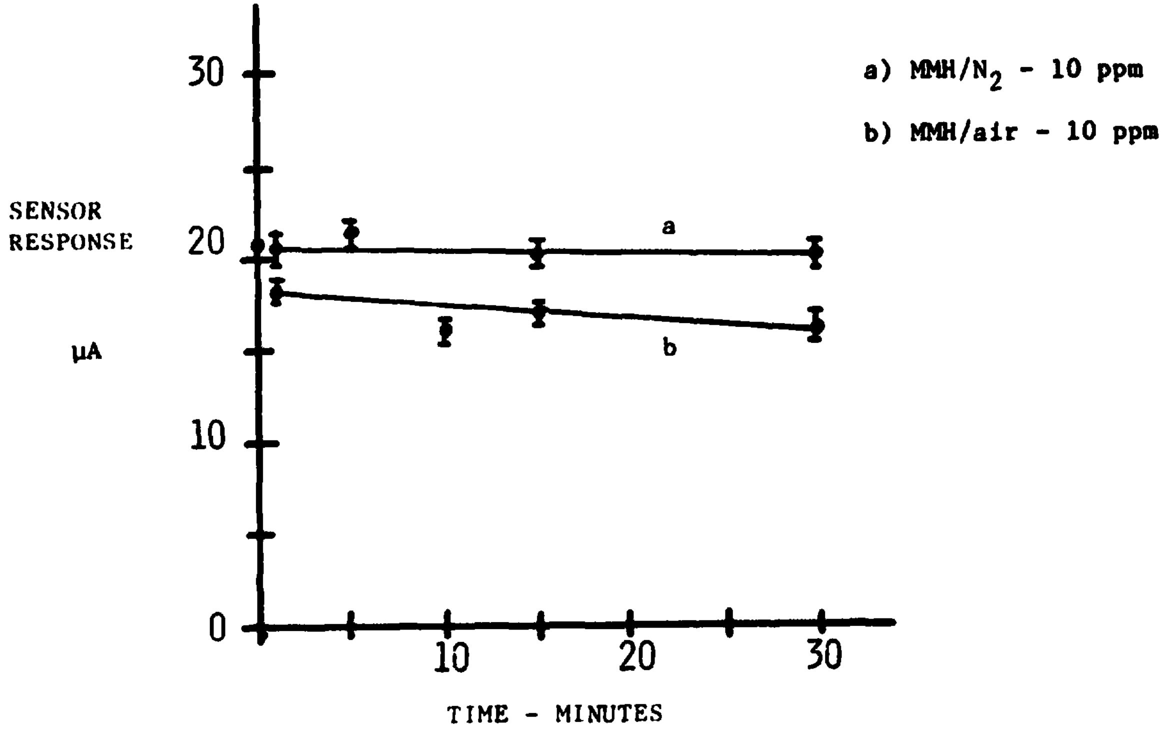
Experiment No.	Gas Mixture	Sampling Technique	Sensor Response (μA)
1	N_2H_4/air	Direct	13.5
2	N_2H_4/air	Bag	3.5
3	MMH/air	Direct	1.7
4	MMH/air	Bag	0
5	N_2H_4/N_2	Direct	33.9
6	N_2H_4/N_2	Bag	11.5
7	MMH/N_2	Direct	2.2
8	MMH/N_2	Bag	0
9*	N_2H_4/air	Direct	29.3
10*	N_2H_4/air	Bag	8.3
11*	MMH/air	Direct	3.6
12*	MMH/air	Bag	0

* H and MMH concentrations measured by a Drager tube were 2.8 ppm and 1.3 ppm, respectively. The syringe pump setting was twice as high as that used in the experiments 1-8.

of experiments 1 with 5, 2 with 6, and 3 with 7). A comparison of experiments 5 with 6 and 7 with 8 shows that the hydrazines concentration decreases when it is collected in the same sample bag using nitrogen or air as the diluent exhibiting approximately 66-75% degradation over the same time span. Also indicated is that a larger fraction of the MMH disappears than H.

Subsequently, we evaluated vinyl and Teflon sample bags in order to determine the contribution of wall reactions and gas phase reactions to the observed instability of MMH mixtures. Vinyl sample bags resulted in similar stability characteristics as those observed with Mylar. Improved stability was observed with Teflon and the results are illustrated in (FIGURE 11). For MMH/N_2 mixtures (using 99.9995% N_2, dry) no significant degradation was observed over 30 minutes of storage at the 10 ppm level, while approximately 7% loss of the MMH was observed in 30 minutes using dry air as the diluent. An earlier study (21) has reported a half life of 34 minutes for 4.6% MMH vapors in a glass chamber while complete degradation was observed in 10 minutes in a polypropylene bottle. This is consistent with our results which show a 12% difference in the initial concentration of MMH produced for the same dilution system preparative setting. Our dilution system is glass and contains a dead volume of approximately 2.2 liters. Since mixtures were prepared at 700 cc/min, the residence time of the mixture in the glass chamber was three minutes and this would account for the observed 12% initial degradation of MMH/air mixtures. The noted stability of Teflon along

FIGURE 11 STABILITY OF MMH VAPORS IN TEFLON



with the preparative stability of nitrogen diluent leads us to recommend that stable mixtures and hence those for calibration and testing should be prepared using a nitrogen diluent and stored in Teflon containers. Further, it is apparent that instability of MMH/N_2 mixtures in glass, polyester and vinyl is due to wall reactions while the instability of MMH/air mixtures is due to both wall reactions and gas phase reaction, the former being more important than the latter in Teflon vessels.

With these remarks in mind we have evaluated three techniques, two chromatographic and one colorimetric, for hydrazines analyses and the results are now reported.

b) Chromatographic Analysis

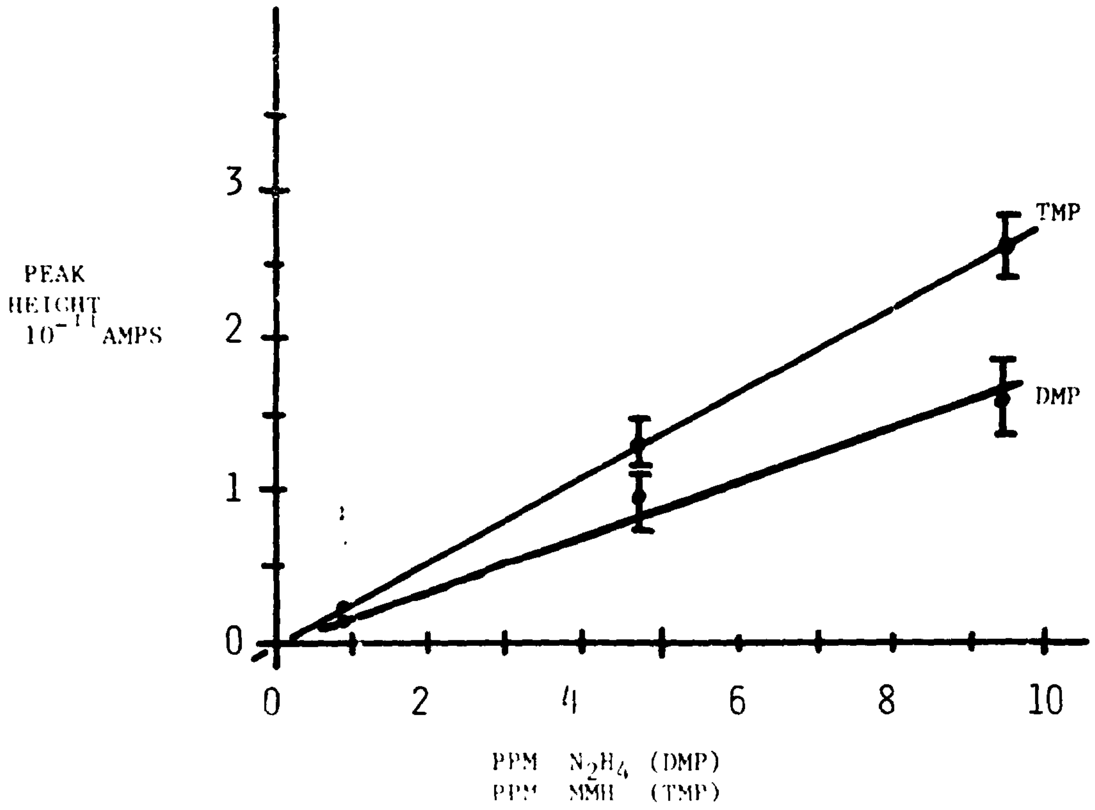
The initial experiments were performed by collecting impinger samples of H and MMH, preparing derivatives with 2-furaldehyde and reacting for exactly 3600 seconds at room temperature with subsequent cooling to 0°C for storage. The hydrazone reaction product (18) was then analyzed chromatographically. The results for this technique were erratic especially at higher concentrations (10-100 ppm) of the sampling stream. It is suggested however that improvements in sampling, handling, and analysis are necessary to achieve reasonable ±10% accuracy and precision using this procedure. At present, the technique is complex requiring sophisticated analytical instrumentation and a highly skilled operator for preparation of the derivatives and for their analysis by gas-liquid chromatography.

A second chromatographic scheme for analysis of H and MMH (19) was evaluated by diluting neat H and neat MMH to ppm levels with 0.1N HCl and 0.1N H_2SO_4 solutions. An aliquot of this mixture was then reacted with an excess of 2,4-pentanedione for at least one hour obtaining the derivative products 3,5-dimethylpyrazole (DMP) and 1,3,5-trimethylpyrazole (TMP) from N_2H_4 and MMH, respectively. Several different concentrations were prepared from the 95% hydrazine and 95% MMH reagents (assumed 95% purity) and analyzed with the results shown in FIGURE 12. Each datum point is the result of 3 or more analyses and it is clear that linear analysis is obtained with this chromatographic technique. The derivative mixtures were stable for periods longer than one day offering the potential for storage and/or transportation of standards and samples. However, the repeatability of the determination was at best ±10% for 1.0 μl samples. While increased sensitivity could be obtained and better precision realized with larger samples, this technique also requires a skilled operator for its precise application.

c) Colorimetric Analysis

Calibration curves were determined for the colorimetric method using hydrazine dihydrochloride, neat hydrazine and neat MMH which were quantitatively diluted to ppm and sub-ppm levels in acid solution. These samples were reacted with p-DMAB and the product dye determined after 20 minutes of reaction with a Spectronic 20 (Bausch and Lomb) colorimeter at 457 nm. The results are given in FIGURES 13 and 14 where typical day to day precision is illustrated for hydrazines and monomethylhydrazine analyses, respectively.

FIGURE 12 HYDRAZINES CALIBRATION USING GC FID TECHNIQUE



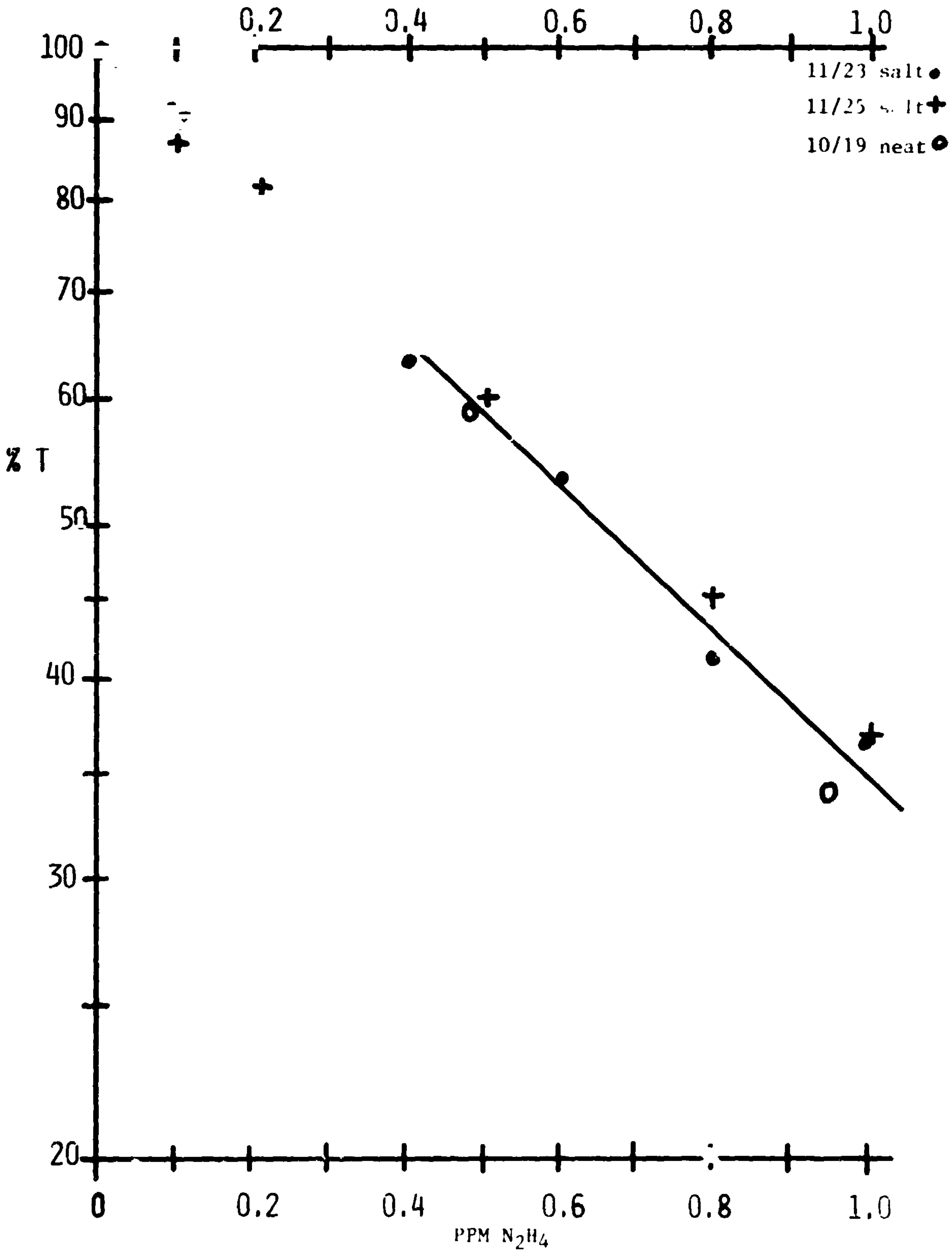
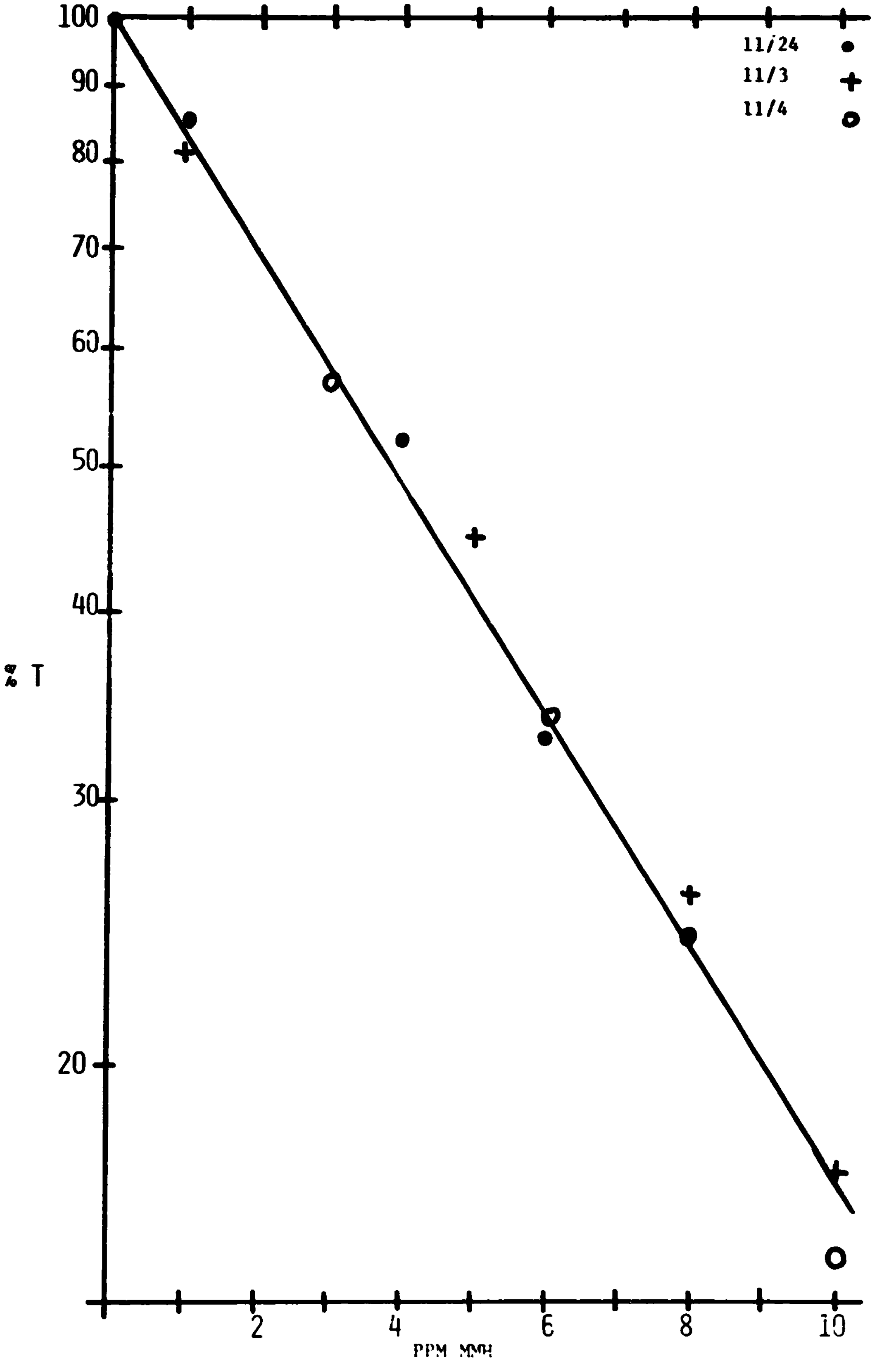


