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NASA CR-
150947

THE DEVELOPMENT OF AN ELECTROCHEMICAL TECHNIQUE FOR IN SITU CALIBRATION OF COMBUSTIBLE GAS DETECTORS

FINAL REPORT

by

J. W. Shumar, J. B. Lantz,
F. H. Schubert

July, 1976

Prepared Under Contract NAS9-14658

by

Life Systems, Inc.
Cleveland, Ohio 44122

for

LYNDON B. JOHNSON SPACE CENTER
National Aeronautics and Space Administration

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FOREWORD

This report was prepared by Life Systems, Inc., for the National Aeronautics and Space Administration Lyndon B. Johnson Space Center in accordance with the requirements of Contract NAS9-14658, "Air Revitalization and Hydrogen Sensor Development." The period of performance for the program was September 1, 1975 to August 31, 1976. The objective of the program was to test a One-Man, Electrochemical Air Revitalization System and to develop an in situ calibration concept for combustible gas detectors.

For simplicity, the work performed has been reported in two separate final reports. The results of the One-man, Electrochemical Air Revitalization System test program is reported in Life Systems' ER-284-4, while this report describes the development of the in situ calibration concept for combustible gas detectors.

All measurements and calculations contained in this report are expressed in SI (metric) units; conventional units are given in parentheses.

The overall Program Manager was F. H. Schubert with the in situ calibration development activities directed by J. W. Shumar. Technical support for the in situ calibration development was provided by J. B. Lantz, PhD, P. Y. Yang, PhD, R. R. Woods, R. A. Wynveen, PhD and G. A. Little.

The Contract Technical Monitor was Mr. Nick Lance, Jr., Crew Systems Division, Lyndon B. Johnson Space Center, Houston, Texas 77058.

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LIST OF ACRONYMS

| | |
|--------|--|
| CGD | Combustible Gas Detector |
| EC/LSS | Environmental Control/Life Support Systems |
| EDC | Electrochemical Depolarized Concentrator |
| FSS | Fluid Supply System |
| LEL | Lower Explosive Limit |
| MSS | Modular Space Station |
| NGS | Nitrogen Generating Subsystem |
| OGS | Oxygen Generation Subsystem |
| RLSE | Regenerative Life Support Evaluation |
| SSP | Space Station Prototype |
| TSA | Test Support Accessories |
| WES | Water Electrolysis System |
| WVE | Water Vapor Electrolysis |

SUMMARY

Current designs for future space vehicles incorporate several systems that utilize and/or produce combustible gases. In order to provide crew safety it is necessary to incorporate Combustible Gas Detectors to provide for crew warning and system shutdown in the event of a combustible gas leak. Existing calibration procedures for Combustible Gas Detectors are tedious, time consuming and require support equipment. The development of an in situ calibration technique for Combustible Gas Detectors which minimizes required crew time and support equipment is desirable.

A program to determine the feasibility of performing in situ calibration of Combustible Gas Detectors was successfully completed. Several possible techniques for performing the in situ calibration were proposed. The approach that showed the most promise involved the use of a miniature Water Vapor Electrolysis cell for the generation of hydrogen within the flame arrestor of a Combustible Gas Detector to be used for the purpose of calibrating the Combustible Gas Detectors. A preliminary breadboard of the in situ calibration hardware was designed, fabricated and assembled. The breadboard equipment consisted of a commercially available Combustible Gas Detector, modified to incorporate a Water Vapor Electrolysis cell, and the instrumentation required for controlling the Water Vapor Electrolysis and controlling and calibrating the Combustible Gas Detector.

Test Support Accessories required for evaluation of the Combustible Gas Detector and Water Vapor Electrolysis were designed, fabricated and assembled. The Test Support Accessories included an environmental chamber for establishing the various hydrogen-in-air concentrations for characterizing the Combustible Gas Detector, a Fluid Supply Section providing for the delivery and control of the calibration gases and an Instrumentation Section to allow monitoring of the Combustible Gas Detector and Water Vapor Electrolysis performance.

Characterization tests were performed individually on the commercial Combustible Gas Detector and on the Water Vapor Electrolysis cell. The Combustible Gas Detector's linearity, position sensitivity, reproducibility, zero drift and repeatability were determined. The Water Vapor Electrolysis cell's current versus voltage characteristics at an ambient air relative humidity of 50% were determined and the Water Vapor Electrolysis voltage, as a function of in situ calibration trials, was recorded.

Testing was performed on the breadboard in situ calibration equipment. Time, current density and hydrogen concentration profiles were obtained in order to establish the operating parameters of the Water Vapor Electrolysis cell for hydrogen generation required for calibrating the Combustible Gas Detector. The results showed that operation of the Water Vapor Electrolysis at a given current density for a specific time period resulted in the attainment of a hydrogen concentration plateau within the flame arrestor of the Combustible Gas Detector. Initially, operation of the Water Vapor Electrolysis at 9.4 mA/cm^2 (8.7 ASF) for eight minutes yielded a plateau at 0.5% hydrogen. Further

experimental work was performed in order to reduce the hydrogen generation time required for performing in situ calibrations. It was found that the calibration time could be reduced from eight to two minutes by maintaining a constant voltage of 1.5V on the Water Vapor Electrolysis followed by a pre-plateau of 19 mA/cm² (17.7 ASF), followed by the calibration point plateau of 9.4 mA/cm² (8.7 ASF). An in situ calibration procedure was established and the repeatability and accuracy of the procedure was determined. The three-sigma variation for the selected in situ calibration sequence was ±0.008% hydrogen. The experimental work performed revealed that in situ calibration of Combustible Gas Detectors using a Water Vapor Electrolysis cell for the generation of the hydrogen calibration gas mixture is a viable technique for calibrating Combustible Gas Detectors.

At the conclusion of the program it was apparent that the next effort for advancing the in situ calibration technology should include the development of an in situ zero calibration technique, the development of the electronics required for automatic calibration and the incorporation of a triple redundant sensor head with the in situ calibration hardware. In addition, it is also recommended that supporting studies aimed at defining and evaluating advanced concepts for the detection of combustible gases for future manned space vehicles be prepared.

INTRODUCTION

Space vehicles for future extended duration manned spaceflight will require regenerative Environmental Control/Life Support Systems (EC/LSS). Many subsystems currently being developed to make up the EC/LSS utilize or produce hydrogen (H₂) gas. Some of these subsystems are the Water Electrolysis System (WES)⁽¹⁾ which generates breathable oxygen (O₂) and produces the by-product H₂, the Bosch⁽²⁾ or Sabatier⁽³⁾ Carbon Dioxide (CO₂) Reduction Subsystems which use H₂ in the process of regenerating O₂ from CO₂, the Electrochemical Depolarized Concentrator (EDC)⁽⁴⁾ which uses H₂ to depolarize the anode in the process of removing CO₂ from the cabin atmosphere, and the Nitrogen (N₂) Generating Subsystem (NGS)⁽⁵⁾ which uses hydrazine (N₂H₄) or ammonia (NH₃)⁽²⁾ as the primary N₂ source with H₂ as the by-product.

In addition to those subsystems in the EC/LSS that utilize H₂, NASA Modular Space Station (MSS) design studies have included the use of H₂ in the electrical power system and reaction control system.⁽⁶⁾ The energy storage assembly of the control system uses H₂ and O₂ for the engines.

The Space Station Prototype (SSP) program sponsored by the NASA Johnson Spacecraft Center (JSC) involved the design, development, fabrication and assembly of an advanced EC/LSS. The SSP EC/LSS included three subsystems which produced or utilized H₂ are an O₂ Generation Subsystem (OGS), the EDC and a Sabatier CO₂ Reduction Subsystem.

The Regenerative Life Support Evaluation (RLSE) experiment planned for the mid-1980's will include H₂-bearing subsystems. Current plans for the RLSE

(a) References cited in parentheses are at the end of this report.

incorporate the EDC, an OGS and a Sabatier CO₂ Reduction Subsystem.⁽⁷⁾ In addition, Combustible Gas Detectors (CGDs) are utilized on the launch pad to monitor for H₂ leaks during the H₂ fueling of rockets prior to launch. This program, therefore, has application to subsystems that make up the EC/LSS of spacecrafts, to hardware that make up the electrical power and reaction control system of spacecrafts and to support equipment on the launch pad.

The H₂ gas molecule, being small and highly mobile, can leak through air-tight seals. If it leaks into confined spaces or is permitted to accumulate, it can produce a combustible gas mixture. Prevention of these situations by incorporating H₂ safety design criteria is mandatory. Hence, a definite requirement for future space vehicles is to automatically sense for the presence of H₂ so that corrective measures can be taken before the crew would be exposed to danger.

A study⁽⁸⁾ was performed to assess the effectiveness of the H₂ detection concepts that were selected for regenerative EC/LSS of the SSP. The results of the study pointed out that frequent CGD calibrations are required and that these calibrations are time consuming, tedious and require several items of support equipment such as an environmental chamber and a calibration gas supply. The study also pointed out that presently available CGDs could not be used as triple redundant detectors and, therefore, automatic fault detection and fault isolation of the CGDs was not possible. A recommendation presented at the conclusion of the referenced study suggested the development of a Triple Redundant Hydrogen Monitor and the development of an in situ calibration technique.

The objective of this program was to design and develop an in situ calibration procedure for CGDs. This included evaluating several techniques for performing in situ calibration of CGDs, selecting one approach that showed the most promise, preparing a preliminary design of a partial breadboard, and performing bench top testing in order to arrive at an in situ calibration procedure. Once the procedure was established, testing was to be performed to evaluate the repeatability and accuracy of the in situ calibration procedure. The objectives of the program were met. The following sections summarize the work completed.

DISCUSSION

In Situ Calibration Concept

The function of a sensor is to convert a parameter such as temperature, pressure, or gas composition, to a predictable electrical signal which can then be processed by electronic circuitry for controlling and monitoring purposes. Although sensor designs are based on stable and reproducible physical characteristics, nearly all sensors require periodic calibration to maintain their accuracy and credibility. Aging of the material used in the construction, the influence of various external parameters such as temperature, vibration and shock can cause a sensor to change its characteristics.

Calibration of a sensor is a process in which the input parameter is supplied to the sensor, the resulting electrical signal is measured, and this signal is compared with the normal or standard performance for the device. There are two ways of using the calibration data obtained in this manner. The first is to record the sensor's response to the known parameter and produce a calibration curve which can then be used to accurately measure the parameter. Reference to the calibration curve by the operator then gives the actual value of the parameter. These calibration curves can be put into a computer for automatic readout, if desired.

The second calibration involves making sensor and/or circuit adjustments in response to parameter inputs such that prescribed outputs are obtained from the sensor. This is done when one wants a direct readout of parametric data or when automatic control and monitoring equipment is being used.

Usually these adjustments consist of a span or gain adjustment and an offset or zero adjustment. With these two adjustments, two points on the transfer characteristics of the sensor and electronics can be set at desired values. For a linear sensor the assumption is that the transfer characteristic will fall on the desired curve between these two points.

In summary, calibration involves supplying a known input or inputs to the sensor and measuring the response from the sensor and in some cases, making adjustments to the circuits to compensate for variations in sensor performance. This generally requires that the sensor be removed from its normal installed position and taken to a place where there is a source of known inputs. This is generally a long, time-consuming, difficult procedure. For a CGD this involves removing the instrument from its normal location and providing an environmental chamber and calibration gases or bringing the environmental chamber and calibration gases to the sensor location.

There are several disadvantages to the existing calibration procedures for CGDs which make them unattractive for manned space flight applications. These disadvantages are:

- The weight penalty at launch associated with carrying compressed calibration gases and an environmental chamber.
- The excess crew time required for performing frequent CGD calibrations.
- Flight maintainability and safety ground rules prohibit performing maintenance on subsystems while they are operational. (9) Frequent manual calibration of CGDs located on subsystems would require frequent subsystem shutdowns or a violation of the maintainability and safety rule.
- Due to the position sensitivity of certain CGDs, special mounting provisions and precautions would have to be employed to ensure that the configuration of the CGD, during the calibration, is similar to that used in its monitoring location.

Based on these disadvantages, it became apparent that the in situ calibration technique for CGDs would be an attractive development for future space vehicles. Several possible in situ calibration techniques were initially considered. Among them were the plumbing of the calibration gas from a central source to the flame arrestor of the CGD with subsequent activation of a solenoid valve to admit the calibration gas for a prescribed time period required to reach the calibration percent H₂-in-air mixture. Another proposed technique was the use of a Water Vapor Electrolysis (WVE) cell for the generation of H₂ into the confines of the flame arrestor of the CGDs in order to establish the calibration H₂-in-air mixture. The latter in situ calibration technique was selected as the one most attractive for further development. For this in situ calibration technique, a miniature WVE cell is packaged into the flame arrestor of the CGD. Then at prescribed intervals (e.g., hourly, daily, weekly, monthly), current is supplied to the WVE cell for the required time to produce a constant H₂-in-air concentration within the confines of the flame arrestor. The output of the CGD can then be automatically adjusted to the calibration gas concentration, thus completing the span calibration sequence. A sketch describing this concept is presented in Figure 1. By knowing the volume of the flame arrestor and making assumptions for the volume of gas lost through the flame arrestor and consumed on the catalyzed sensing element, it is possible, using Faraday's Law, to calculate the current density and time required to generate a given H₂-in-air concentration in the confines of the flame arrestor for various WVE cell diameters.

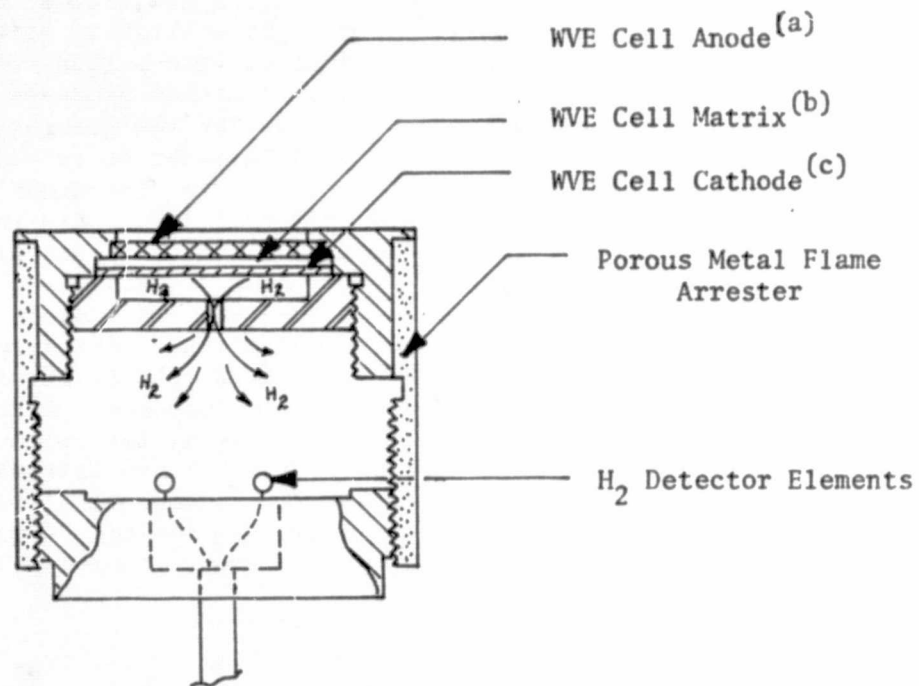
Figure 2 is a plot of detector volume versus WVE cell diameter for 20 seconds of WVE operation at various current densities required to attain a 2% H₂ mixture within the flame arrestor. The curve assumes that 30% of the H₂ generated by the WVE cell is lost through the flame arrestor and by consumption at the catalyzed sensing beads. The primary advantages inherent in the in situ calibration concept for CGDs are listed in Table 1.

Hardware Description

The breadboard in situ calibration equipment consists of a commercial CGD, a Life Systems Inc. (LSI) WVE cell and the breadboard electronics required for the operation of the integrated CGD and WVE cell. The flame arrestor of the commercial CGD was modified to incorporate the LSI WVE cell.

Commercial CGD

The commercial CGD selected for use on this program was a General Monitors, Inc. (GMI) Model 180 with a standard industrial sensor assembly (Part No. 10-001-1). The sensor assembly and the electronics package are shown in Figure 3. The sensor assembly consists of two ceramic-type elements. The active element is catalyzed, the reference element is uncatalyzed and provides temperature compensation. Both elements are mounted in an explosion-proof housing behind a screen-type flame arrestor. Both elements contact the gas vapors, however, due to the catalyst coating, only the active element responds to the combustible gas vapors. Any rapid change in temperature of the ambient atmosphere affects



- (a) Generates O_2 which is admitted to atmosphere
- (b) Contains water and electrolyte
- (c) Generates H_2 which is admitted to H_2 detector sensing cavity



FIGURE 1 IN SITU CALIBRATION CONCEPT

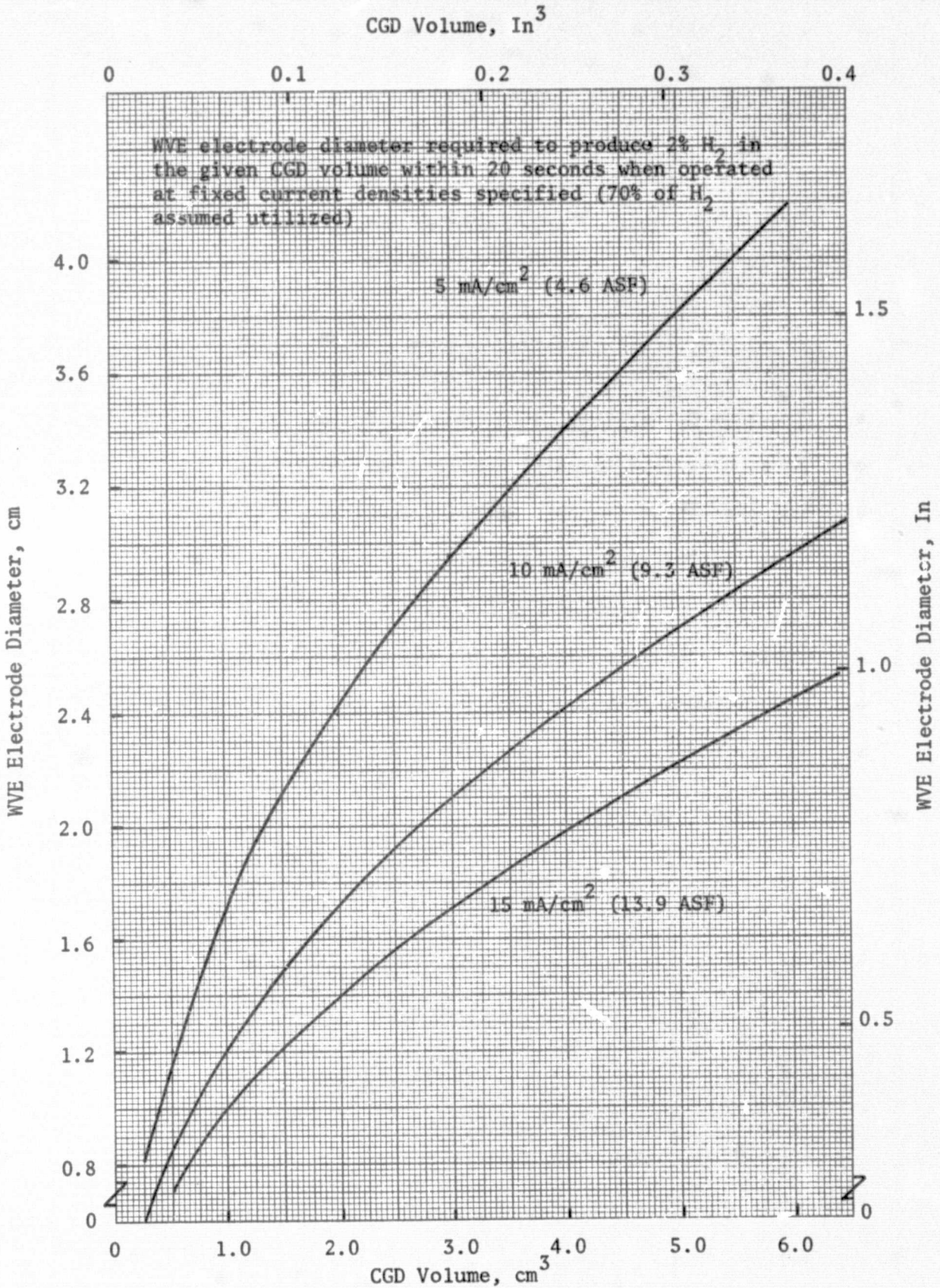


FIGURE 2 WVE ELECTRODE DIAMETER VERSUS CGD VOLUME

TABLE 1 ADVANTAGES OF THE IN SITU
CALIBRATION CONCEPT

- Provides Credibility for H₂ Monitor Output
- Saves Crew Time Normally Required for Calibrations
- Reduces Flight Support Equipment Complexity
 - Calibration Chamber
 - Calibration Gas Source
- Automatic In Situ Calibrations Avoid Human Error
- H₂ Generated is Replenished by Water Vapor in Cabin Air
- Allows Increased Frequency of Calibrations

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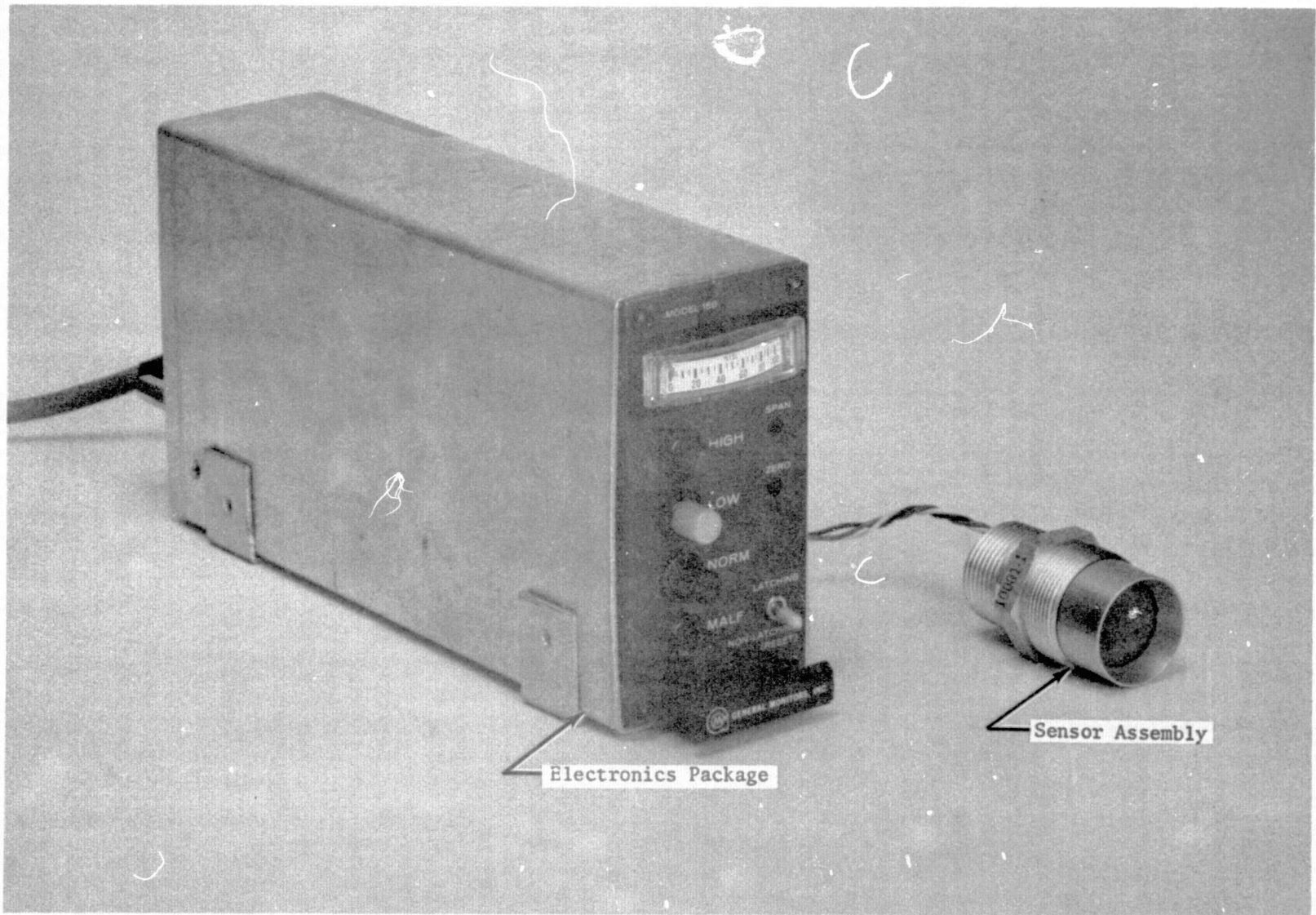