FIGURE 13 COLORIMETRIC CALIBRATION CURVE FOR HYDRAZINE

FIGURE 14 COLORIMETRIC CALIBRATION CURVE FOR MMH



Vapor samples from the dilution system were prepared for analysis by collection on sulfuric acid impregnated silica gel and subsequent elution with triply distilled water and also by using 25 cc of acid solution in a midget impinger apparatus. In this phase of the program the performance of the dilution system was also evaluated. The colorimetric procedure involving the reaction of hydrazine or MMH with p-DMAB with subsequent measurement of the per cent transmittance was used to calibrate the syringe pump dilution system. Samples of the H and MMH vapor mixtures were collected on 200 mg of 20% H_2SO_4 impregnated silica gel. Typically one or two liters of vapor were passed through a filter tube containing the acidic silica gel. The collected sample was eluted with triply distilled water for one hour with subsequent addition of the p-DMAB reagent to an aliquot of the supernatant. Results in FIGURE 15 represent vapor samples collected at various speed settings of the syringe pump in the dilution system. FIGURE 15I is illustrative of diluter performance in the preparation of high concentrations while FIGURE 15II shows low concentration collections on acidic silica gel and FIGURE 15III represents vapor samples collected using a midget impinger apparatus. Results show that the syringe pump is linear in vapor output for N_2H_4 mixtures and good agreement between the silica gel and impinger collection techniques is observed.

For the various syringe pump dilution system conditions a theoretical concentration (i.e. assuming 100% efficiency of the diluter) can be calculated. This ideal concentration has been compared to the analysis of

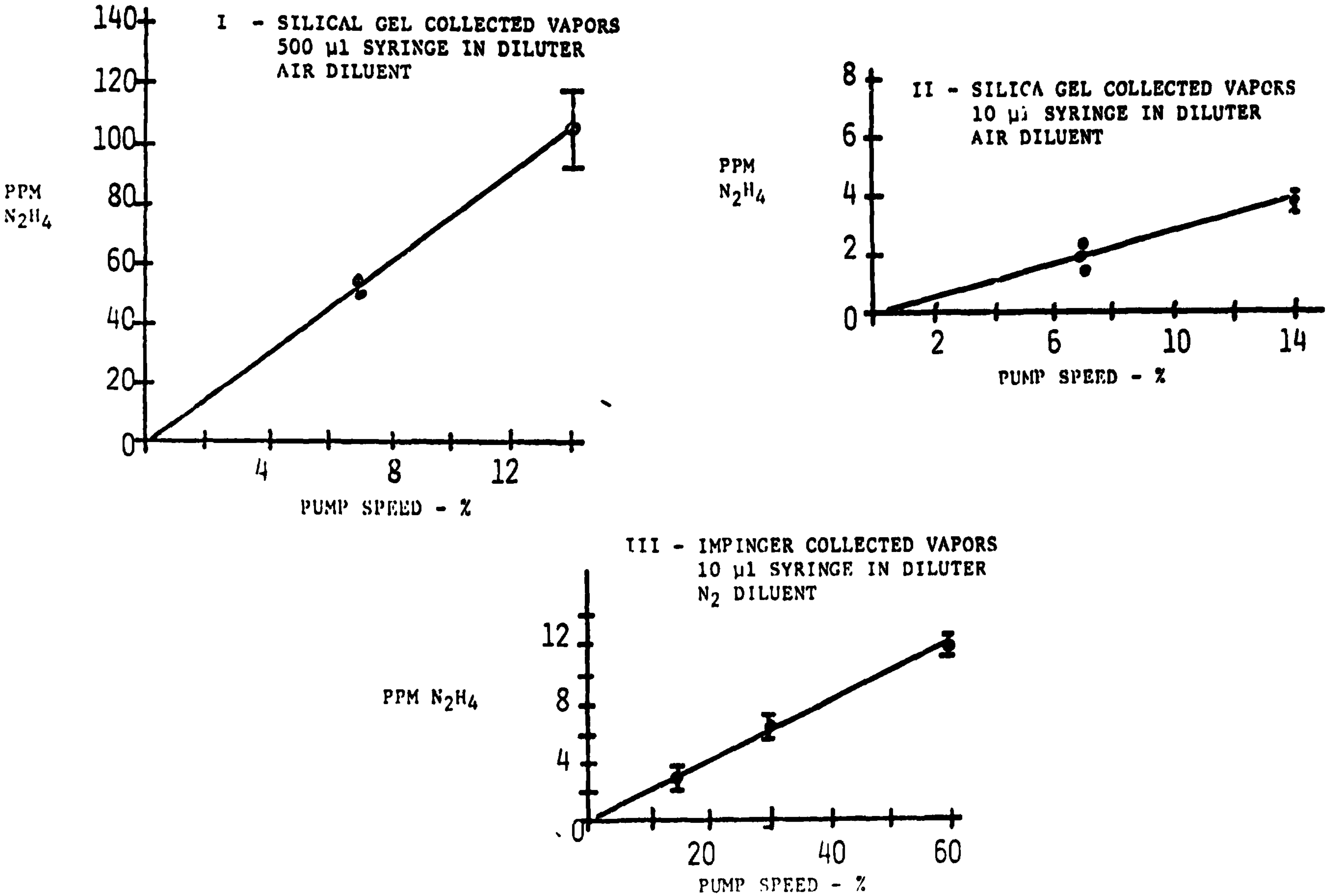


FIGURE [illegible] CALIBRATION OF SYRINGE PUMP DILUTION SYSTEM vapor mixtures which were collected in an impinger and analyzed colorimetrically with the results shown in Table IV. It is noted that good agreement is obtained for H and MMH mixtures prepared in nitrogen and the repeatability of the syringe pump dilution system is similar to that of the colorimetric analvsis scheme although absolute concentrations are somewhat lower than predicted values in most cases.

TABLE IV

HYDRAZINES MIXING APPARATUS PERFORMANCE

Syringe Pump Setting	Diluent UHP-N_2	Liquid Delivery	Theoretical Concentration	Actual Concentration (Colorimetric)
	cc/min	µl/min		
1/1000, 60% 10 µℓ	700	0.0155	11.2 ppm MMH	9.2± 1.6 ppm MMH
			15.9 ppm H	10± 2 ppm H
1/1000, 30% 10 µℓ	700	0.00775	5.6 ppm MMH	
			7.9 ppm H	
6%, 1/1000 10 µℓ	700	0.00155	1.12 ppm MMH	
			1.59 ppm H	∿ 2 ppm H

2) NO$_2$ Sensor Development

The NO$_2$ analysis scheme utilized in the final instrument package was determined by evaluation of the following criteria for a variety of electrochemical sensor systems: response time, zero and span drift, sensitivity, reproducibility (precision), linearity, power requirements (portability), background, and specificity. The two schemes evaluated for the analysis of NO$_2$ are shown in FIGURE 16 and scheme B depends upon development of a selective adsorbent filter while scheme A depends upon development of a selective NO$_2$ electrochemical sensor. Method A is preferable since filters add additional maintenance and cost to the instrument while adding to the internal volume of the sensing system and thus affecting instrument rise and decay performance characteristics.

The selective reduction of NO$_2$ was studied on a series of electrochemical sensor electrodes at various potentials. Responses for the most promising systems are reported in Table V at the electrode bias (electrode potential vs. a Pt/air reference electrode in acid electrolyte) for which the maximum selectivity was achieved. The sensors constructed from these electrode materials were tested using a sample flow rate of 700 cc/min and typical responses are shown in FIGURES 17 and 18 for the Au/H$^+$ and Ru/H$^+$ systems, respectively. The graphite electrode system also exhibited a well behaved response and is shown in FIGURE 19.

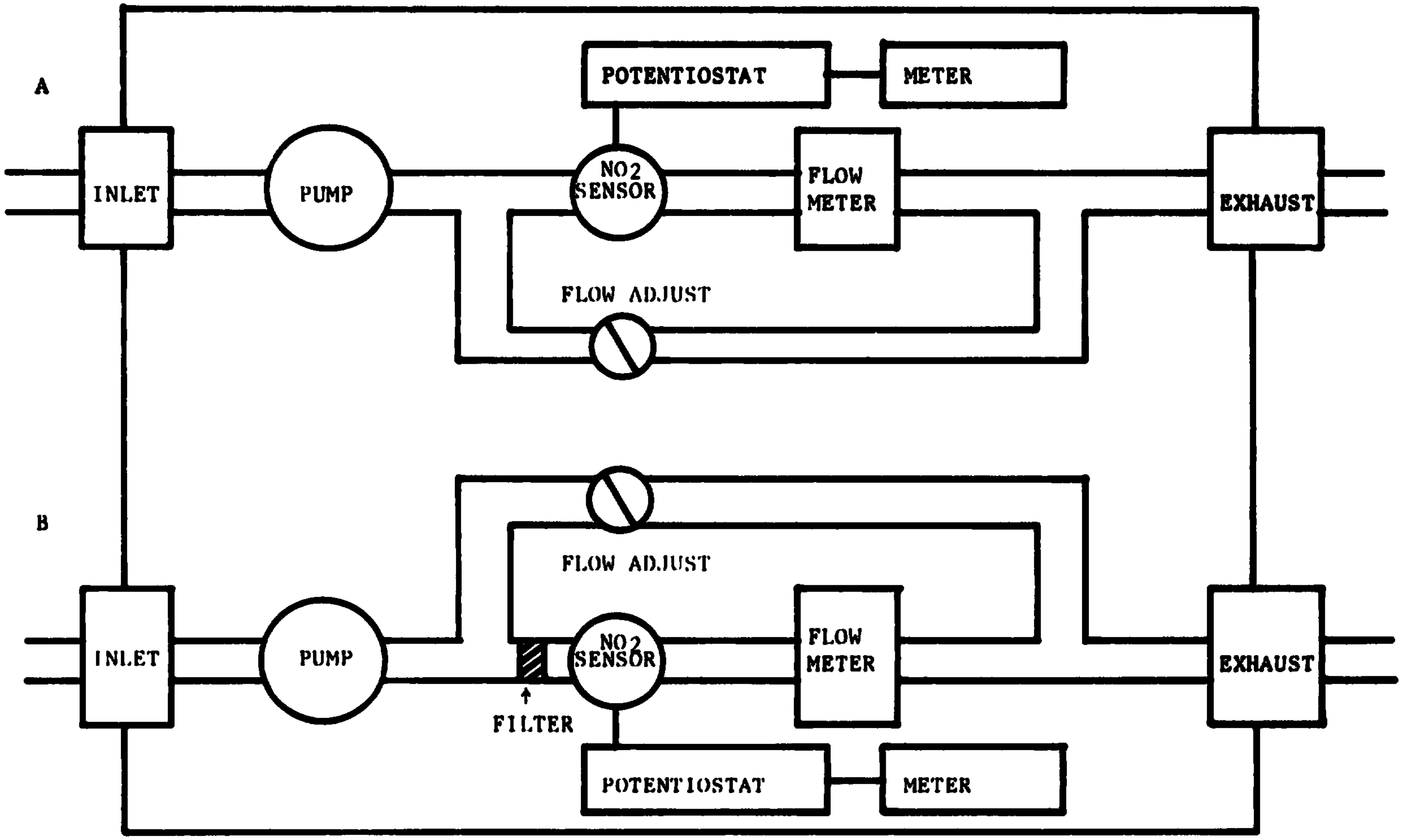
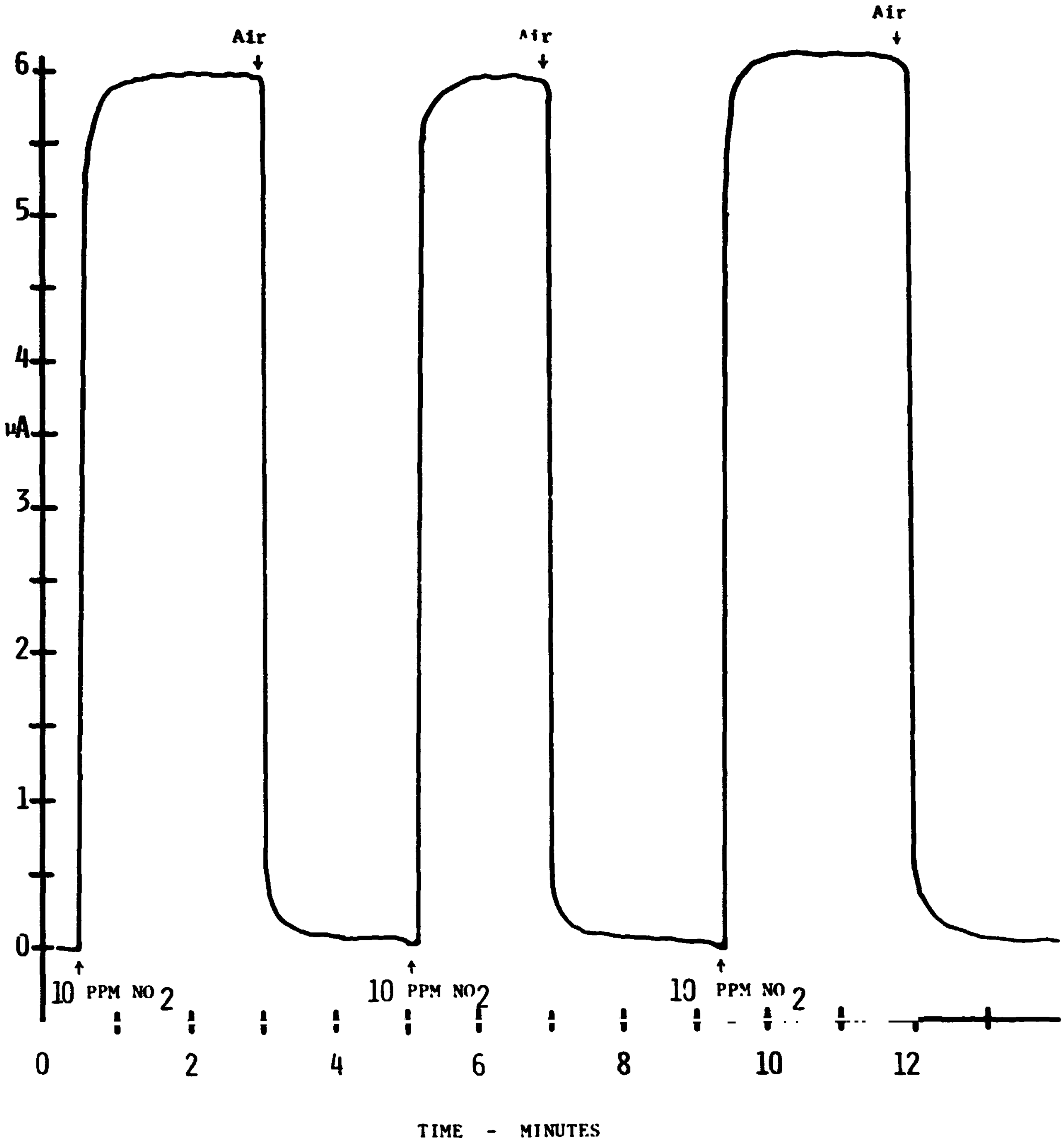