FIGURE 3 GENERAL MONITORS, INC. MODEL 180 COMBUSTIBLE GAS DETECTOR

both elements and results in no output voltage, therefore, no drift. As a result, only the presence of combustible gas vapors produces a signal. The GMI sensor operates at about 672K (750F). The Model 180 electronics package includes circuits which provide the constant current supply to the sensor to maintain its operating temperature, alarm circuits, indicators and controls. The characteristics of the GMI CGD are listed in Table 2. (10)

WVE Cell

The WVE cell used for the program is shown in Figure 4. The WVE cell contains a platinized screen cathode, a crocidolite asbestos matrix and an activated porous titanium anode. The cell body was made from polycarbonate. The H₂ cavity spacer was 0.025 cm (0.010 in) teflon screen and the H₂ gas manifold consisted of six 0.025 cm (0.010 in) diameter holes in the polycarbonate cell body. The seal between the anode and cathode side of the cell is made with a Viton A O₂ ring. The WVE cell was designed to have a cell active area of 6.45 cm² (1 in²). The cell size was dictated by the H₂ generation rate requirement and by the configuration of the CGD flame arrestor into which it was to be integrated. Electrical connections were made by spot welding platinum wires to the anode and cathode.

Integrated CGD and WVE

A sketch of the cross section of the integrated CGD/WVE showing the calculations for the sensing cavity volume (the volume that must be filled with calibration gas) is presented in Figure 5. Photos of the integrated WVE/CGD assembled and disassembled are shown in Figures 6 and 7, respectively. The commercial CGD was modified in order to be integrated with LSI's WVE cell. The modification involved the removal of the screen-type flame arrestor to allow the insertion of the porous 316 stainless steel flame arrestor and the addition of the WVE cell at the end of the flame arrestor. The characteristics of the integrated CGD/WVE assembly are described in Table 3. Based on the designed cell active area of 6.45 cm² (1 in²) and the calculated H₂ sensor volume of 4.0 cm³ (0.24 in³) for the configuration shown in Figure 5, the design WVE operating characteristics for in situ H₂ generation were determined based upon the data presented in Figure 2. Referring to Figure 2, one sees that a current density of 8.0 mA/cm² (7.4 ASF) is required. A current density of 10 mA/cm² (9.3 ASF) was selected to provide an overdesign margin of 25%. The design operating characteristics are listed in Table 4. These operating characteristics result in a design where up to 44% of the H₂ generated by the WVE could either be lost by consumption at the active sensing element or by diffusion through the porous flame arrestor. In actual testing, discussed later in this report, it was found that this assumption for H₂ loss was greatly underestimated. The testing indicated that H₂ generation times in excess of six minutes at 10 mA/cm² (9.3 ASF) are required to attain a 0.5% H₂ concentration within the flame arrestor. Based on this experimental data and the desire to initiate a H₂ warning alarm at a lower H₂ concentration, the calibration point for the CGD was established at 0.5% H₂-in-air.

TABLE 2 COMBUSTIBLE GAS DETECTOR CHARACTERISTICS

Sensor

| | |
|----------------------------------|--|
| Type | Diffusion, low temperature catalytic bead |
| Operating Temperature, K (F) | 672 (750) |
| Ambient Temperature Range, K (F) | 219.1 to 366.3 (-65 to +200) |
| Response Time | Less than one second (H ₂) |
| Drift | Less than 5% per year |
| Life | Normally up to three years |
| Wiring | Three wires; shielding not normally required |

Controller

| | |
|--------------------------|---|
| Size, cm (In) | 5.1 x 10.2 x 20.3 (2 x 4 x 8) |
| Weight, kg (Lb) | 1.36 (3) |
| Mounting | Panel mount |
| Temperature Range, K (F) | 233.0 to 338.5 (-40 to +150) |
| Power Requirements | 105 to 130 VAC, 50 to 60 Hz; or 11 to 15 VDC; 8W |
| Meter Span | 0 to 100% Lower Explosive Limit (LEL) |
| Repeatability | ±2% full scale |
| Alarm Circuits | Three: High, Low and Malfunction |
| Controls | Current Adjust, Bias Adjust, Low and High Alarm Set points, Zero Adjust, Span Adjust, Alarm Reset, (Latching or Non-latching) |
| Indicators | Percent LEL Meter, Low Alarm Lamp Amber, High Alarm Lamp (Red), Malfunction Lamp (Blue), Normal Lamp (Green) |
| Output | Individual, isolated latching or non-latching relay contacts for Low and High Alarm, Malfunction relay is normally energized, non-latching. Contacts are SPDT, rated at 2A, 26VDC or 2A, 117 VAC, resistive. Analog signal of 0 to IV for recording purposes. |

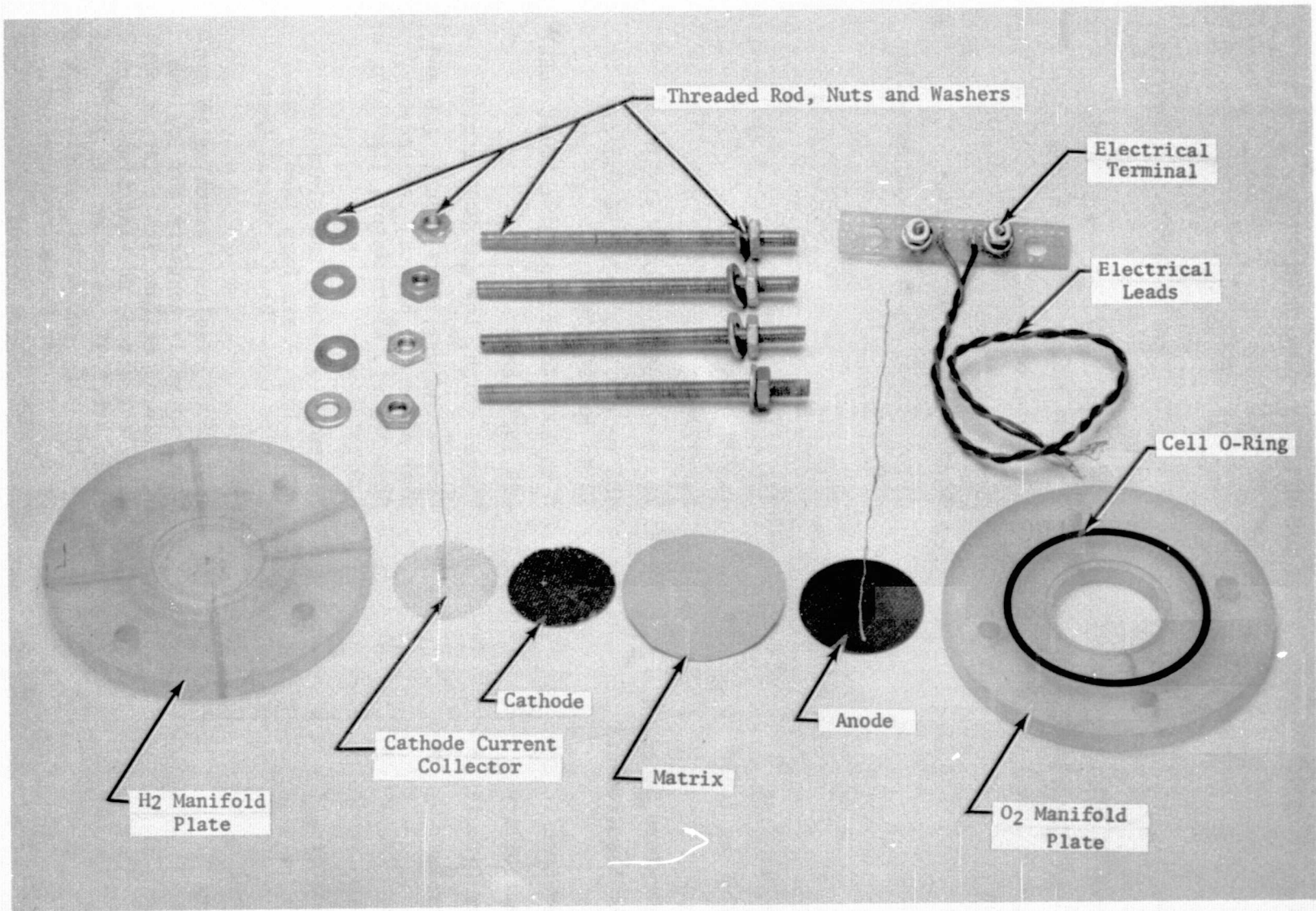
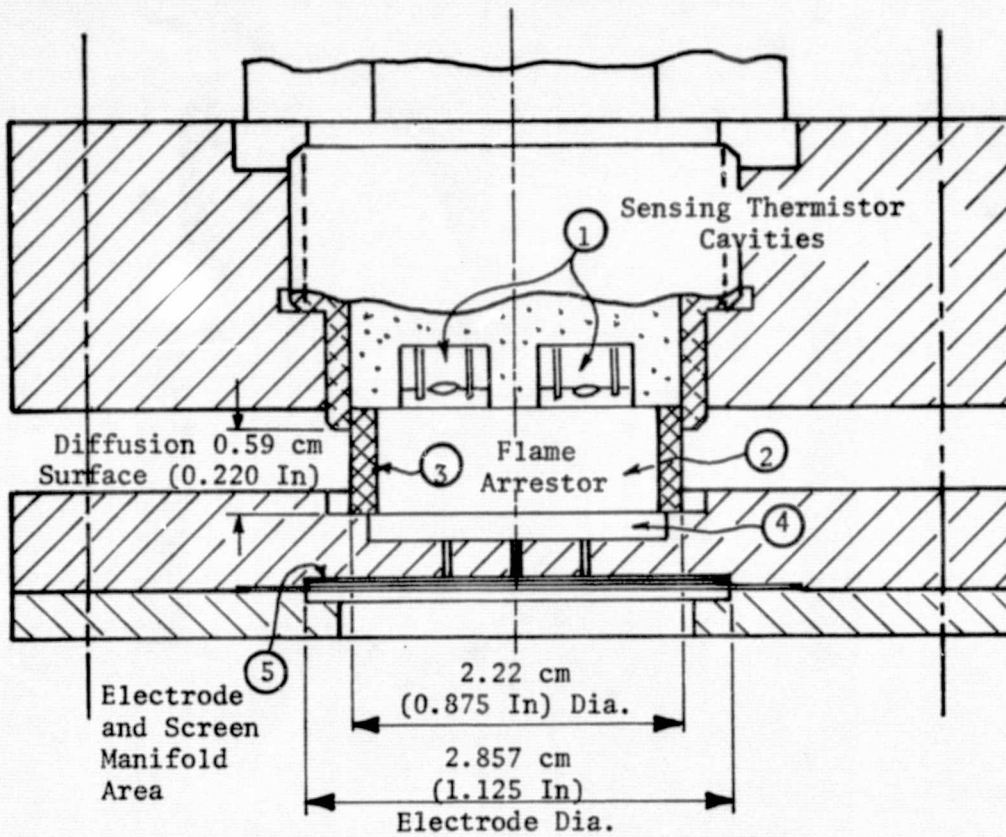