FIGURE 16 NO_2 ANALYSIS SCHEMES

FIGURE 17 NO_2 RESPONSE FOR Au/H+ SENSOR



ANALYSIS CONDITIONS: 700 cc/min, Background = 1.95µA, Bias = -200mv vs Pt/air

FIGURE 18 NO_2 RESPONSE FOR Ru/H+ SENSOR

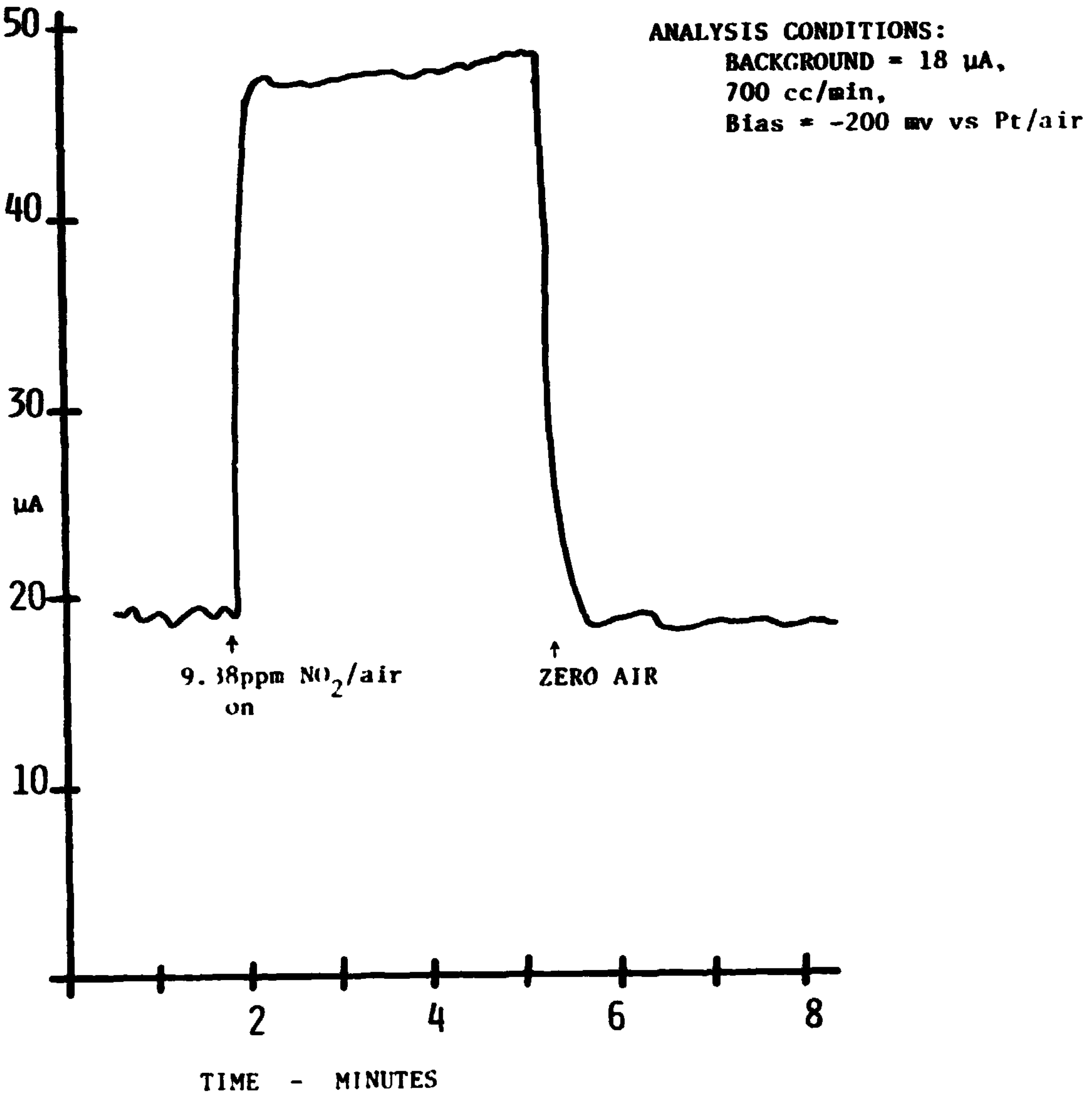
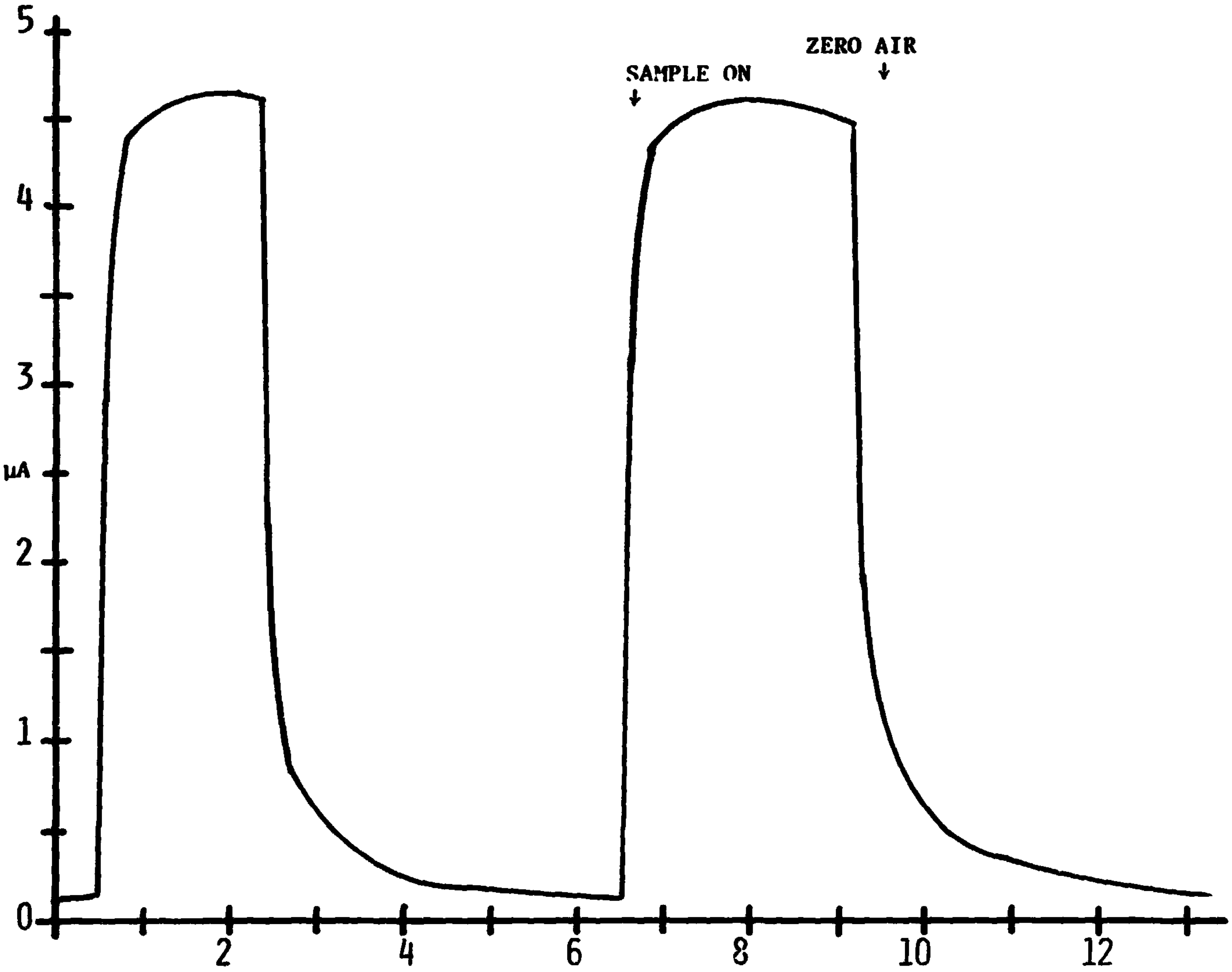


FIGURE 19 NO_2 RESPONSE FOR GRAPHITE/H+ SENSOR



TIME - MINUTES

ANALYSIS CONDITIONS: Background 8.3 μA, 700 cc/min,
Bias = 500mv vs Pt/air,
9.38ppm NO_2/air mixture.

TABLE V

NO_2 Sensor Performance

Gas Mixture	Au -200 mv*	Au-Graphite -400 mv	Ruthenium -200 mv
	[μA/ppm]	[μA/ppm]	[μA/ppm]
Hydrazine	0.94	0.7	< 0.2
Monomethyl hydrazine	0.83	2.0	< 0.2
NO_2/Air	0.7	1.6	3.0
NO/N_2	0.02	1.9	< 0.04
CO/Air	0.009	0.002	< 0.01
NH_3/Air	0.036	0.1	< 0.01
Background	2.5 μA	25 μA	15 μA

The signals obtained with the ruthenium electrode sensor were irreproducible and spurious span changes were observed for NO_2 analyses, therefore no further work was carried out on this system.

The rise time with the Au sensors was fast and the signals due to NO_2 were stable and reproducible being 0.59 μA/ppm ± 0.01 (FIGURE 17). However, 10 ppm hydrazine gave the same signal as -1 ppm NO_2 (a negative signal means that the interferent signal was in the reverse direction). This interference varied between 10 and 30 for a variety of Au electrodes.

The characteristics of the graphite catalysed sensors (FIGURE 19) depended on the pre-treatment of the graphite sensing electrode. The best selectivity was obtained with a sensing electrode which had been pre-treated by potentiostatting at +0.20V for 2 days (i.e., under conditions where the graphite surface is oxidized). With this treatment, there was no interference at low hydrazine concentrations, but at high hydrazine concentrations the selectivity ratio of NO_2/H was -1.

In none of these cases was the hydrazine/NO_2 selectivity considered to be satisfactory for a practical instrument. As a result the scheme FIGURE 16B was investigated for NO_2 analysis using a standard NO_2 ECOLYZER filter. It consisted of a combination of mercuric chloride and glycerol absorbed on firebrick. The filter was capable of removing 100 ppm hydrazine for at least 6 hours (the duration of the test). This scheme offers excellent selectivity in a practical instrument design.

3) Hydrazines Sensor Development

a) By Gas Phase Oxidation of Hydrazines to NO

The first proposed analysis scheme is the oxidation of hydrazine to nitric oxide and subsequently analyzing the nitrogen oxide by the appropriate electrochemical analysis technique.

Hydrazine may be oxidized in the presence of oxygen to either nitric oxide (high temperatures) or to nitrogen dioxide (low temperatures). The former is preferred since although it will require a higher weight of batteries per unit operating time the latter will cause interference in the selected electrochemical analytical technique. Before discussing the selection of the catalyst for this process, we will consider some of the possible reactions which may occur in the catalytic reactor. He, Ar, and CO_2 cannot be oxidized and will not cause any interference. Also the reaction between N_2 and O_2 is thermodynamically unfavorable (22) at the probable catalyst operating temperatures of 400°C to 800°C, and therefore, no nitrogen oxides will be formed by this reaction. H_2, CO, CH_4, and Freon can be oxidized in the catalytic reactor to various degrees (23) but these oxidized products will not cause any interference on the electrochemical sensor.

The ambient concentrations of NO in the vicinity of the analyzer will be between 20 ppb and 50 ppb, and this is sufficiently low that it will cause errors in the accuracy only at very low levels of hydrazine which can be compensated for by inclusion of a specific NO sensor if required.

The nitrogen dioxide levels may be greater than the hydrazine concentration and hence some consideration needs to be given to the effect of this gas. If hydrazine were to be analyzed by gas phase oxidation to NO_2 then the ambient NO_2 levels must be corrected for by either: 1) selectively pre-filtering NO_2 from hydrazine prior to the catalytic reactor, or 2)electronically subtracting the NO_2 reading on the NO_2 sensor from the NO_2 reading on the hydrazine sensor. This again suggests rejection of this scheme for hydrazine analysis due to its complexity.

Since hydrazine is to be measured by gas phase oxidation to NO, there may still be a possible interference caused by NO_2 since the reactor operating conditions may be such as to thermodynamically favor the conversion of NO_2 to NO. However, the kinetics of this reaction is not known. If it occurs at an insignificantly slow rate, it will pose no problems in the hydrazine analysis. If the conversion of NO_2 to NO does occur at a significant rate, it will be necessary to either: 1) selectively pre-filter the NO_2, or 2) electronically subtract the NO_2 concentration from the apparent hydrazine reading.

The catalyst selected will be such as to give the maximum conversion efficiency, highest stability and lowest reactor operating temperature. There have been a large number of studies of hydrazine decomposition to ammonia, nitrogen, and hydrogen (24-30) which suggests **possible** hydrazine oxidation catalysts. This has shown that the general sequence of reactivity of the hydrazine decomposition catalysts is: metals > semi-conductors > solid bases > solid acids > solid salts. Studies of the catalyst electrical conductivity and work function during N_2H_4 adsorption and decomposition using semiconductors demonstrated that N_2H_4 is an electronic donor molecule and an increase in catalytic activity is observed with decreasing width of the semiconductor forbidden zone (31). It is understandable, therefore, why transition metal oxides with their low forbidden energy gaps make good N_2H_4 decomposition catalysts, and doping of NiO and Li_2O results in an increase in N_2H_4 decomposition rate. There has been much less work on hydrazine oxidation to the nitrogen oxides. However, studies at NRL (32) showed that N_2H_4 is oxidized to NO with a 60% conversion efficiency with a steel wool catalyst heated to 850°C in a stainless steel tube reactor.