FIGURE 4 WATER VAPOR ELECTROLYSIS CELL, DISASSEMBLED



Sensing Cavity Volume

| | | | |
|----------|---|----------------------|--------------------------|
| Volume 1 | = | 0.94 cm ³ | (0.057 In ³) |
| Volume 2 | = | 2.03 cm ³ | (0.124 In ³) |
| Volume 3 | = | 0.33 cm ³ | (0.020 In ³) |
| Volume 4 | = | 0.52 cm ³ | (0.032 In ³) |
| Volume 5 | = | 0.20 cm ³ | (0.012 In ³) |
| <hr/> | | | |
| V Total | = | 4.02 cm ³ | (0.245 In ³) |

FIGURE 5 WVE/CGD INTEGRATED BREADBOARD

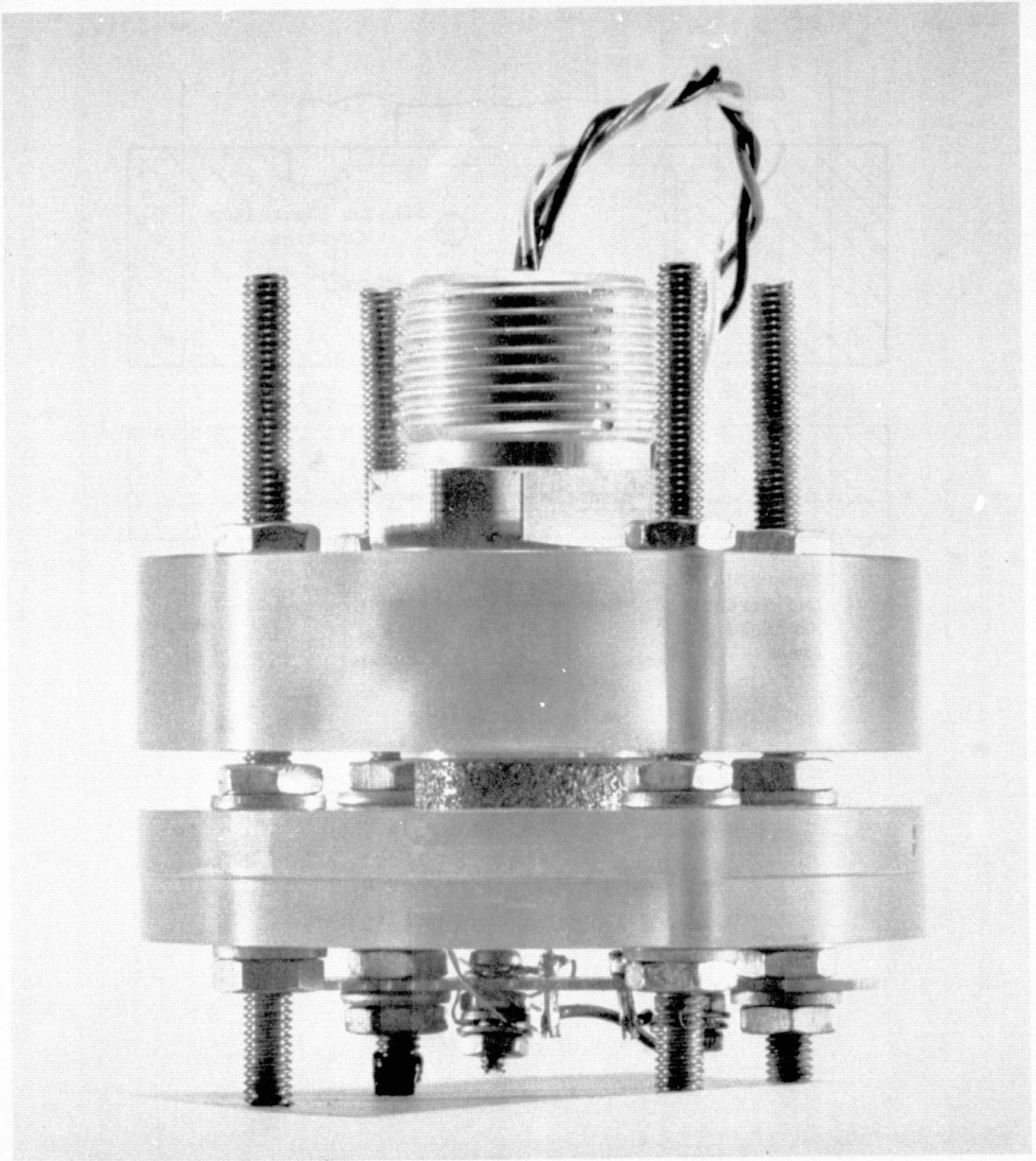


FIGURE 6 INTEGRATED WVE/CGD, ASSEMBLED

TABLE 3 CHARACTERISTICS OF INTEGRATED WVE/CGD

WVE Cell Characteristics

| | |
|--|---|
| Cell Body | Polycarbonate |
| Anode, cm (In) | 0.076 (0.030) Activated Porous Titanium |
| Cathode, cm (In) | 0.025 (0.010) Platinized Screen |
| Matrix, cm (In) | 0.025 (0.010) Crocidolite Asbestos |
| Electrolyte | 33.3% Sulfuric Acid (H ₂ SO ₄) |
| H ₂ Cavity Spacer, cm (In) | 0.025 (0.010) Teflon Screen |
| H ₂ Gas Manifold, cm (In) | 0.025 (0.010) Diameter Holes |
| Cell Active Area, cm ² (In ²) | 6.452 (1.0) |

CGD Characteristics

| | |
|---|------------------------|
| Type | General Monitors, Inc. |
| H ₂ Sensor Volume, cc (In ³) | 4.0 (0.24) |
| Flame Arrestor | |
| Material | 316 Stainless Steel |
| Porosity | 50 to 55% |
| Mean Pore Size, μ(In) | 75 (0.003) |
| Maximum Pore Diameter, μ ^(a) (In) | 375 (0.015) |
| Sensing Element | Activated Thermistor |
| Principle of Operation | Catalytic Combustion |

(a) Quenching diameter for H₂-in-air is 0.06 cm or 600μ⁽¹¹⁾

TABLE 4 WVE OPERATING CHARACTERISTICS
FOR IN SITU H₂ GENERATION

| | |
|--|---------------------------|
| WVE Cell Active Area, cm ² (In ²) | 6.452 (1.0) |
| H ₂ Sensor Volume, cm ³ (In ³) | 4.0 (0.24) |
| WVE Cell Operating Current Density, mA/cm ² (ASF) | 10 (9.3) |
| H ₂ Generation Time, | 20 (est.) |
| H ₂ Calibration Concentration | 2% H ₂ -in-air |
| Expected WVE Cell Voltage, V | 1.6 |
| WVE Cell Voltage Shutdown, V | 1.9 |
| Cabin Atmosphere Relative Humidity, % | 26 to 70 |

Overdesign - Assumes that up to 44% of the H₂ generated could be lost by consumption of the active sensing element, or by diffusion through the porous flame arrestor.

Breadboard Electronics

The instrumentation required for performing the in situ calibration experiments consisted of the Model 180 instrumentation package for control and calibration of the CGD, two variable current sources for the WVE cell, and the electrical circuits required for maintaining a constant potential on the WVE cell and for varying, in step changes, the current to the WVE cell. Also included were a digital multimeter for reading out WVE cell current and a two-pen recorder with an event marking circuit for recording WVE cell voltage and CGD output voltage. A block diagram of the in situ calibration instrumentation is presented in Figure 8. The block diagram shows three separate signal sources connected to the WVE cell. The WVE cell could be connected to any one of the three signal sources to initiate a portion of the in situ calibration sequence by means of a source selection switch. The current sources were repeatable to within 1% and the constant idle voltage source was repeatable to within 1.5%. Each position change of the switch caused an event marking circuit to superimpose a small voltage spike on the calibration data recorder to facilitate timing of any portion of the calibration sequence. Switching from one signal source to the other was performed manually and was timed using a stopwatch. The calibration current could be set and measured without the WVE cell connected using a current preset circuit and a digital multimeter. Currents could also be read during the actual calibration sequence with a digital multimeter, in combination with the current shunt, in series with the WVE cell.

Test Support Accessories

The Test Support Accessories (TSA) required to perform the testing task of the program consisted of an Environmental Chamber and a Fluid Supply Section (FSS).

Environmental Chamber

The Environmental Chamber was required for two purposes. First, to maintain a constant environment for the integrated CGD/WVE during the in situ calibration experiments. This was necessary in order to eliminate the effect of variations in relative humidity, room temperature and background combustible gas concentrations on the performance of the in situ calibration evaluation. Second, the Environmental Chamber was used to confine the H_2 /air gases used for calibrating the CGD. The Environmental Chamber, which is a photograph of the TSA, is shown in Figure 9. The Environmental Chamber was composed of a polycarbonate bell jar with a volume of approximately 9,000 cm^3 (0.3 ft^3) that sealed via a closed cell neoprene gasket against a 1.59 cm (0.625 in) thick acrylic plate. Gas entered the Environmental Chamber at the top through a large area porous stainless steel sparger and exited at the bottom. The porous stainless steel sparger was used to diffuse the gas uniformly through the chamber so that concentration gradients could be eliminated. The inside of the chamber was fitted with a terminal block for making electrical connections to the WVE and CGD and with a thermocouple which permitted temperature measurements of the inside of the chamber. Electrical wiring ran through gas-tight feed-throughs at the bottom of the chamber.