There have been many more studies of ammonia oxidation (33, 34) and these aid in the hydrazine oxidation catalyst selection since ammonia is one product of hydrazine decomposition. Ammonia is oxidized to NO with yields of 80-100% with a platinum gauze catalyst maintained at 750°C-950°C in a tube reactor (33). In addition, the transition metal oxides are also active catalysts with the maximum activity being exhibited by MnO, Cu_3O_4 and CuO (35).

Each catalyst tested was placed in the portable catalytic reactor shown in FIGURE 5. A usual charge of 25-100 mg of catalyst was used. The reactor was then placed in the apparatus illustrated in FIGURE 7 where it was evaluated. In a typical experiment the catalyst was slowly heated in an air stream. The temperature was held constant at a series of temperatures for example, 100°C, 150°C, 200°C, etc. as the sample was heated. At each of these isothermal points a stream of N_2H_4/air was introduced and the output of the reactor was sampled and analyzed for NO content. The results utilizing the various catalysts is reported in Table VI. The flowrate through the catalyst bed was maintained constant in all cases until a constant conversion (steady state) was obtained. Typical flowrates were 400 cc/min since this is practical from an instrument design view.

The major problem associated with all of the results reported here was the poor reproducibility of the conversion from catalyst charge to catalyst charge and with time. For most samples a continuous deterioration of activity with time was observed. Maximum conversions obtained are given in Table VI. It should be noted that while practical development is not attained here the feasability of the approach is clearly demonstrated. A combination of higher temperature (> 400°C) and lower flow rate (5-10 cc/min) will produce entirely different catalytic specificity, however this would also necessitate consideration of instrument redesign not within the scope of this program.

TABLE VI

CATALYTIC CONVERSION OF HYDRAZINE TO NO

CATALYST	MAXIMUM CONVERSION ≠
Pt wire	10% at 200°C
Pt on alumina (10%)	10-12% at 300°C and 650°C 50% at 803°C (for 100 mg catalyst)
CuO	16-20% at 250°C
Ru on asbestos (2% Ru)	70% at 450°C
Pd on copper (.01% Pd)	50% at 450°C @ 1.55 CFH } unstable 80% at 450°C @ .65 CFH
Zinc-Chromium Oxide	60% at 500°C
Cobalt Nickel Oxide Spinel	70% at 450°C
Iridium black	35% at 300°C
Ga doped ZnO	30% at 250°C
Li doped NiO	30% at 400°C

≠ Conversion is defined by 1 ppm Hydrazine yielding 1 ppm NO being 100% conversion. An Hydrazine instrument in this case would respond as an NO analyzer.

b) Hydrazine Analysis by Direct Electrochemical Oxidation

The second analysis scheme is measurement of the current produced by the direct electrochemical oxidation of hydrazine in a three-electrode electrochemical sensor. In order to optimize this technique it is necessary to select the combination of electrode catalyst, electrode potential, and electrolyte to maximize the signal (i.e., current) due to hydrazine electro-oxidation and to minimize the signal due to other potential atmospheric constituents (e.g., NO, NO_2, CO). Further, the electrode catalyst must be stable (i.e., non-corrosive) at the electrode operating potential. This restricts the selection of the catalyst to the noble metals such as Pt, Rh, Au, Ru, Ir, Pd, and Carbon. Each of these metals was obtained commercially as high area metal blacks for evaluation with the carbon being in graphitic form.

The selection of the electrode potential is restricted to a range of approximately 0.7V to 1.9V vs. the reversible hydrogen electrode in acid depending on the nature of the catalyst. This potential range is determined by the requirement that neither oxygen reduction nor water oxidation occurs at a significant rate. With some catalysts this range is further restricted either due to the catalysts high activity for oxygen reduction and water oxidation (e.g., Pt) or to corrosion of the metal (e.g., Pd).

The electrochemical oxidation of hydrazine has been previously investigated by a number of people (36, 37) due to its applicability as a fuel for fuel cells (38). It is readily oxidized in alkaline electrolyte according to the equation

$$N_2H_4 + 4OH^- \longrightarrow N_2 + 4H_2O + 4e^- .$$

Hydrazine electro-oxidation in acid electrolyte has been less throughly investigated since it is protonated in acid electrolyte (i.e., forms $N_2H_5^+$) which precludes the obtaining of power in a fuel cell. However, it was evaluated in both acid and alkaline electrolyte during these studies.

Twelve systems (electrode catalyst, electrolyte) were evaluated for use in the selective direct analysis of hydrazines at a series of bias potentials and the results are reported in Table VII.

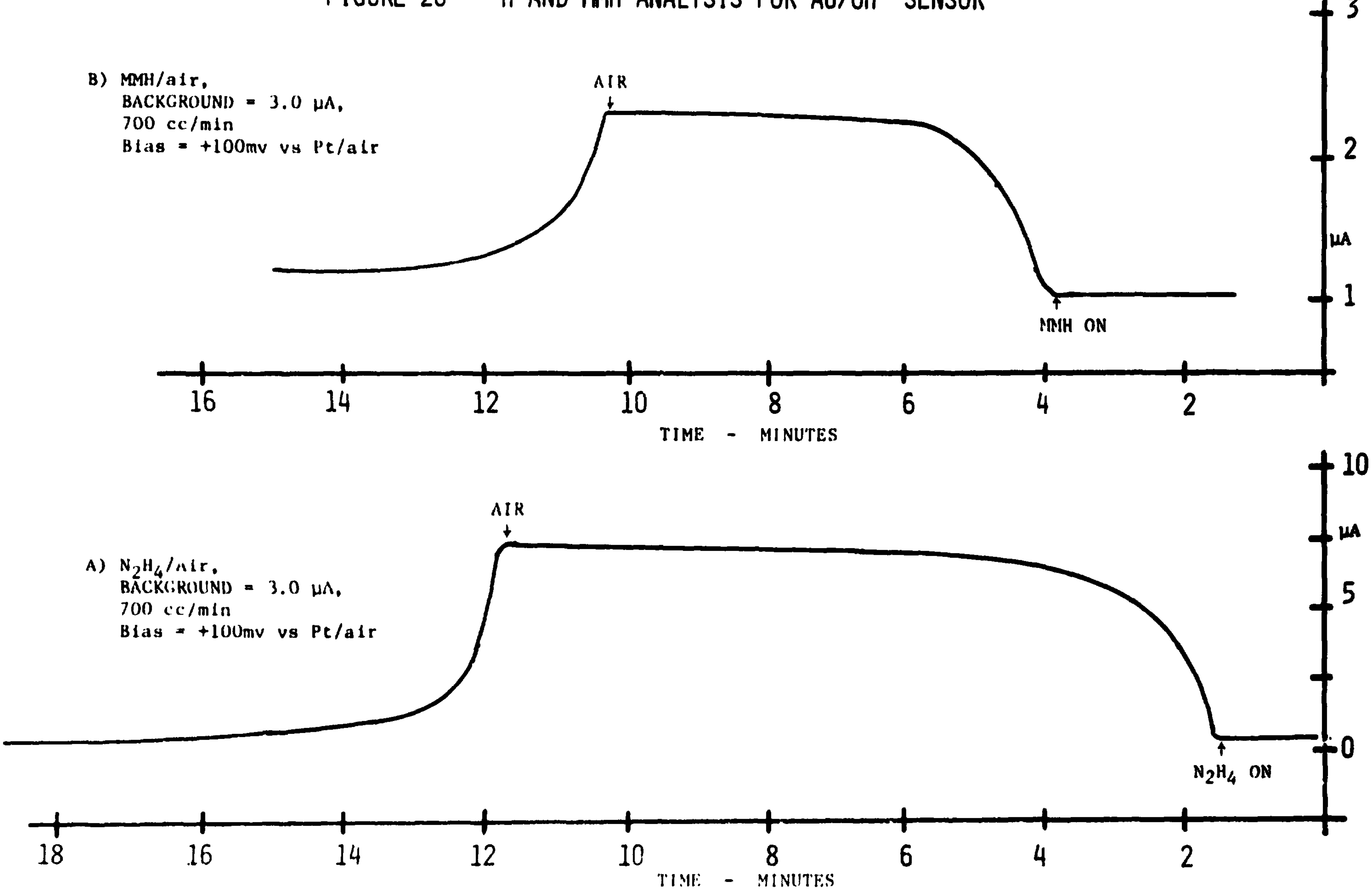
TABLE VII

ELECTROCHEMICAL SENSORS FOR N_2H_4 ANALYSIS

Sensing Electrode Catalyst	Electrolyte	Comments
Pt	H_2SO_4	Non-selective responses at all positive potentials.
Au	H_2SO_4	Non-selective responses at all potentials.
Pt	KOH	Non-selective.
Au	KOH	Non-selective at potentials >+100 mv. Low potential responses selective for hydrazine vs NO_2.
Pd	H_2SO_4	Low reactivity and non-specificity.
Ru	H_2SO_4	Non-steady state response at all potentials 0 mv.
Ir	H_2SO_4	Some H, MMH response at low potential, non-steady state responses at high >+100 mv potentials.
Rh	H_2SO_4	Non-steady-state responses at >+100 mv; selective hydrazine and MMH responses at $\sim$0.0 mv potential.
Vitreous Carbon	H_2SO_4	No steady-state signals observed.
Au on graphite	H_2SO_4	Larger responses for NO_2 than H or MMH.
Graphite	H_2SO_4	Non-selective.

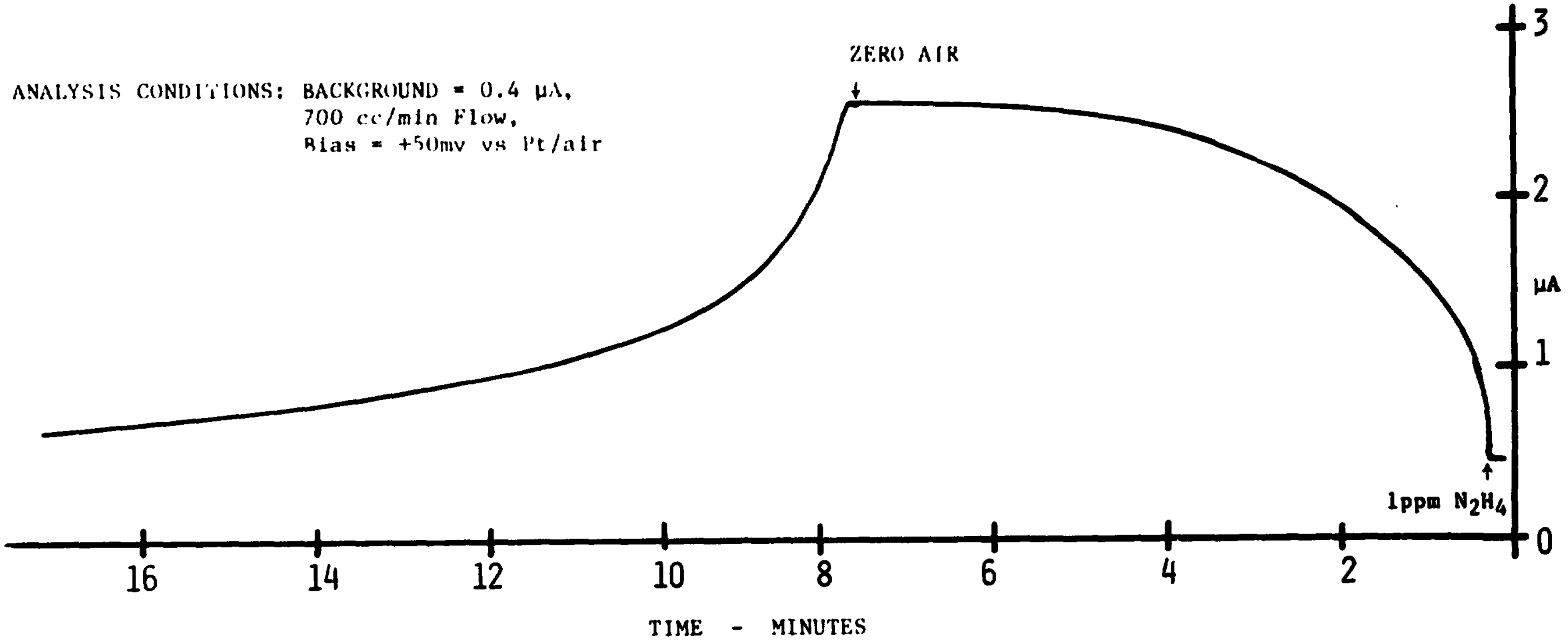
Non-selective responses are indicative of those sensors which responded to a number of gases including NH_3, H_2, CO, NO, and NO_2. These sensors were screened at potentials of 0V, +0.1V, +0.2V and +0.3V versus the Pt/Air reference electrode. From Table VII it is seen that three systems offer potential application to hydrazine/air analysis and they are Au/KOH, Rh/H_2SO_4 and Ir/H_2SO_4. Representative responses for these systems are shown in FIGURES 20-23 and these illustrate response/time characteristics of the sensors. The selectivities of these systems is given in Table VIII and the Rhodium catalyst is the most selective of all the electrodes while the Au/KOH system was the most repeatable and stable (background and noise). The signals for the Rh/H^+ sensor were irreproducible and the rise and decay times were long. Therefore, work with this sensor was discontinued. Similar findings were obtained with the Iridium system in addition to its extreme sensitivity to slight pressure changes. Therefore, optimization of sensor response and instrument design proceeded with a Au/KOH hydrazines sensor.