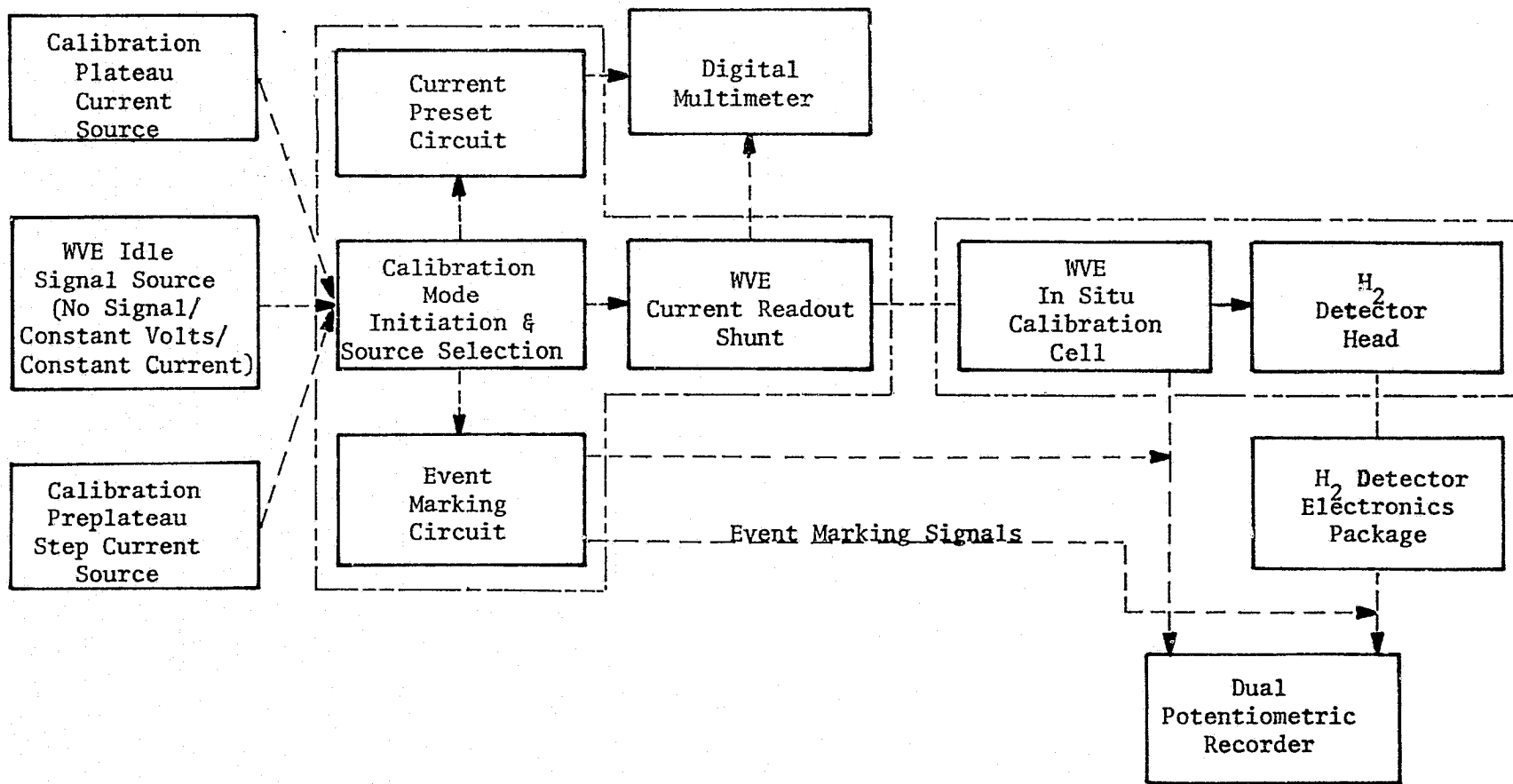


FIGURE 8 FUNCTIONAL BLOCK DIAGRAM OF IN SITU CALIBRATION TEST INSTRUMENTATION

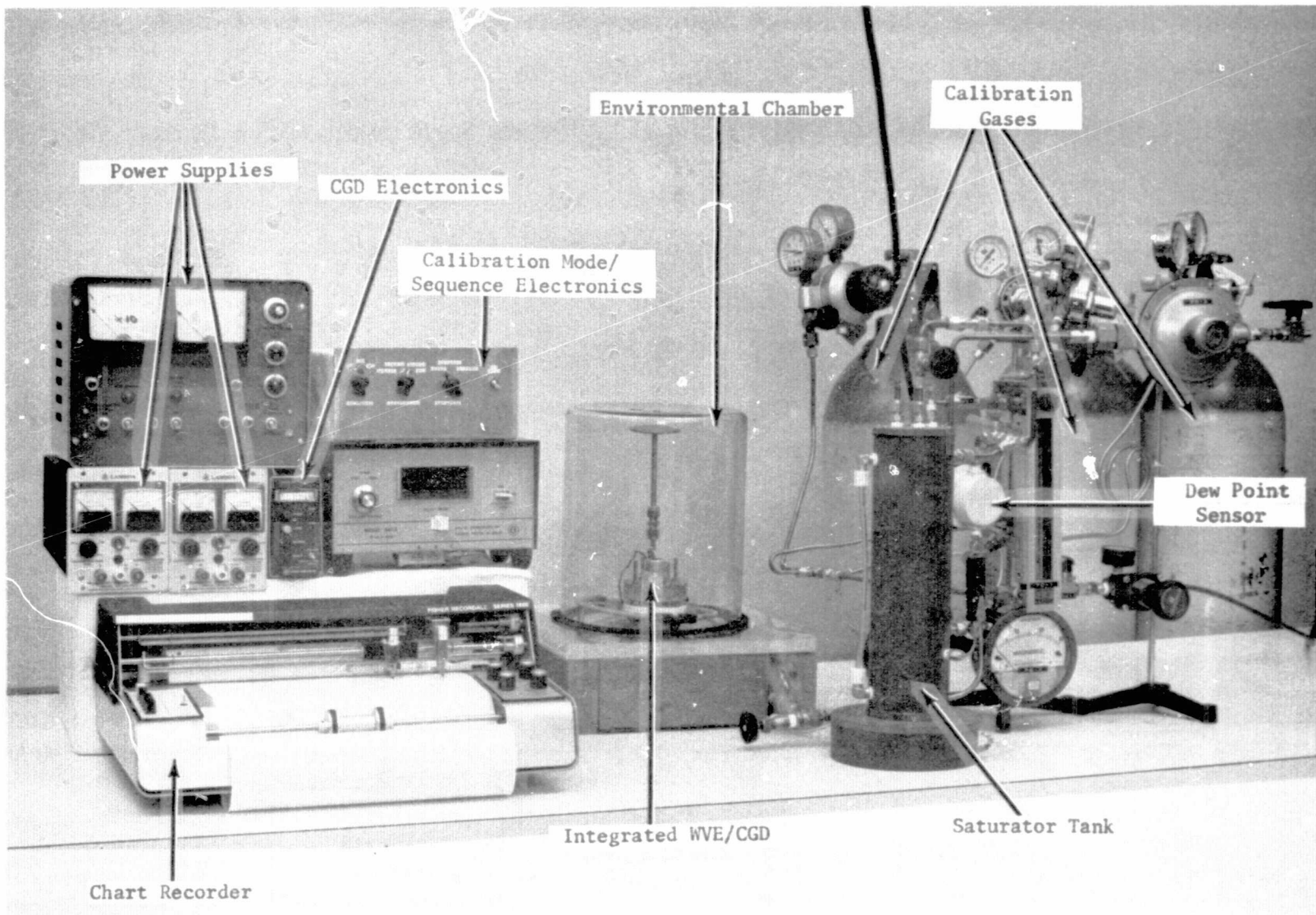


FIGURE 9 IN SITU CALIBRATION TEST SUPPORT ACCESSORIES

Fluid Supply Section

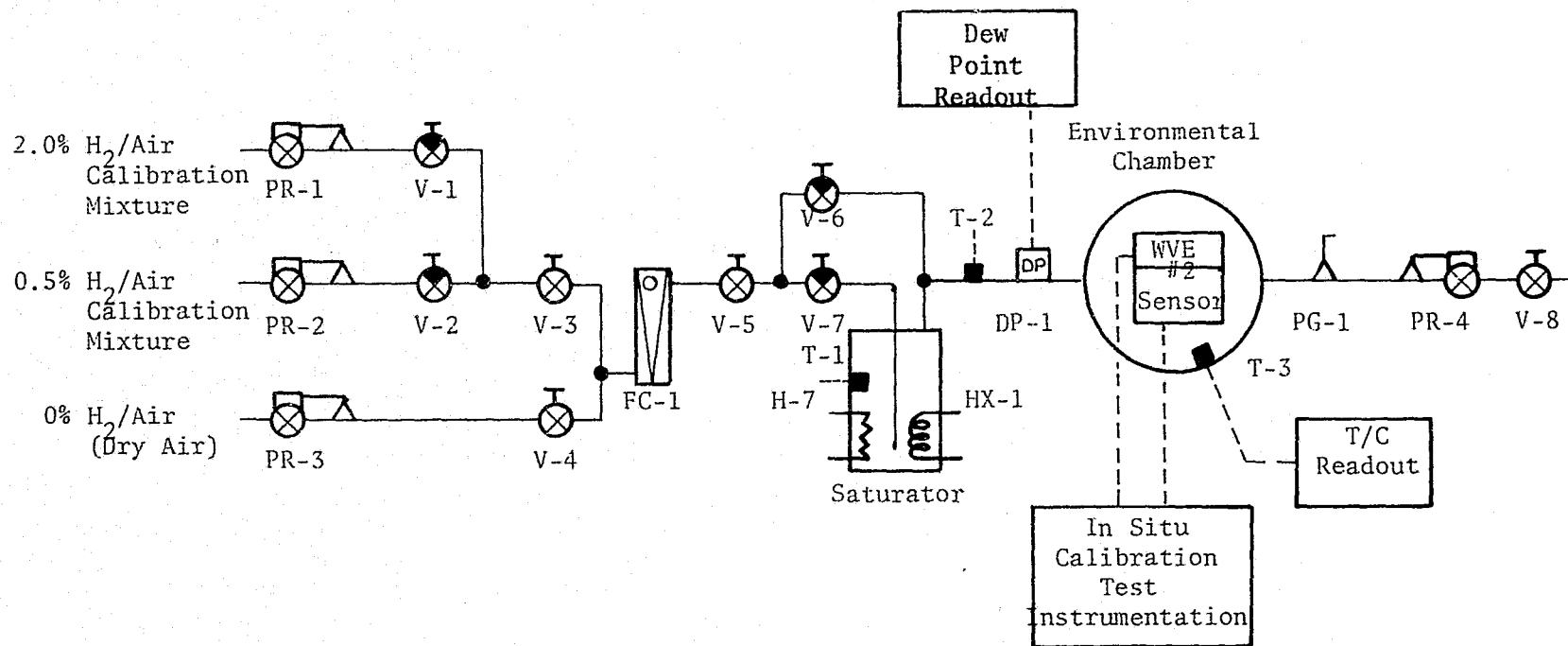
The FSS was required to provide for the delivery and control of the calibration gases to the Environmental Chamber. In addition, the FSS provided for the delivery and control of conditioned laboratory air for delivery to the Environmental Chamber. A schematic of the FSS is shown in Figure 10. Premixed H₂/air mixtures, certified to better than 0.1% H₂, could be selected for calibrating the CGD by means of valves V-1 through V-4. The flow of these gases, normally 940 cc/min (2 scfh), was monitored and maintained by flow controller FC-1. The gas was humidified to approximately 283K (50F) dew point by passing a portion of the gas through a saturator. The ratio of dry gas to wet gas and thus the dew point was controlled by varying the position of valves V-6 and V-7. The dew point of the gas prior to entry into the Environmental Chamber was monitored by a dew point hygrometer. Pressure² regulator PR-4 was used to maintain a backpressure of approximately 125 N/m² (0.5 in water) on the Environmental Chamber. This pressure was indicated on pressure gauge PG-1.

Test Program

The test program consisted of characterizing the WVE cell and the CGD individually and characterizing the integrated WVE/CGD for performing in situ calibrations. The characterization of the WVE involved determining cell voltage as a function of current density. The characterization of the CGD involved determining its linearity, position sensitivity, reproducibility, zero drift and repeatability. The evaluation of the integrated WVE/CGD included determining the H₂ concentration indicated by the CGD as a function of WVE current density, selection of the WVE current density required for in situ calibration, determining the repeatability of H₂ concentrations generated by the WVE for constant operating conditions and determining the accuracy and repeatability of simulated CGD in situ calibrations. Further experimental testing was performed on the integrated WVE/CGD in order to determine if the time required for carrying out in situ calibrations could be reduced.

WVE Characterization

Before starting in situ calibration experiments it was necessary to establish whether the WVE cell voltage would stay within established safe limits in the maximum current range considered for H₂ generation. Figure 11 is a plot of cell voltage versus WVE current over the range 5 to 40 mA/cm² (4.6 to 37.2 ASF) current density. The data for this curve was obtained by increasing the current density step-wise and observing the resulting cell voltages after an average of four minutes at a particular current. The cell was operated in a static atmosphere of air at approximately 283K (50F) dew point. The data gathered for Figure 11 was obtained while the WVE was operating continuously for 46 minutes. Since the in situ calibration concept calls for operating the WVE for only a few minutes at a time (i.e., daily, weekly, monthly) depending on the desired calibration frequency, an endurance test for continuous operation of the WVE is not required.