FIGURE 20 H AND MMH ANALYSIS FOR Au/OH⁻ SENSOR



B) MMH/air,
BACKGROUND = 3.0 μA,
700 cc/min
Bias = +100mv vs Pt/air

A) N_2H_4/air,
BACKGROUND = 3.0 μA,
700 cc/min
Bias = +100mv vs Pt/air



ANALYSIS CONDITIONS: BACKGROUND = 0.4 μA,
700 cc/min Flow,
Bias = +50mv vs Pt/air

FIGURE 21 HYDRAZINE ANALYSIS FOR RH/H+ SENSOR

FIGURE 22 MMH ANALYSIS FOR RH/H+ SENSOR

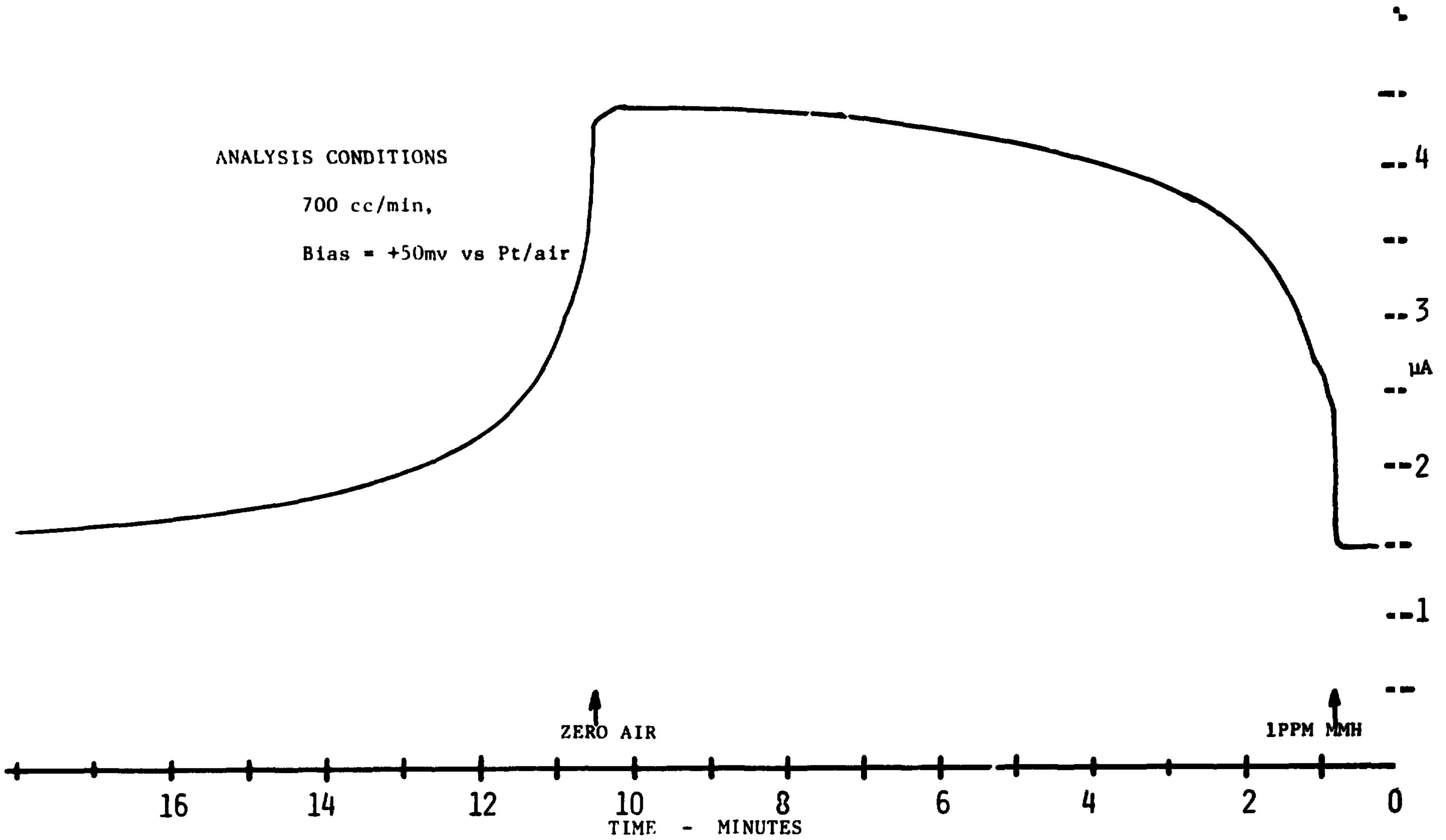
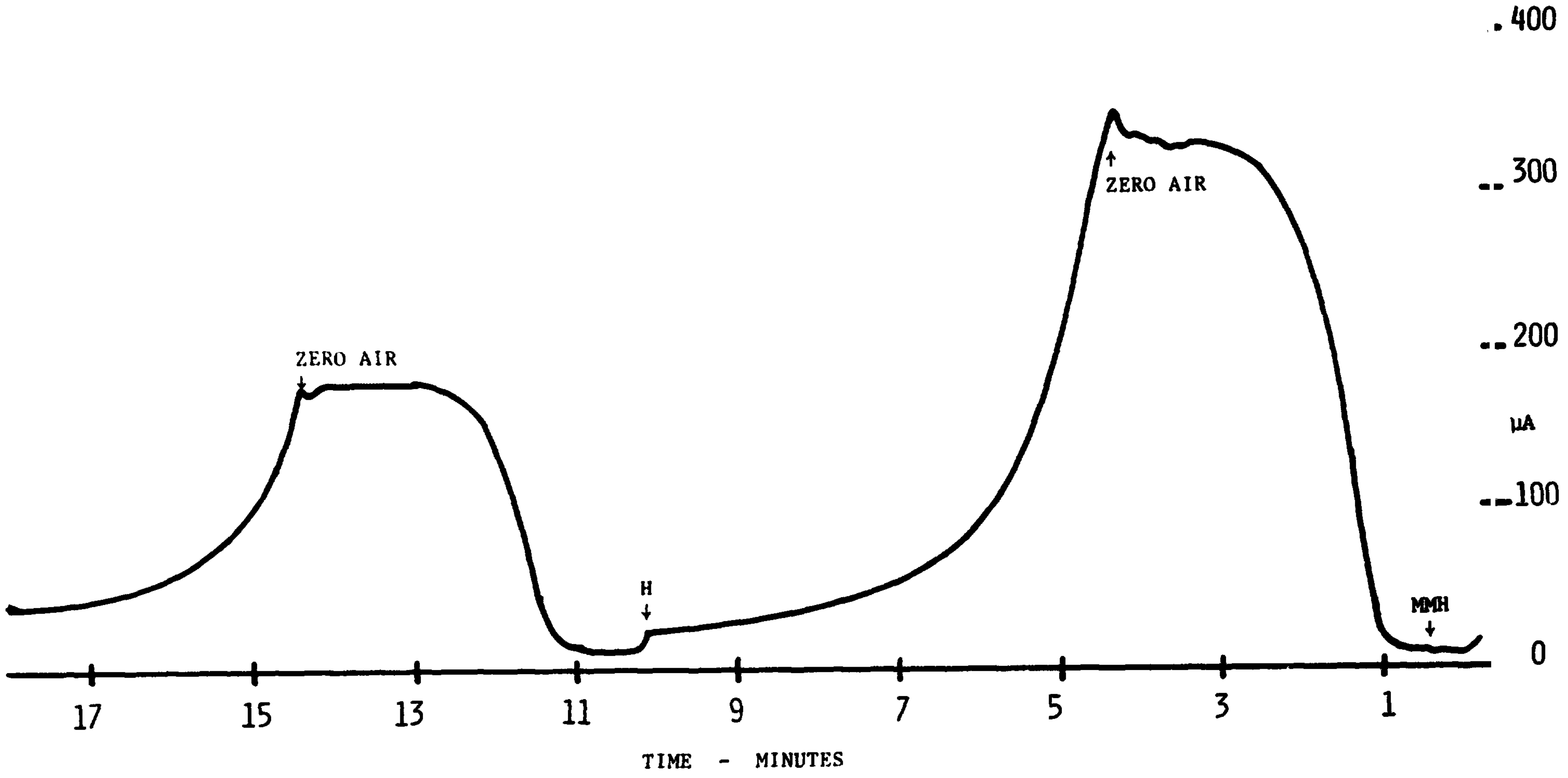


FIGURE 23   H AND MMH RESPONSE FOR IRIDIUM/H+ SENSOR



ANALYSIS CONDITIONS: Background = 15µA, 700 cc/min, Bias = -100 mv vs Pt/air

TABLE VIII

SELECTIVITY OF HYDRAZINE SENSORS

Gas Mixture	Rhodium: Signal [μA/ppm]	+20 mv bias Selectivity* [ppm H/ppm]	Iridium Signal [μA/ppm]	-100 mv bias Selectivity [ppm H/ppm]	Gold/KOH: Signal [μA/ppm]	+11 mv bias Selectivity [ppm H/ppm]
Hydrazine/air	2.1	1.0	68	1.0	1.7	1.0
MMH/air	2.8	0.75	53.3	1.3	1.5	$\sim$1
NO_2/air	-0.03	70	-2.1	32	< .05	34
NO/Nitrogen	0.005	420	<.02	3400	.09	19
CO/air	<0.002	1050	<.01	6800	.14	12
NH_3/air	0.009	233	.05	1360	.30	5.7
H_2/air	6×10^{-5}	3.5×10^{4}	-	-	0.025	680

*Selectivity is defined as the gas concentration required to give the same signal as 1 ppm hydrazine.

IV. INSTRUMENT DESIGN AND CHARACTERIZATION

During this phase of the program all design modification to the 7000 Series ECOLYZER were made including chassis modification, special mounting brackets, sensor endplates, special Teflon pump and plumbing, and front panel meter modifications. Internally, the electronics were modified to accomodate the sensor, instrument, and readout specifications. All instrument changes were documented for presentation in the instrument manual.

For hydrazine analysis, the sensor will consist of a Au catalysed sensing electrode biased at +0.1V vs. the reference Pt/Air electrode and contain 23% KOH electrolyte solution, and the electrode will be fabricated with the membrane used to obtain the results in FIGURE 20. The reasons for the selection of this system are: 1) high sensitivity, 2) fast response time, 3) high selectivity, 4) ESI's previous experience in fabricating Au electrodes, 5) reproducibility, and 6) Au black can readily be obtained commercially.

For NO_2 analysis, the sensor will consist of an Au catalysed sensing electrode biased at -0.20V vs. Pt/Air electrode and containing 28% H_2SO_4 solution, and a filter will be used to achieve high instrument selectivity.

FIGURE 24 is a picture of the front instrument face and control panel of the ECOLYZER MODEL 7630 prototype instrument. FIGURE 25 and Table IX can be used to determine the utilization of the instrument functional controls. The two prototype instruments constructed were ECOLYZER