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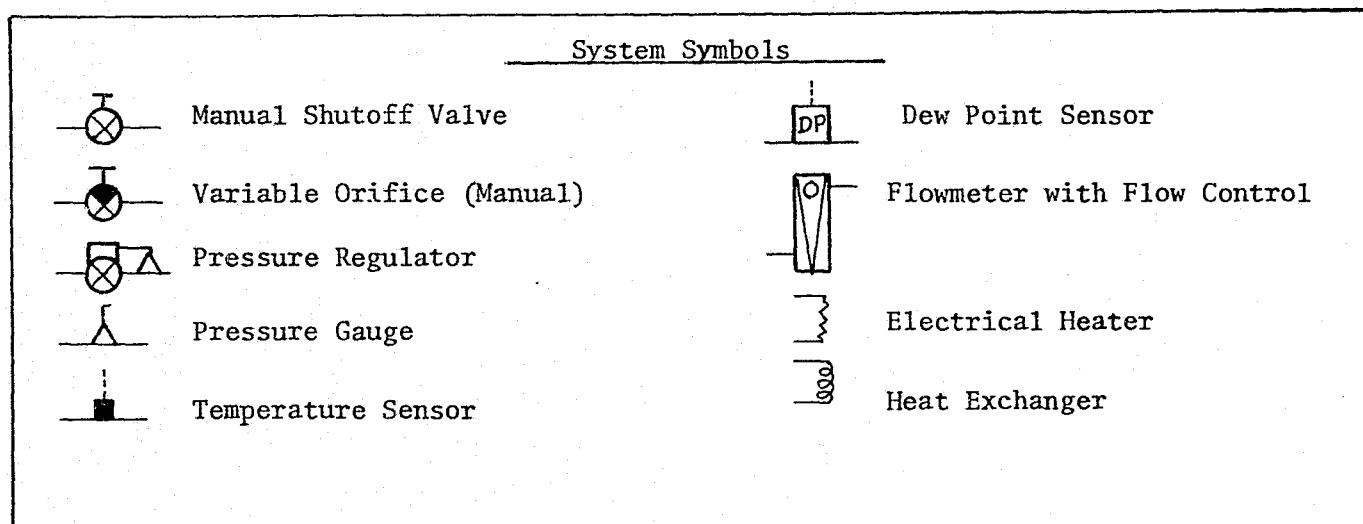


FIGURE 10 FLUID SUPPLY SECTION

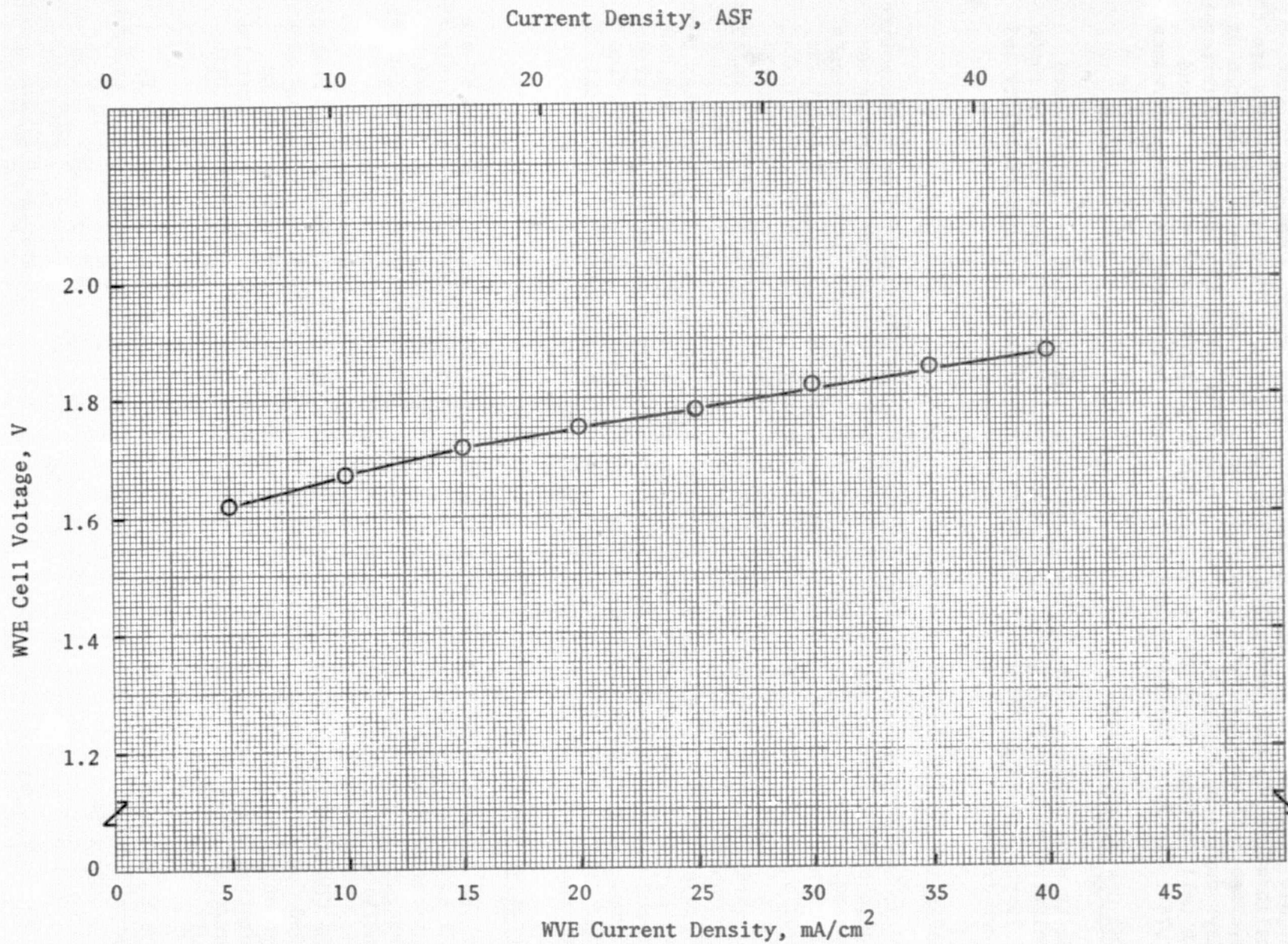


FIGURE 11 WVE VOLTAGE VERSUS CURRENT DENSITY

During the course of the in situ calibration experimental work, the WVE cell voltage was recorded each time an in situ calibration₂ profile was completed. Figure 12 is a plot of cell voltage for all 9.4 mA/cm² (8.7 ASF) in situ calibration plateaus generated during the program. The plotted points are the average cell voltage for a particular day. This data covers a time span of 41 days during which the WVE cell was operated at least 73 times. No deterioration in cell voltage was noted as the voltage throughout was between 1.73 and 1.78V. In fact, the data indicates a slight improvement in WVE performance.

CGD Characterization

Tests were performed on the CGD in order to characterize its performance relative to linearity, position sensitivity, effects of variations in input voltage, simulated effect of long-term exposure to 2% H₂, repeatability and zero drift.

Linearity of the CGD

If accurate H₂-in-air concentration measurements are required over the entire range of possible H₂ concentrations, the CGD must be linear. In order to determine the linearity of the CGD, the CGD was mounted in the Environmental Chamber. The CGD was then calibrated by alternately exposing it to 0% and 2.0% H₂ calibration gases and making the appropriate zero and span adjustments. Once calibration was completed the CGD output was recorded for the calibration gases and an additional H₂-in-air gas mixture between the calibration points, (0.55% H₂). The results₂ of this task are presented in Figure 13. Observation of the data reveals that the CGD's response is nearly linear over the H₂-in-air concentration range evaluated. At the 0.55% H₂ point the CGD output departs only 10 mV from the expected output based on the calibration curve. This 10 mV variation corresponds to 0.04% H₂. This variation from linearity is considered insignificant since the repeatability specification for the CGD is ±2% of full scale or ±0.08% H₂.

Position Sensitivity

It was reported that the CGD selected for application with the EC/LSS of the SSP exhibited position sensitivity.⁽⁸⁾ The off-the-shelf CGD selected for the integrated WVE/CGD in situ calibration testing was believed to have been designed to minimize such effects; however, it was necessary to determine its position sensitivity when combined with the WVE.

The CGD output was first recorded as the sensing head was rotated 6.3 radians (360 degrees) about its own axis while in an air atmosphere. Figure 14 is an output versus rotation plot of this data, including a description of the rotation axis. Note that the output fluctuates a maximum of ±100 mV over the range of rotation. This fluctuation is equivalent to approximately ±10% of full scale output.

The H₂ detector was also rotated 6.3 radians (360 degrees) about an axis perpendicular to its own axis and perpendicular to the g vector while observing its output in air.