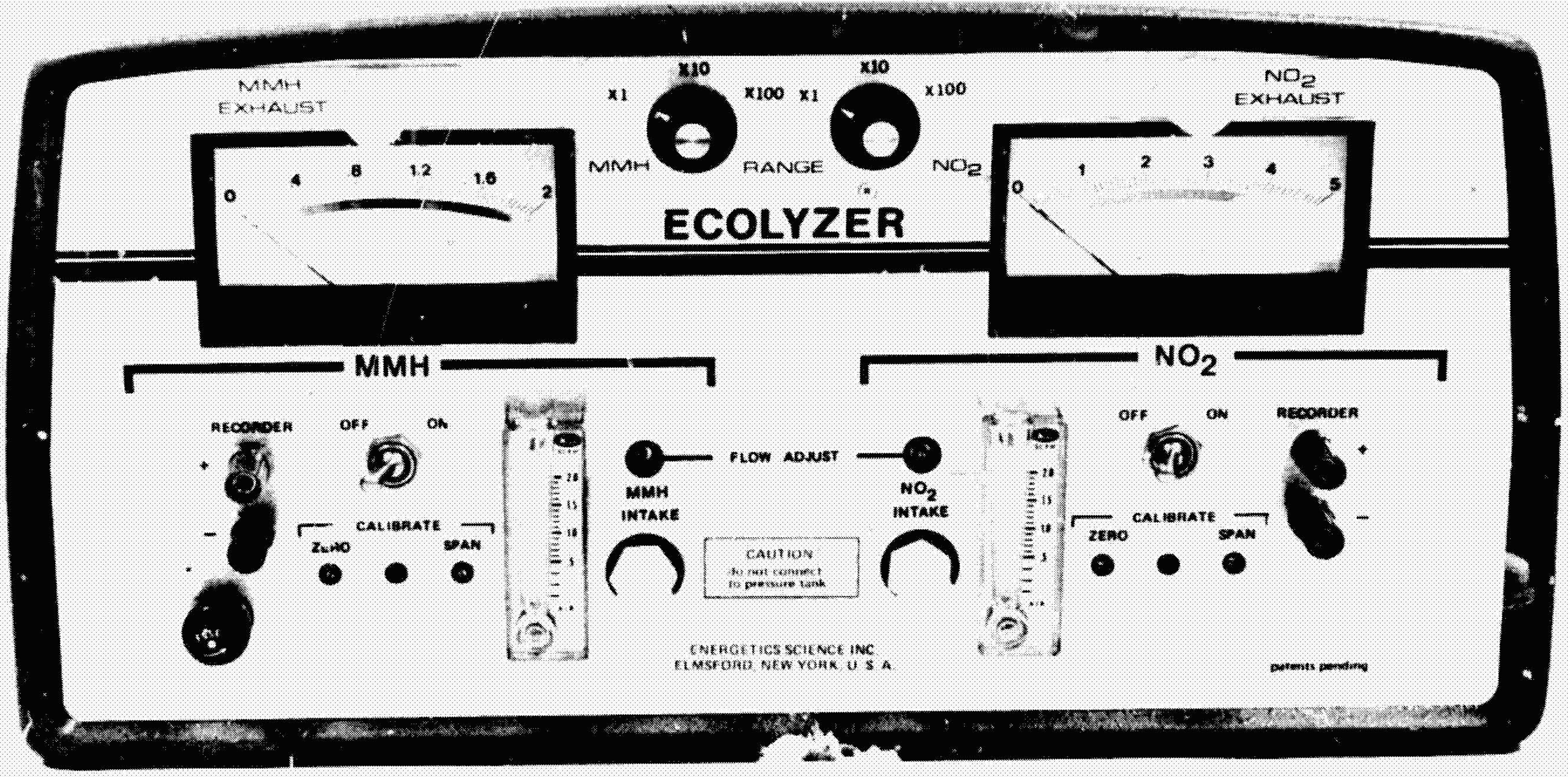


FIGURE 24 ECOLYZER MODEL 7630

FIGURE 25 ECOLYZER OPERATING CONTROLS

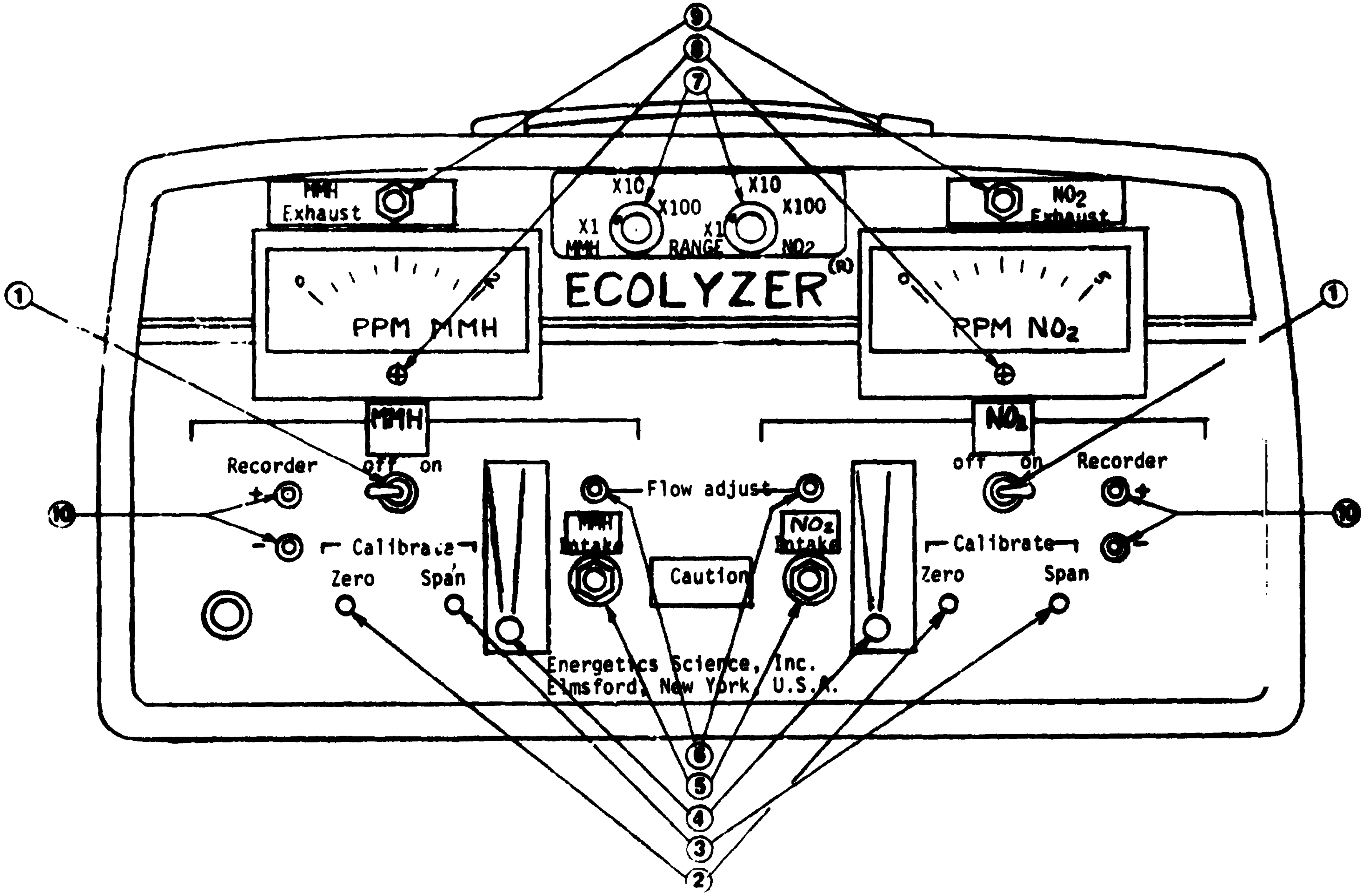


TABLE IX

FUNCTION OF THE ECOLYZER CONTROLS

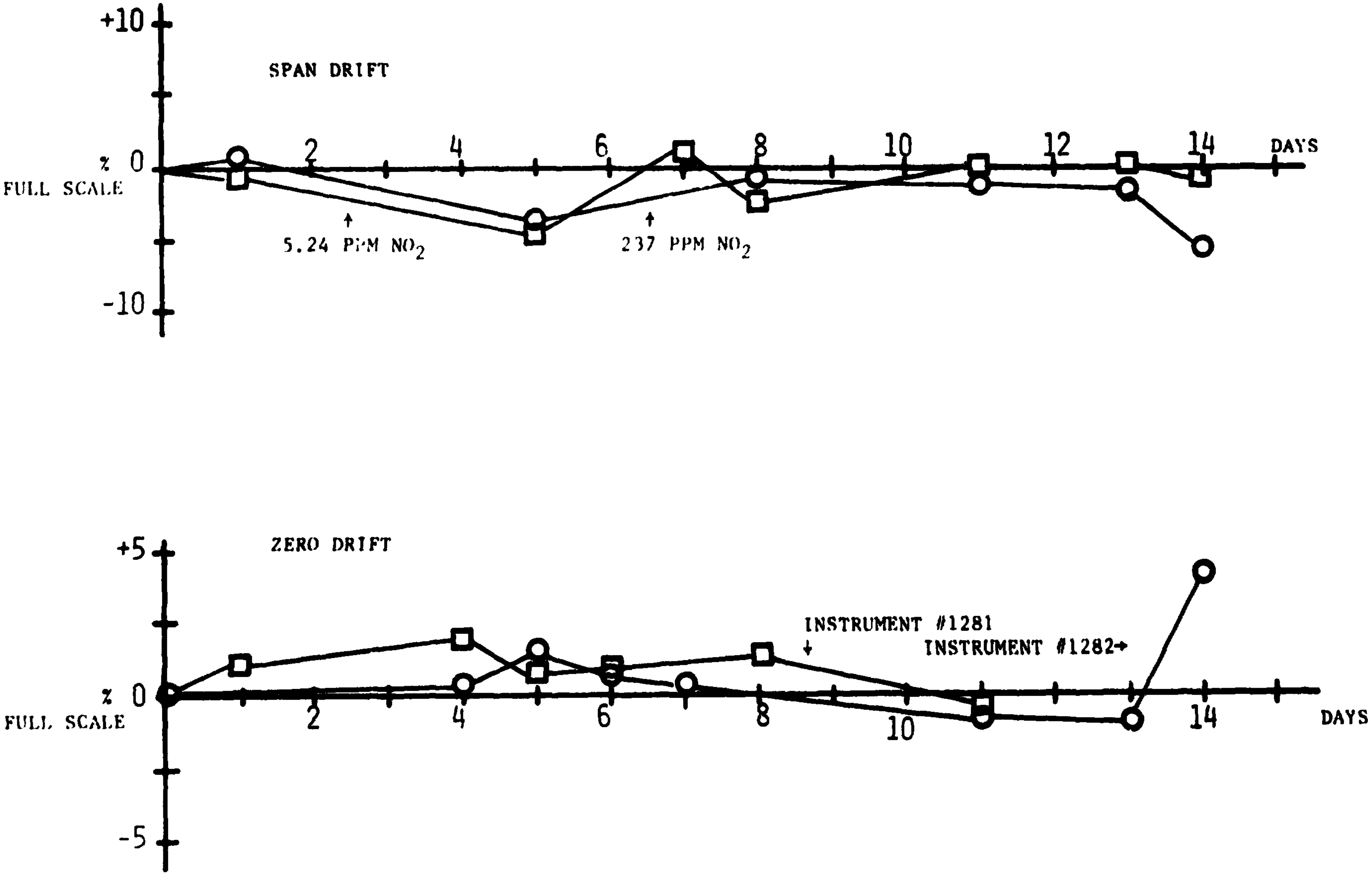
	CONTROL	FUNCTION
1)	Selector Switch	
	"on"	Instrument power is "on".
	"off"	Instrument Power is "off".
2)	Zero	Provides precise setting of instrument electronic zero.
3)	Span	Provides for calibrating the instrument response with known MMH and NO_2 span gas mixtures.
4)	Flowmeter	Provides for reading the sampling gas flow rate through the sensor in s.c.f.h.
5)	Intake	Provides ¼" TFE Teflon compression fitting for connecting gas samples or ambient gas probes.
6)	Flow Adjust	Provides a needle valve for adjusting gas flow through MMH and NO_2 sensors.
7)	Range Selector Switch	Provides for selection of the instrument ranges of 0-2, 0-20 and 0-200 ppm full scale for MMH sensing and 0-5, 0-50 and 0-500 ppm NO_2 full scale for NO_2 sensing.
8)	Panel Meter Zero	Provides a means for setting the mechanical zero of the front panel meters.
9)	Exhaust	Provides ¼" compressing fitting for remote exhausting or sampled gas mixtures.
10)	Recorder Inputs	Provides plug terminals for connection of a C-5V full scale recorder.

Model 7630, Serial Numbers 1281 and 1282.

In order to estimate field performance of the developed instrument, the span and zero drift of the NO_2 instruments is given in FIGURE 26. Long term zero and span drift tests are in progress but it is anticipated that results will be similar to those reported here. Similar data for the MMH sensor are reported in FIGURE 27 where the span drift was evaluated at approximately 5 ppm MMH/N_2 and 0.2 ppm MMH corresponds to 10% of full scale on the most sensitive range. This test was performed on a production type sensor and the useful life of this sensor was evaluated under most severe conditions (0% R.H. and continuous 24 hr/day operation) to be ten work weeks (8 hr/day). Further tests are designed to determine and extend the maximum useful life possible for a typical production grade MMH instrument sensor.

FIGURES 28 and 29 show sample instrument responses for NO_2 and MMH, respectively for prototype instrument Number 1282. The circles mark 90% rise and decay points being less than 12 seconds for NO_2 at two concentrations and approximately 36 seconds for 7.2 ppm MMH/N_2. The response for MMH is concentration dependent requiring up to three minutes to attain 100% response (21 minutes to 90%) at low levels (<1 ppm) and similar response is observed for 100% instrument decay. Maximum rise and decay times are achieved by using inert (Teflon) analyzer parts which contact the gas stream which minimizing the surface area in contact with the vapor mixture. Similar results for instrument 1281 are shown in FIGURES 30 and 31. The 237 ppm NO_2 and 5.24 ppm NO_2/air

FIGURE 26 ZERO AND SPAN DRIFT FOR NO_2 INSTRUMENTS



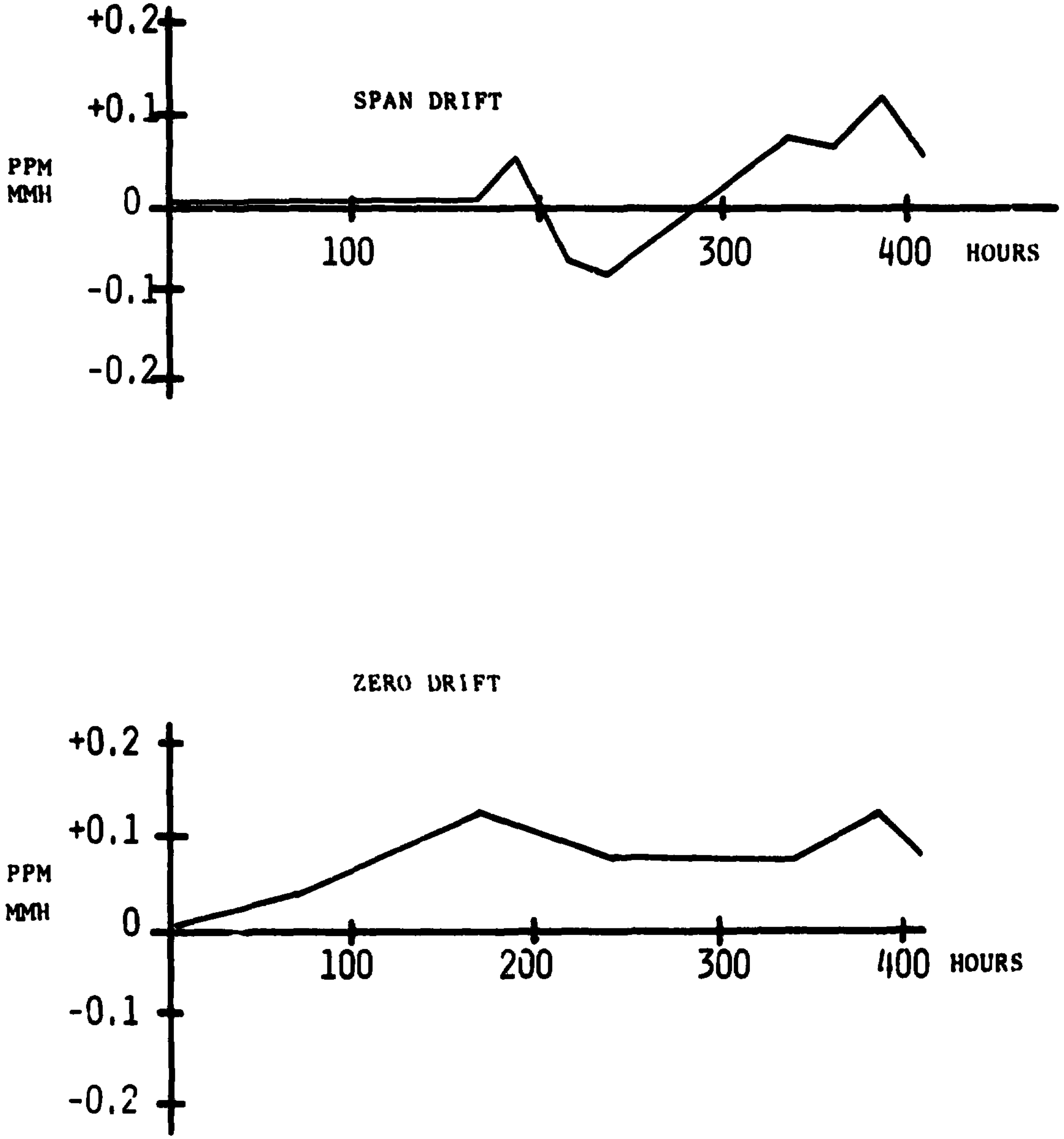


FIGURE 27 ZERO AND SPAN DRIFT FOR MMH INSTRUMENT SENSOR

FIGURE 28 NO$_2$ RESPONSE FOR PROTOTYPE INSTRUMENT #1282

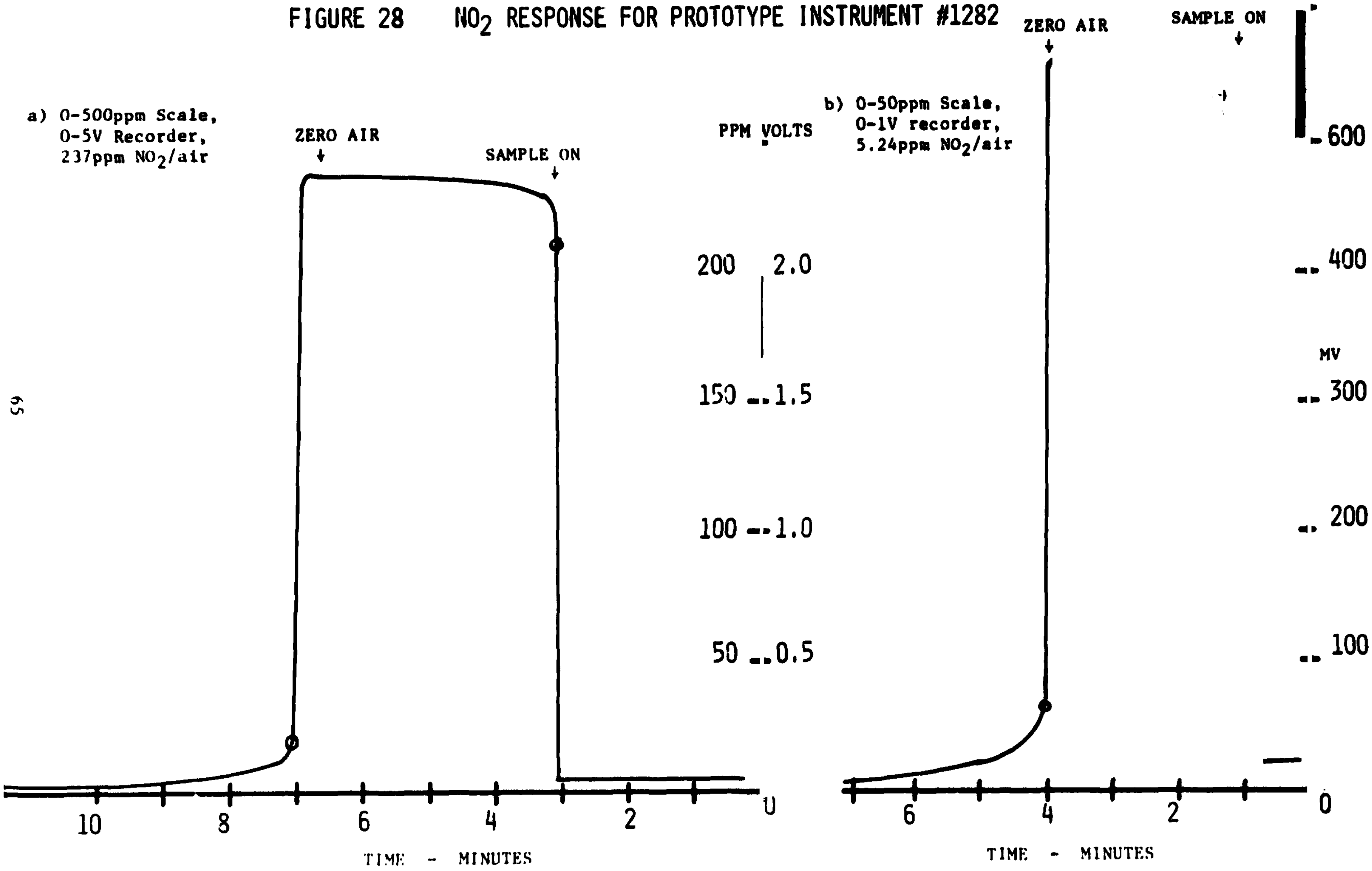
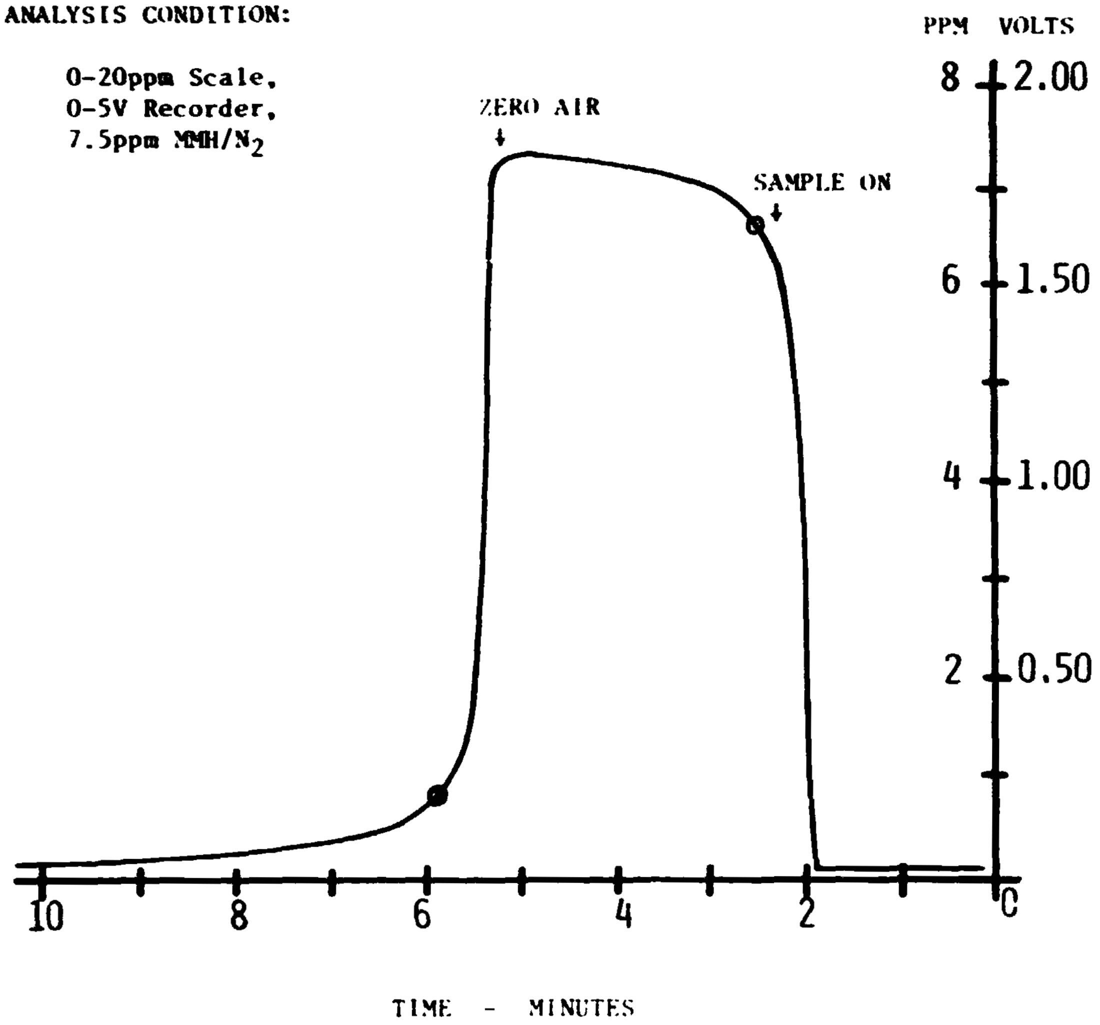