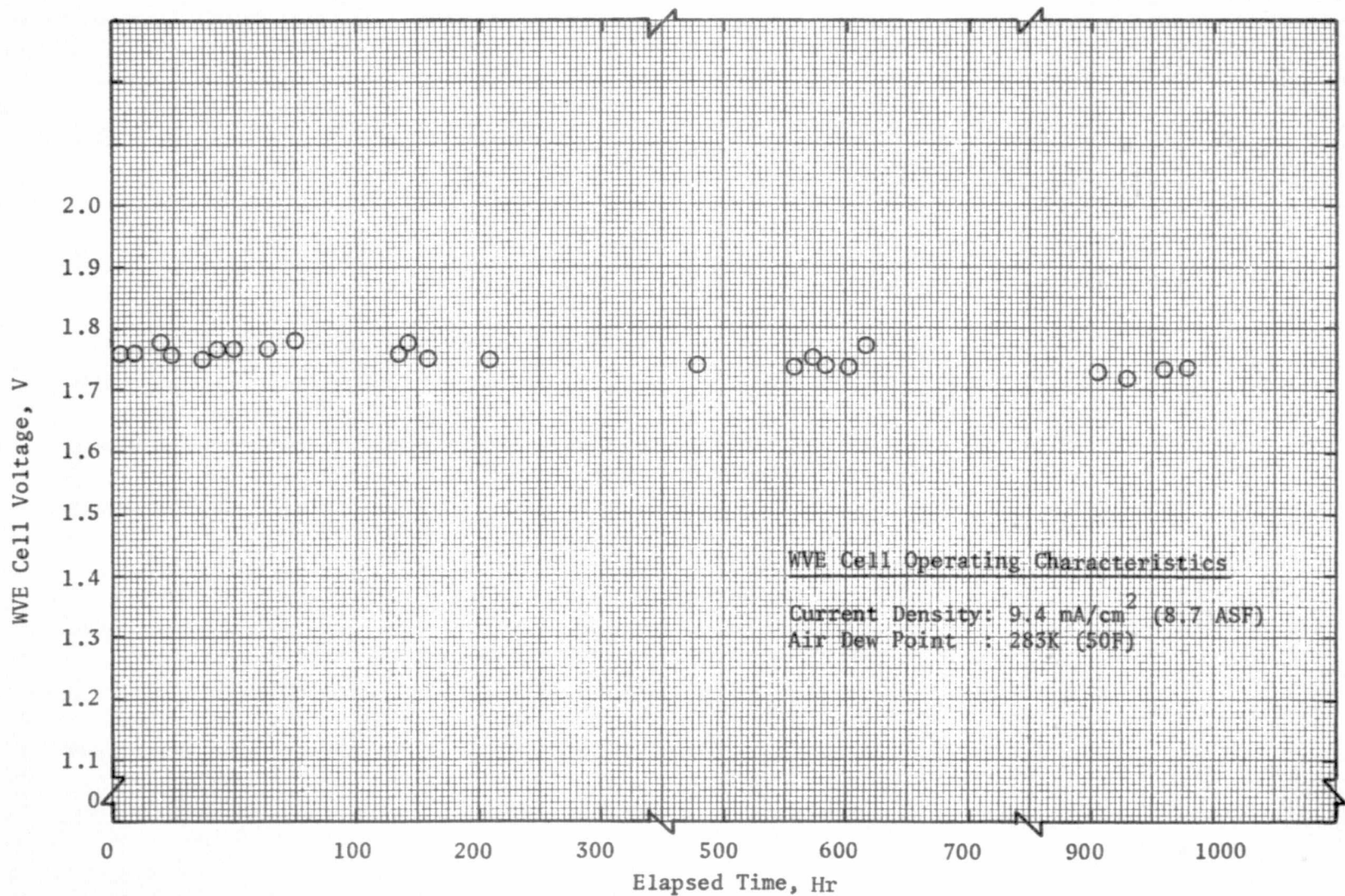


FIGURE 12 WVE CELL VOLTAGE FOR EACH IN SITU CALIBRATION

CGD Output, mV

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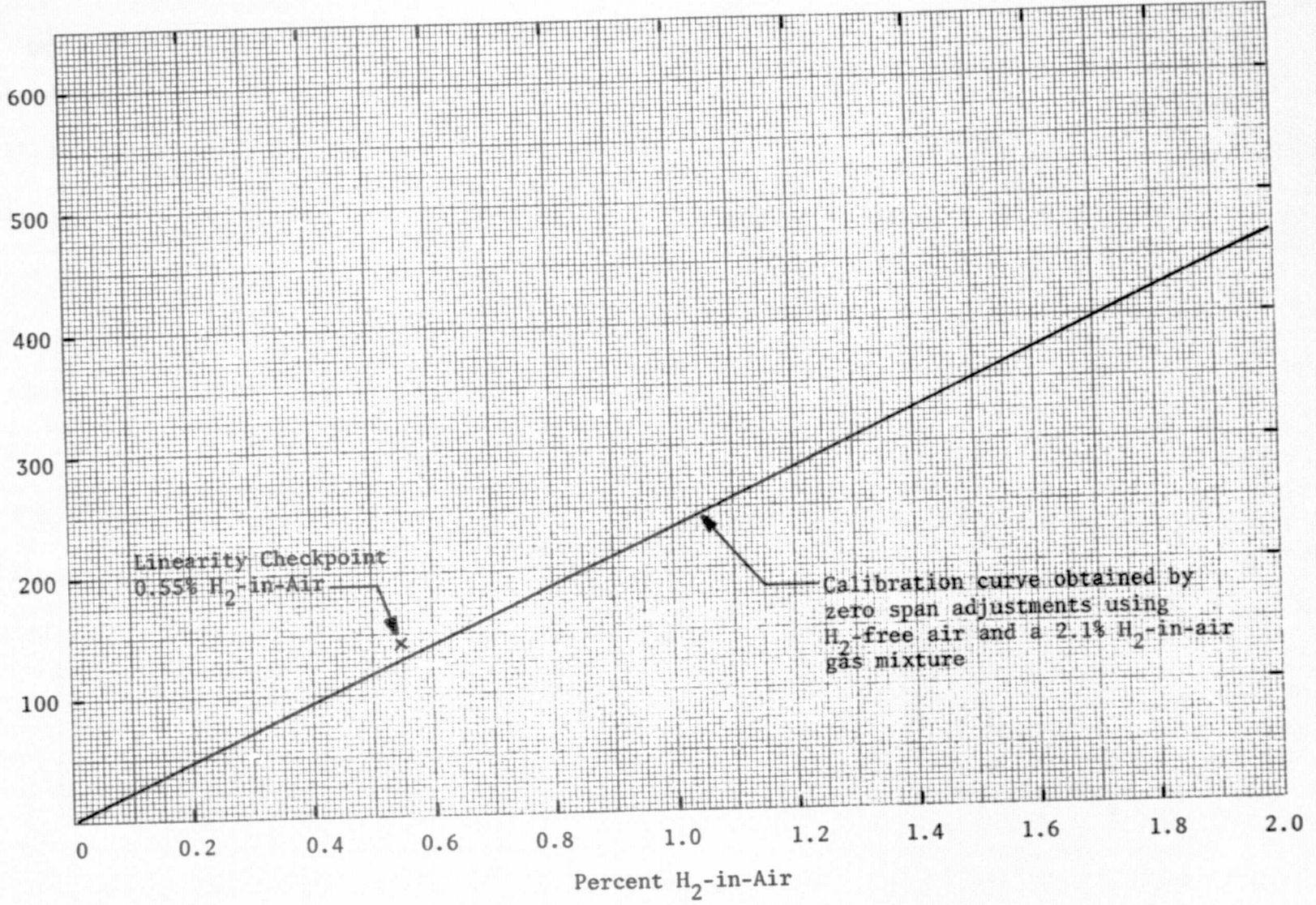


FIGURE 13 LINEARITY OF CGD

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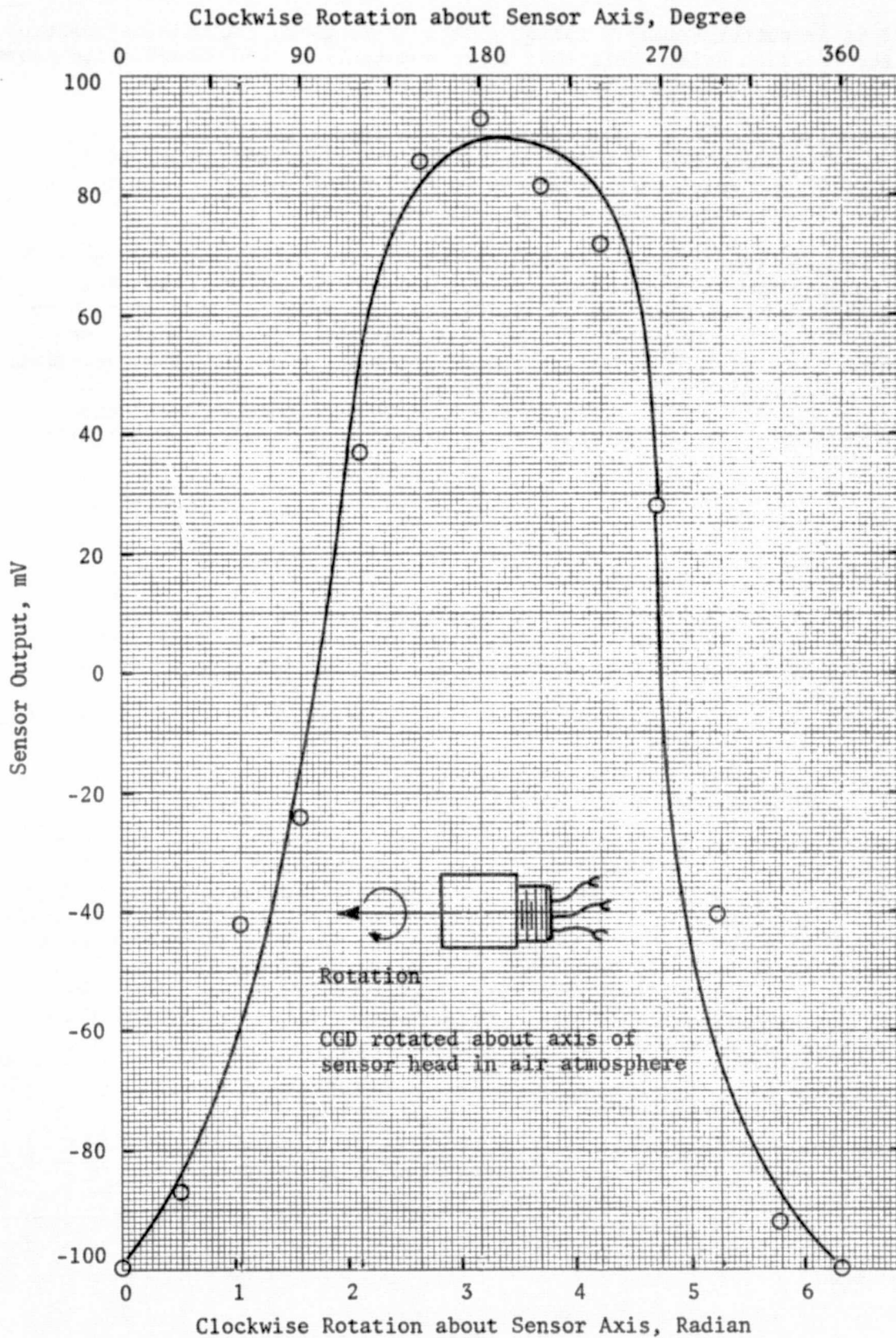


FIGURE 14 CGD OUTPUT VERSUS ORIENTATION ABOUT SENSOR AXIS

Figure 15 is an output versus rotation plot of this data, including a description of the rotation axis. Note that there was again a ± 100 mV deviation over the rotation range corresponding to $\pm 10\%$ of full scale.

A $\pm 10\%$ deviation from full scale corresponds to approximately a $\pm 0.4\%$ H_2 -in-air error. This magnitude of error due to the position sensitivity of the CGD is unacceptable and resulted in the need to define and maintain constant the position of the CGD during the in situ calibration experiments.

It was determined that this dependence on orientation was created by the fact that the sensing and reference beads in the sensor are heated. When the sensor is oriented such that the two beads are in a vertical line (i.e., one right above the other) with the sensing bead over the reference bead, convective heat transfer will cause the sensing bead to be hotter than the reference bead. This will unbalance the bridge and provide an output. If the sensor is rotated 3.1 radians (180 degrees) to reverse the two beads the reference bead will now be hotter than the sensing bead and the output will decrease.

Reproducibility

The reproducibility of the CGD was characterized by determining:

1. the effects of variations in input power on CGD output,
2. the effect of a constant H_2 exposure on the output of the CGD,
3. the magnitude of zero drift observed for the instrument over a period of time and
4. the repeatability of CGD output for consecutive exposures to a given H_2 -in-air mixture.

Variation of Input Voltage

The CGD was mounted in the Environmental Chamber and power to the electronics was supplied through a variable transformer. By manipulating the variable transformer setting the input voltage to the CGD electronics was varied from 105 to 120V. The CGD output voltage for exposure to ambient air and 2% H_2 -in-air was monitored as a function of the input voltage. The results of this test are presented in Figure 16. Observation of the data reveals that the total fluctuation in CGD output for line voltage variations from 105 to 120V was only 5 mV, corresponding to 0.04% H_2 . This fluctuation is within the $\pm 2\%$ of full scale repeatability specified for the instrument.

Long-Term Effect of H_2 Environment

The off-the-shelf CGD was operated in a constant 2% H_2 -in-air environment for 24 hours to simulate the effects of accumulated exposure to H_2 . Figure 17 is a plot of CGD output versus elapsed exposure time. The data shows that the output variation was less than ± 5 mV or $\pm 0.04\%$ H_2 for the 24 hours of exposure time. This variation is also within the $\pm 0.08\%$ H_2 repeatability specified for the instrument.