FIGURE 29 MMH RESPONSE FOR PROTOTYPE INSTRUMENT #1282



ANALYSIS CONDITION:

0-20ppm Scale,
0-5V Recorder,
7.5ppm MMH/N_2

FIGURE 30 NO_2 RESPONSE FOR PROTOTYPE INSTRUMENT #1281

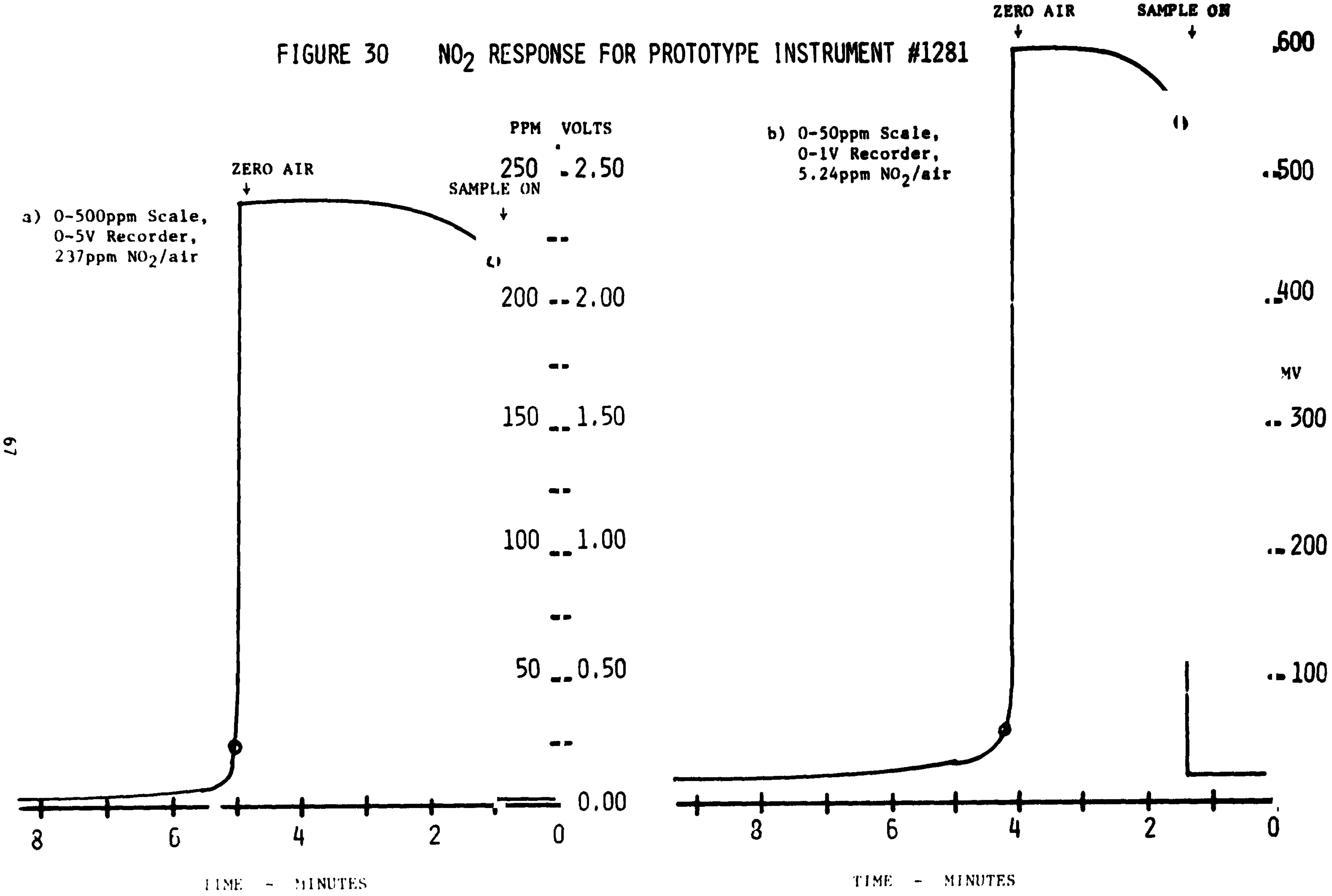
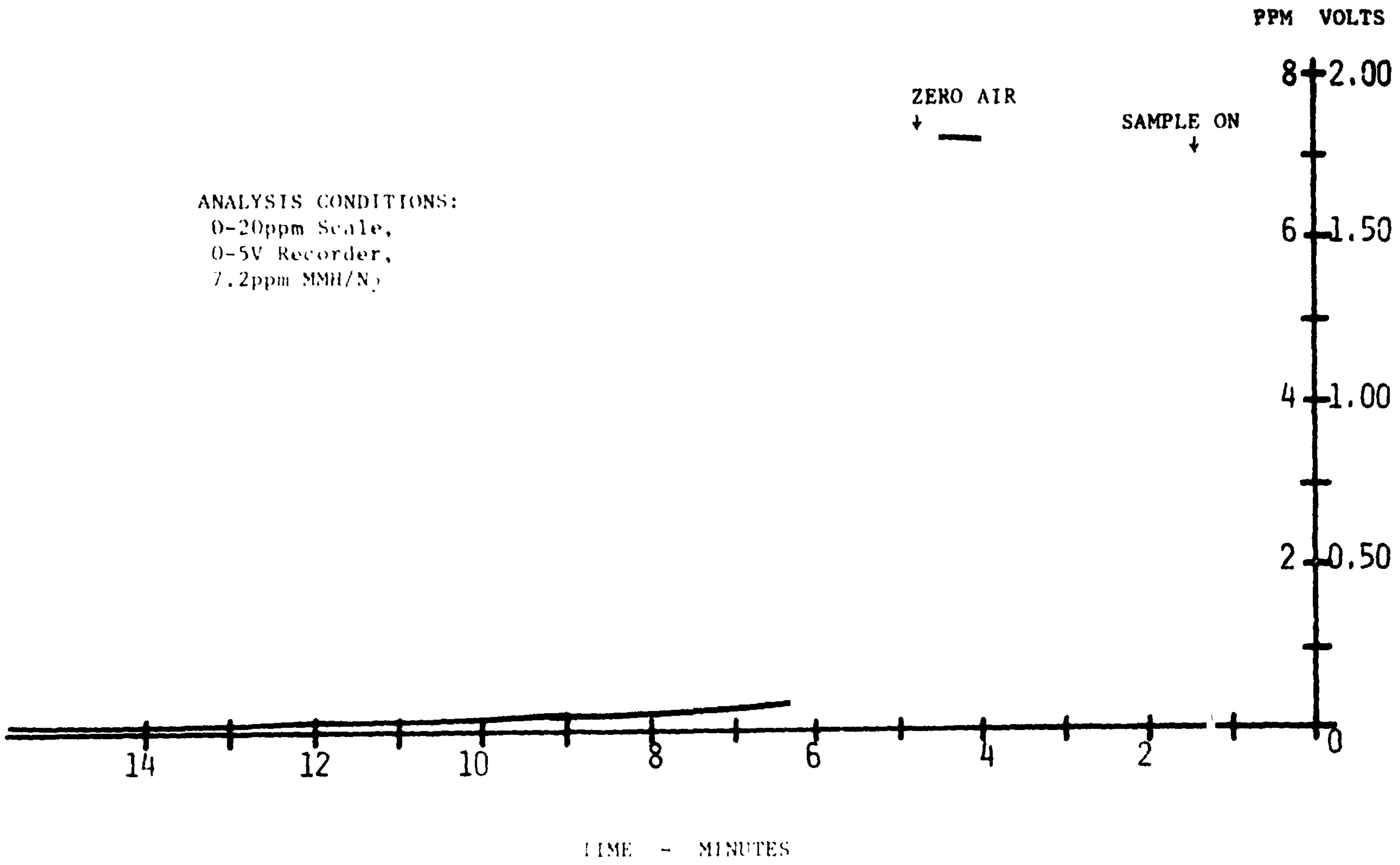


FIGURE 31 MMH RESPONSE FOR PROTOTYPE INSTRUMENT #1281



ANALYSIS CONDITIONS:
0-20ppm Scale,
0-5V Recorder,
7.2ppm MMH/N_2

mixtures are separate preparations each accurate to ±2% of full value and the instruments were spanned using the 237 ppm NO_2/air mixture.

Temperature dependence of the instrument response is given in Table X. FIGURE 32 reports this data for a hydrazines and an NO_2 sensor. For the NO_2 sensor little or no variation is seen over the range 0-35°C, while for the MMH sensor the variation noted is difficult to determine precisely since much scatter is found in the data due to the difficulty in the preparation, calibration, handling, analysis, and the stability of the MMH/N_2 gas mixtures (±10%). At the low temperature (<10°C) results of the MMH analysis were erratic. This was attributed to condensation of the vapor in the instrument tubing, pump, and sensor. It is apparent that for most precise and accurate results at low temperatures a heated sampling and analysis system is preferable, especially if the sample is transported over a long distance. This problem, however, is not inconsistent with the fact that hydrazines in the ambient air will also be condensed on cold surfaces.

Table XI gives a list of the instrument interferences. These are for one typical sensor and, while results may vary with the individual sensor, this data is representative of a production quality sensor. The interferences are listed as to the signal generated for the particular gas mixture tested, i.e., for H_2 in the NO_2 instrument 23,400 ppm H_2 was found to give a negative signal of 1.35 ppm NO_2 this means that H_2 has an interference ratio of-17333 to 1 on this instrument.

TABLE X

TEMPERATURE DEPENDENCE OF MMH/NO_2 INSTRUMENT

GAS MIXTURE	TEMP.	NOISE Mv	ZERO Mv	SPAN Mv/ppm
MMH/N_2	25°C	± 1	0	185
MMH/N_2	35°C	± 1	+ 1	182
MMH/N_2	15°C	± 1	-45	187
NO_2/Air	25°C	± 1	+85	8.82
NO_2/Air	35°C	± 1	+85	8.61
NO_2/Air	12°C	± 1	--	8.44

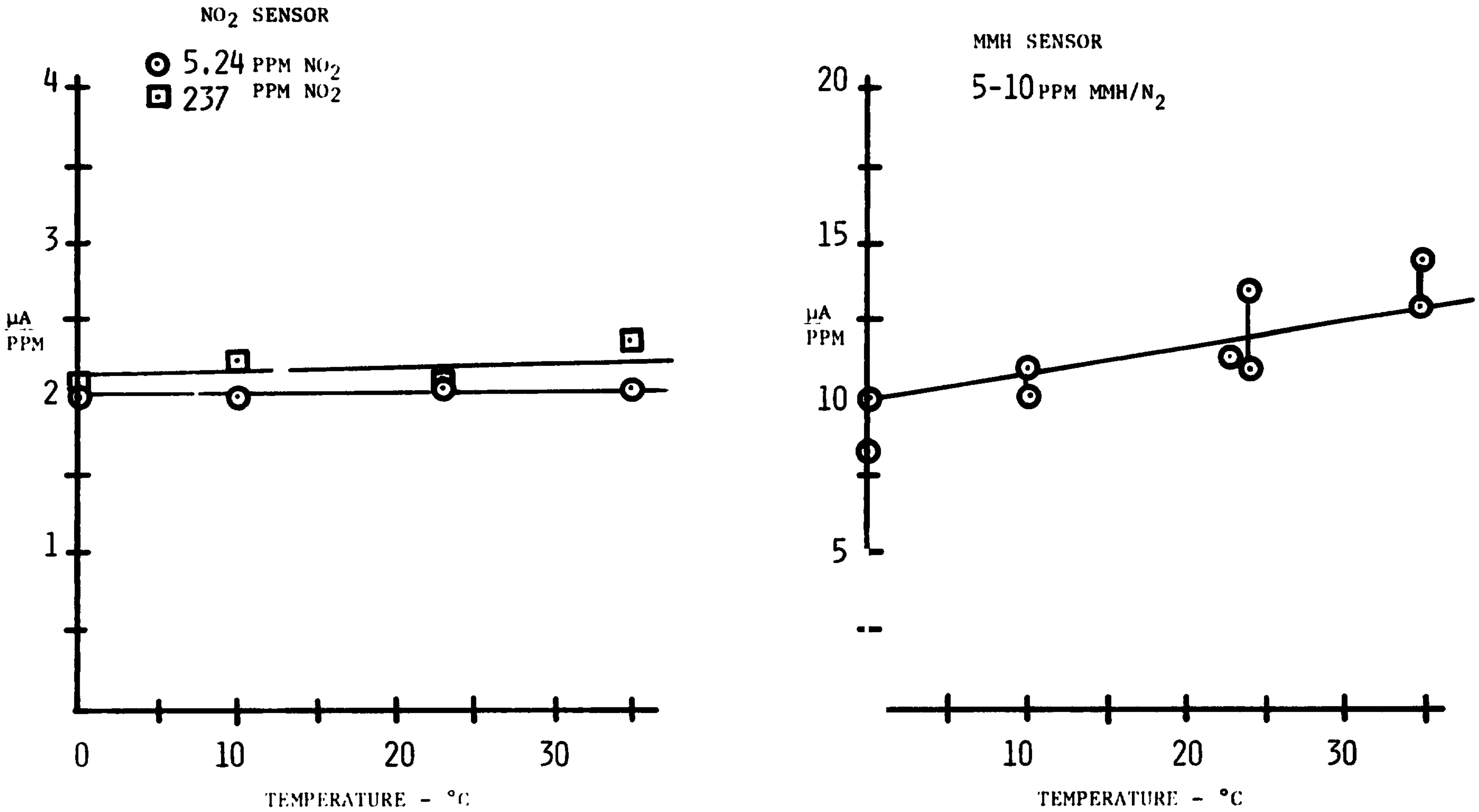


FIGURE 32 TEMPERATURE DEPENDENCE OF NO_2 AND MMH SENSORS

TABLE XI

INTERFERENCE EQUIVALENTS OF SELECTED POLLUTANTS

Gas Mixture		Reading Due to Interferent - PPM	
		MMH Analyzer	NO_2 Analyzer
MMH	5 ppm/N_2	5	0.0
NO_2	5 ppm/Air	-0.3	5
H_2	23,400 ppm/Air	+4	-1.35
CO	248 ppm/Air	+0.25	-0.1
CO_2*	- - -	0.0	0.0
CH_4	1000 ppm/N_2	0.00	0.00
NH_3	111 ppm/N_2	+40	0.00
C_2H_4	2.27 ppm/N_2	+0.1	0.0
N_2	10^6 ppm	0.0	0.0
O_2	±100,000 ppm/N_2	0.0	±0.015
Ar*	- - -	0.0	0.0
He	10^6 ppm	0.06	0.0
Freon TF(60% EtOH Azeotrope)	1000 ppm/N_2	+0.2	0.0

* Estimate

From the reported data we developed the instrument specifications given in Table XII for the ECOLYZER 7630. The minimum detectable sensitivity is given as 1/2 of 1 division on the front panel meter readout. The zero drift and span drift is estimated for thirty days from the long term data determined for sensors, and the short term instrument data which was performed during this program. Accuracy of 5% for MMH analysis is feasible only if extreme care is taken in utilization of the reference method for hydrazine analysis. The precision of the electrochemical sensor is better than 2% F.S. and is normally limited by gas mixture sampling and handling techniques rather than instrument response. These specifications compare favorably with the original program design goals (TABLE I). These instruments have the capability to provide continuous real time monitoring for H and MMH in ambient air at ppm and sub-ppm levels. While these instruments were not designed for portable use the low power requirements of this instrument allow redesigned to provide at least 8 hours of continuous battery operation.

TABLE XII

INSTRUMENT SPECIFICATIONS

	MMH ANALYZER	NO_2 ANALYZER
Multi-ranges	0-2, 0-20, 0-200 ppm	0-5, 0-50, 0-500 ppm
Minimum Detectable Sensitivity	20 ppb	50 ppb
Rise Time 90%	36 seconds	<12 seconds
Fall Time 90%	36 seconds	<12 seconds
Zero Drift*	±10%/30 Days	±10%/30 Days
Span Drift*	±10%/30 Days	±10%/30 Days
Precision	2% F.S.	2% F.S.
Accuracy**	5% F.S.	2% F.S.
Noise	<1% F.S.	<1% F.S.
Operating Temperature Range	0-35°C	0-35°C
Operating Relative Humidity	10-95%	10-95%
Dimensions	← 8" x 8" x 16" →	
Weight	← 17 lbs. - 7.7 Kg. →	
Readout	Meter, 50 Divisions Mirrored Recorder, 0-5V DC	Meter, 50 Divisions Mirrored Recorder, 0-5V DC
Power	← 105 - 125V AC →	

* Estimate using data reported for short term studies

** Using a reference standard gas mixture of the same accuracy. With a more accurate standard reference method an accuracy within the specified precision can be achieved for Hydrazines.

V. CONCLUSIONS AND RECOMMENDATIONS

During the performance of this program the problems of the modern day hydrazine analyst became readily apparent. While several methods are available for sensitive hydrazine determinations they lack, for one reason or the other, certain vital characteristics necessary for the solution of environmental hydrazine problems. They are either insufficiently sensitive, complex, or non-continuous. In this area the prototype ECOLYZER MODEL 7630 represents a significant advance is the state-of-the-art of hydrazine analysis. It is simple, sensitive, and can be used for continuous or intermittent hydrazine analysis requiring only minutes to obtain accurate ppb level determinations.

Brought to light during the program was the extreme sensitivity of the diffusion electrode and its potential application to continuous and non-continuous analytical techniques for hydrazines. Although only H and MMH were studied in detail during this program UDMH was observed to behave similar to MMH in this instrument.

Some instrument limitations were encountered such as the shorter lifetimes observed for the basic electrolyte-diffusion electrode system than for sensors with acid electrolyte. This is not surprising since past fuel cell work has encountered similar problems. It appears that the severity of this limitation strongly depends upon electrode-sensor design and therefore is not fatal to instrument design. Further, the experiments with acid systems reveal that with future development these could provide [illegible] solutions for hydrazine sensor longevity problems.

One of the most basic implications of the study is the present state of the analytical chemistry of hydrazine. Methods available, (it was necessary to choose one for a reference method for our electrochemical instrument calibration) are plagued by limitations of complexity, precision, and absolute accuracy. This electrochemical sensor method shows the promise of increasing hydrazine analysis precision by an order of magnitude and accuracy by at least as much with an adaptation of the technique. These concepts are important since new regulation is requiring measurement of hydrazines in the ppb range thus demanding improved analytical methods. Effective worker and workplace protection is placing even more stringent demands upon the utility of the analytical method in terms of real time monitoring capability.

While the instrument developed under this program can by no means fill all of these requirements, improvements have become obvious during the performance of this program which will significantly broaden the scope of this work. Of these improvements, some are easily implemented, such as minimizing the sampling tubing within the instrument for faster responses, and others, such as improved sensor lifetime and selectivity, will demand further research and development effort.

We look forward to improvements in both instrument design and instrument capability as it is applied to its specific function, i.e. real time monitoring of hydrazines, while new instruments using this electrochemical technology will evolve to satisfy other requirements such as portable monitors, laboratory analyzers, leak testing equipment and dosimeters. The technique also looks forward to improved methodology that will provide increasing accuracy and precision to hydrazines analyses and eventual application to the development of an absolute analytical method for hydrazine analysis.

This instrument clearly demonstrates that it can be both analytically accurate and cost-effective which makes it not only efficient but also practical in its real world implementation. This is its valuable contribution to solving present technical, legal, and societal requirements concerning environmental hydrazine problems.

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APPENDIX I

AMERICAN SOCIETY FOR TESTING AND MATERIALS

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Standard Method of Test for

HYDRAZINE IN INDUSTRIAL WATER[1]

ASTM Designation: D 1385 - 67

This Standard of the American Society for Testing and Materials is issued under the fixed designation D 1385; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This method[2] covers the colorimetric determination of hydrazine in industrial water.

2. Summary of Method

2.1 Para-dimethylaminobenzaldehyde produces a specific, yellow reaction product with hydrazine. The intensity of the yellow color is proportional to the amount of hydrazine in the water, and follows Beer's law.

3. Definitions

3.1 For definitions of terms used in this method, refer to ASTM Definitions D 1129[3], Terms Relating to Industrial Water and Industrial Waste Water.

4. Interferences

4.1 The substances normally present in industrial water do not interfere with the test; however, the hydrazine content may be diminished by oxidizing agents collected with the sample or absorbed by it prior to testing.

4.2 Colors in the prescribed wavelengths also interfere, as do other dark colors or turbidities that cannot be overcome by the prescribed treatment.

5. Apparatus

5.1 *Colorimeter or Photometer*—A Duboscq-type colorimeter, or a filter photometer or spectrophotometer suitable for measurements at 458 mμ. Table 1 shows the ranges to which various photometers are applicable. The quantities are based on a band width of 10 mμ and are increased by approximately 10 per cent for a band width of 40 mμ. Photometers and photometric practices prescribed in this method shall conform to ASTM Recommended Practice E 60, Photometric Methods for the Chemical Analysis of Metals;[4] spectrophotometers shall conform to the ASTM Recom-

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[1] Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-19 on Water. A list of members may be found in the ASTM Year Book.

Current edition accepted Sept. 8, 1967. Originally issued 1955. Replaces D 1385 - 64.

[2] For further information on this method, the following references may be of interest: Watt, G. W., and Chrisp, J. D., "Spectrophotometric Method for the Determination of Hydrazine," *Analytical Chemistry*, Vol 24, No. 12, 1952, pp 2006–2008; and Wood, P. R., "Determination of Maleic Hydrazide Residues in Plant and Animal Tissue," *Analytical Chemistry*, Vol 25, No 12, 1953, pp. 1879-1883.

[3] Appears in this publication

[4] *1967 Book of ASTM Standards*, Part 32.

mended Practice E 275, Describing and Measuring Performance of Spectrophotometers.[5]

5.2 Certain photoelectric filter photometers are capable of measurements at 425 mμ, but not at 458 mμ. Measurements may be made at 425 mμ, with a reduction in sensitivity of approximately 50 per cent of that possible at 458 mμ.

6. Reagents

6.1 Reagent grade chemicals, or equivalent, as defined in ASTM Method E 200, Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis,[3] shall be used in all tests.

TABLE 1—APPLICATION RANGES OF PHOTOMETERS

Scale Length, mm/per cent transmission	Solution Thickness, mm	Range, micrograms of N_2H_4 in 60 ml of final solution
1	10	0.20 to 25.0
	50	0.05 to 5.0
2.5	10	0.05 to 25.0
	50	0.02 to 5.0
5.0	10	0.05 to 25.0
	50	0.01 to 5.0

6.1.1 The purity of hydrazine dihydrochloride may be established[4] by iodimetric methods, making certain that all water used is oxygen free and that all flasks and pipets used are purged with nitrogen. The water for this reagent is best prepared by boiling and then cooling under a nitrogen blanket.

6.1.2 Para - dimethylaminobenzaldehyde reagents obtained from different manufacturers produce different intensities of color in solution. It is necessary that each new supply of reagent be tested on standard solutions before using with previously determined calibration curves.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specifications D 1193, for Reagent Water[3], referee grade. In addition, water shall be freshly boiled and free of dissolved oxygen.

6.3 *Hydrazine, Standard Solution (1 ml = 0.1 mg N_2H_4)*—Dissolve 0.328 g of hydrazine dihydrochloride ($N_2H_4 \cdot 2HCl$) in 100 ml of water and 10 ml of HCl (sp gr 1.19). Dilute with water to 1 liter in a volumetric flask, and mix.

6.4 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

6.5 *Hydrochloric Acid (1:9)*—Mix 1 volume of HCl (sp gr 1.19) with 9 volumes of water.

6.6 *Hydrochloric Acid (1:99)*—Mix 1 volume of HCl (sp gr 1.19) with 99 volumes of water.

6.7 *Para - Dimethylaminobenzaldehyde Solution*—Dissolve 4.0 g of p-dimethylaminobenzaldehyde in 200 ml of methyl alcohol (CH_3OH) and 20 ml of HCl (sp gr 1.19). Store in a dark bottle out of direct sunlight.

7. Sampling

7.1 Collect the sample in accordance with the applicable method of the American Society for Testing and Materials, as follows:

D 510, Sampling Industrial Water,[3]
D 860, Sampling Water from Boilers,[3]
D 1066, Sampling Steam,[3] and
D 1192, Equipment for Sampling Industrial Water and Steam.[3]

7.2 Analyze the sample as soon after collection as practicable, since hydrazine undergoes auto-oxidation as well as oxidation by oxidizing agents. Such agents may be in the sample or may enter the sample from the atmosphere. If it is suspected that oxidation of the

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[5] *1967 Book of ASTM Standards, Part 30*

hydrazine in the sample is occurring in the interval between collection and analysis, or if the sample is not to be analyzed immediately, collect under acid. Place 5.0 ml of HCl (1:9) in a 50-ml volumetric flask, and collect sufficient sample in the flask to bring the total volume to 50 ml.

8. Calibration

8.1 Prepare a series of hydrazine standards by making appropriate dilutions of the hydrazine solution (1 ml = 0.1 mg N_2H_4) with HCl (1:99), so that a 50.0-ml aliquot of each dilution will contain the desired quantity of hydrazine (0.2 to 5.0 μg).

8.2 Pipet 50.0-ml portions of the hydrazine standards into 100-ml beakers, flasks, or cylinders, and proceed as directed in 9. Procedure, except do not add more acid. Plot transmittance against micrograms of hydrazine.

8.3 A separate calibration curve must be made for each photometer and a recalibration must be made if it is necessary to change the cell, lamp, or filter, or if any other alterations of instrument or reagents are made. Check the curve for each series of tests by running two or more solutions of known hydrazine concentrations.

9. Procedure

9.1 To a 100-ml beaker, flask, or cylinder, add from a buret exactly 5.0 ml of HCl (1:9), unless the sample was collected under acid, in which case, proceed directly as described in 9.2, except to use HCl (1:99) instead of water for diluting to 50.0 ml.

9.2 By means of a graduated pipet, transfer to the 100-ml beaker, flask or cylinder a portion of the sample that will contain approximately 0.20 to 5.0 μg of N_2H_4. Add water from a graduated buret or pipet to make a final volume of exactly 50.0 ml, and mix. Add 10.0 ml of p-dimethylaminobenzaldehyde solution with a pipet, and mix. Let the mixture stand at least 10 min and not more than 100 min. Measure and compare the color by means of any of the colorimeters listed in 5. Apparatus. Make photometric measurements at approximately 458 mμ (see 5.2).

9.3 In photometric procedures, with water showing no appreciable color, prepare a blank containing no added hydrazine in order to correct for the color of the unreacted *p*-dimethylaminobenzaldehyde and any optical effects involved in adjusting the photometer for 100 per cent transmission. In the case of highly-colored water, prepare a blank by using the sample, after having first oxidized the hydrazine in the sample by suitable means. Determine the completeness of the oxidation of the hydrazine by making a plot of the percentage transmittance (compared to water to which the reagents have been added) versus wavelength for the spectral region 400 to 500 mμ, and noting whether the characteristic dip of para-dimethylaminobenzalazine occurs at 458 mμ.

10. Calculation

10.1 Calculate the hydrazine concentration, in milligrams per liter, as follows:

$$\text{Hydrazine, mg/liter (ppm)} = \frac{W}{S}$$

where:

W = micrograms of hydrazine found in accordance with 9. Procedure, and

S = milliliters of sample.

11. Precision[6]

11.1 The precision may be expressed as follows:

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[6] Supporting data have been filed at ASTM headquarters.

$$S_0 = \frac{0.99X + 0.041}{s}$$

$$S_t = \frac{1.08X + 0.081}{s}$$

where:

S_0 = single-operator precision expressed in milligrams per liter of hydrazine,
S_t = over-all precision expressed in milligrams per liter of hydrazine,
X = concentration of hydrazine determined in milligrams per liter, and
s = milliliters of sample taken for test.

60-95 X