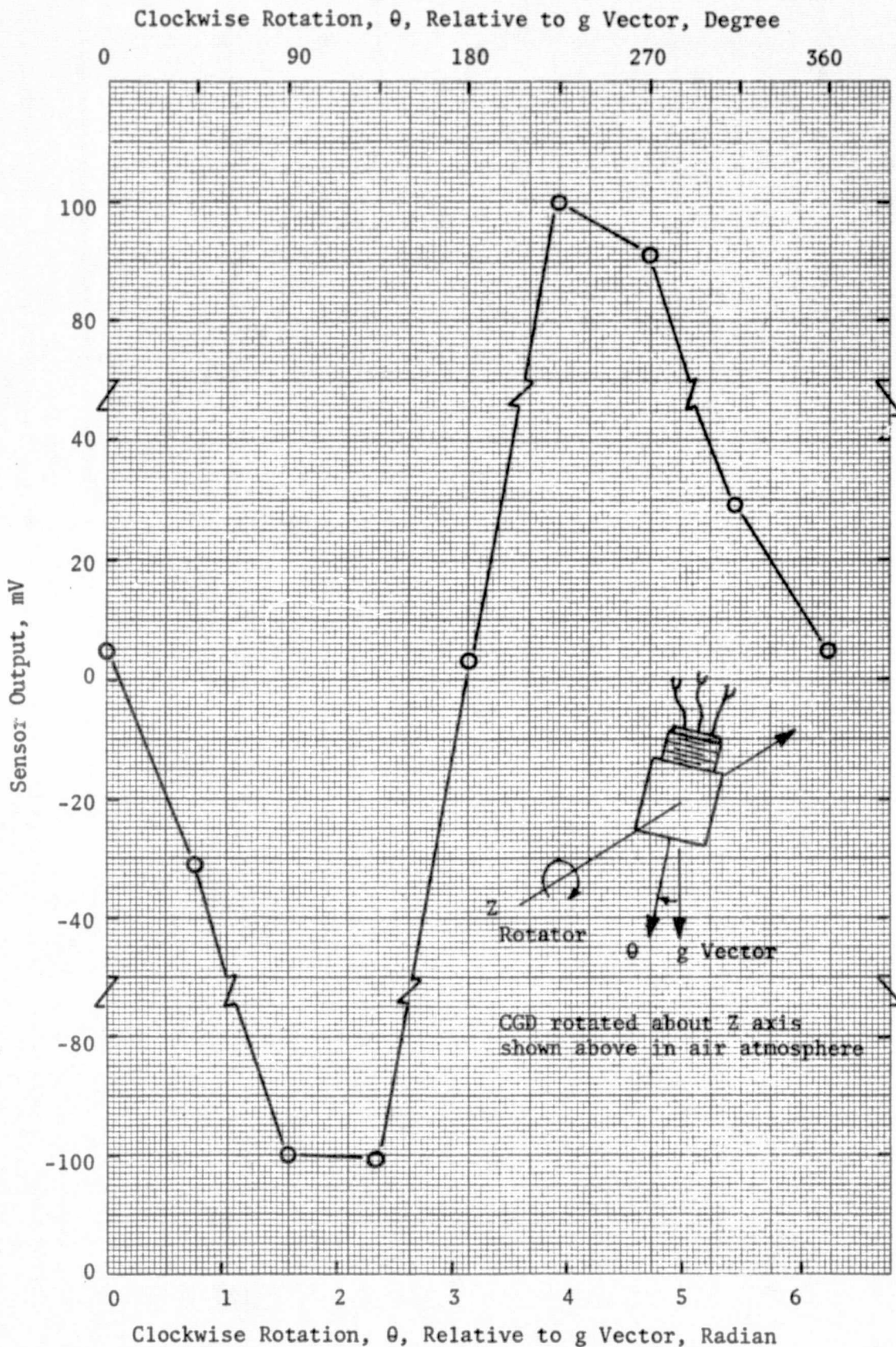


FIGURE 15 CGD OUTPUT VERSUS ORIENTATION ABOUT G VECTOR

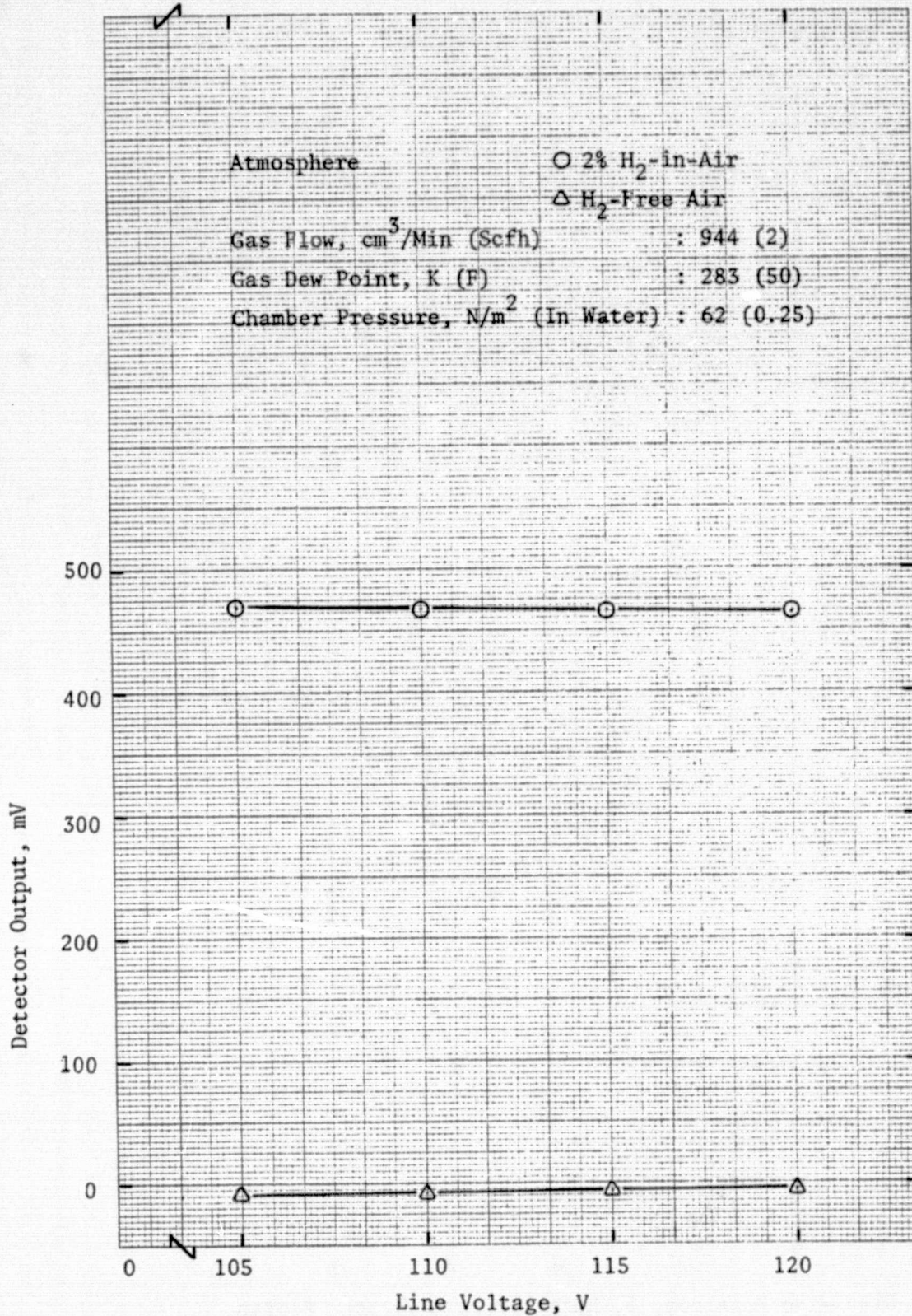


FIGURE 16 (C) OUTPUT VERSUS LINE VOLTAGE

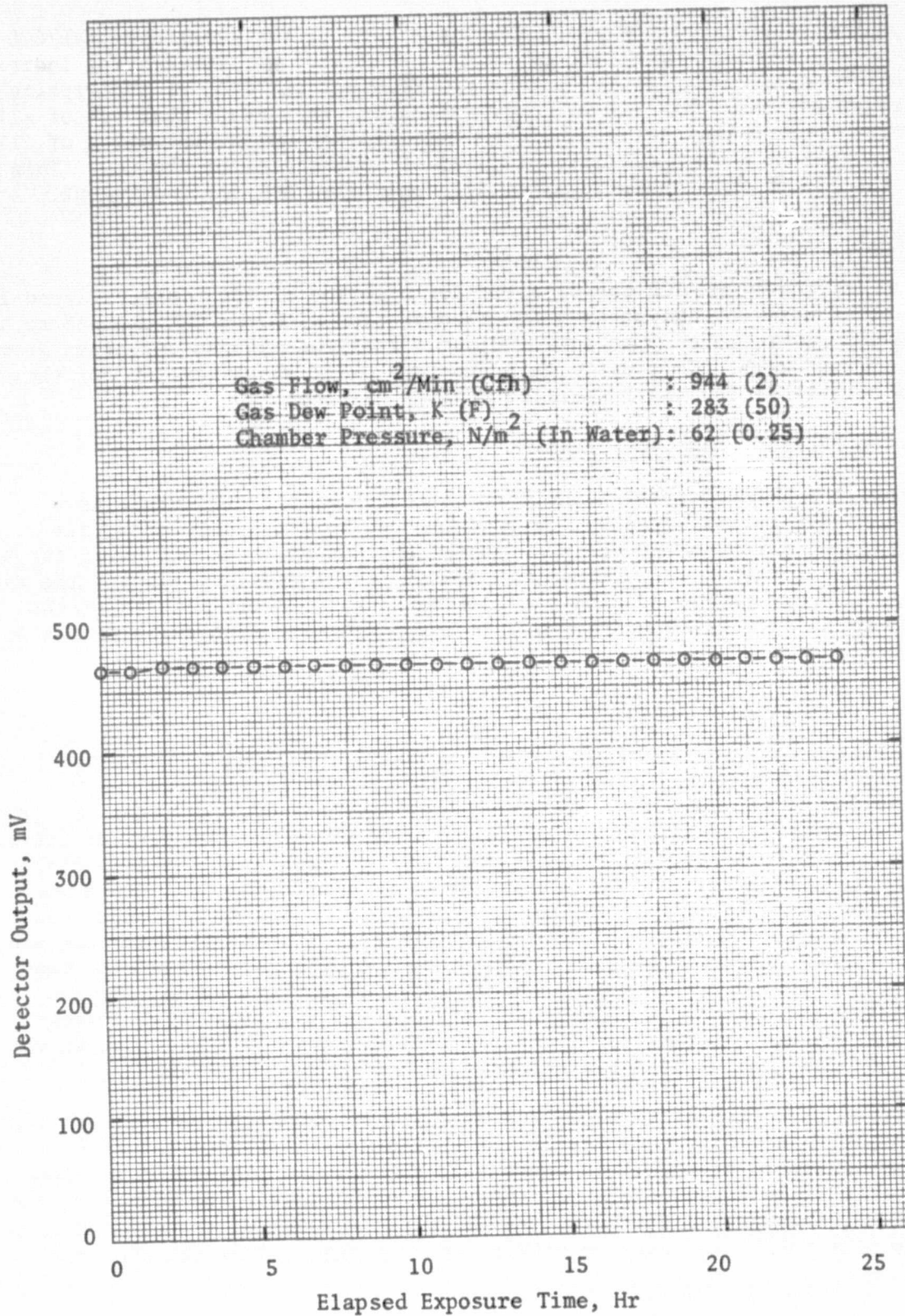


FIGURE 17 CGD OUTPUT VERSUS TIME IN 2% H_2 /AIR ENVIRONMENT

Repeatability

The repeatability of the CGD was demonstrated during the integrated WVE/CGD repeatability testing. The results of the integrated WVE/CGD testing indicated that the standard deviation (σ) of the CGD readings for each of the repeatability experiments was less than 3.7 mV. Statistically, this means that 99% of all data points fall within ± 11.1 mV of the average. An output variation of ± 11.1 mV corresponds to a repeatability of $\pm 1.1\%$ of full scale for the CGD. This is within the $\pm 2\%$ of full scale repeatability specified for the instrument.

Zero Drift

The zero drift for the CGD was observed for a period of 140 hours. Figure 18 is a plot of detector output as a function of time with the CGD exposed to a H_2 -free air environment. The data indicates that the maximum variation from 0 was +5 mV and -2 mV. This was within the zero drift specification for the CGD and was acceptable for the integrated CGD/WVE testing.

Integrated WVE/CGD Characterization

The integrated WVE/CGD testing included establishing the CGD output as a function of WVE current density, determining the repeatability of H_2 /air concentrations generated by the WVE, performing CGD calibrations using the WVE as a source for the H_2 and evaluating several techniques for reducing the time required to carry out an in situ calibration. Based on the results of the testing, an in situ calibration sequence for performing span calibrations of CGDs was defined.

WVE Current Density Versus CGD Output

As the first step in demonstrating the feasibility of using H_2 generated by a WVE cell to perform the in situ calibration of a CGD, it was necessary to determine CGD output as a function of WVE cell current density. The integrated WVE/CGD was mounted in the environmental chamber where the humidity of its environment could be controlled to 283K (50F) dew point. While in the chamber, the WVE was operated at various current densities while the CGD output and WVE cell voltages were recorded. Figure 19 is a plot of CGD output versus minutes of WVE on-time at the indicated current densities. Similar behavior was also noted at higher current densities. Observation of the curves revealed that initially a period occurred during which no CGD output was noted, followed by a sudden rise in CGD output which then leveled into an almost flat plateau. Increasing the current density of the WVE caused a rise in CGD output which then leveled out into a flat plateau at a higher H_2 concentration.

The shape of these curves is explained as follows: when the current is first turned on, H_2 evolved is consumed at the cathode of the WVE to reduce O_2 previously adsorbed there. This occurs for the initial plateau only. When the adsorbed O_2 is consumed the concentration of H_2 inside the flame arrestor of the CGD increases rapidly until the diffusion rate of H_2 through the flame arrestor plus the H_2 consumption rate at the sensing bead of the CGD just

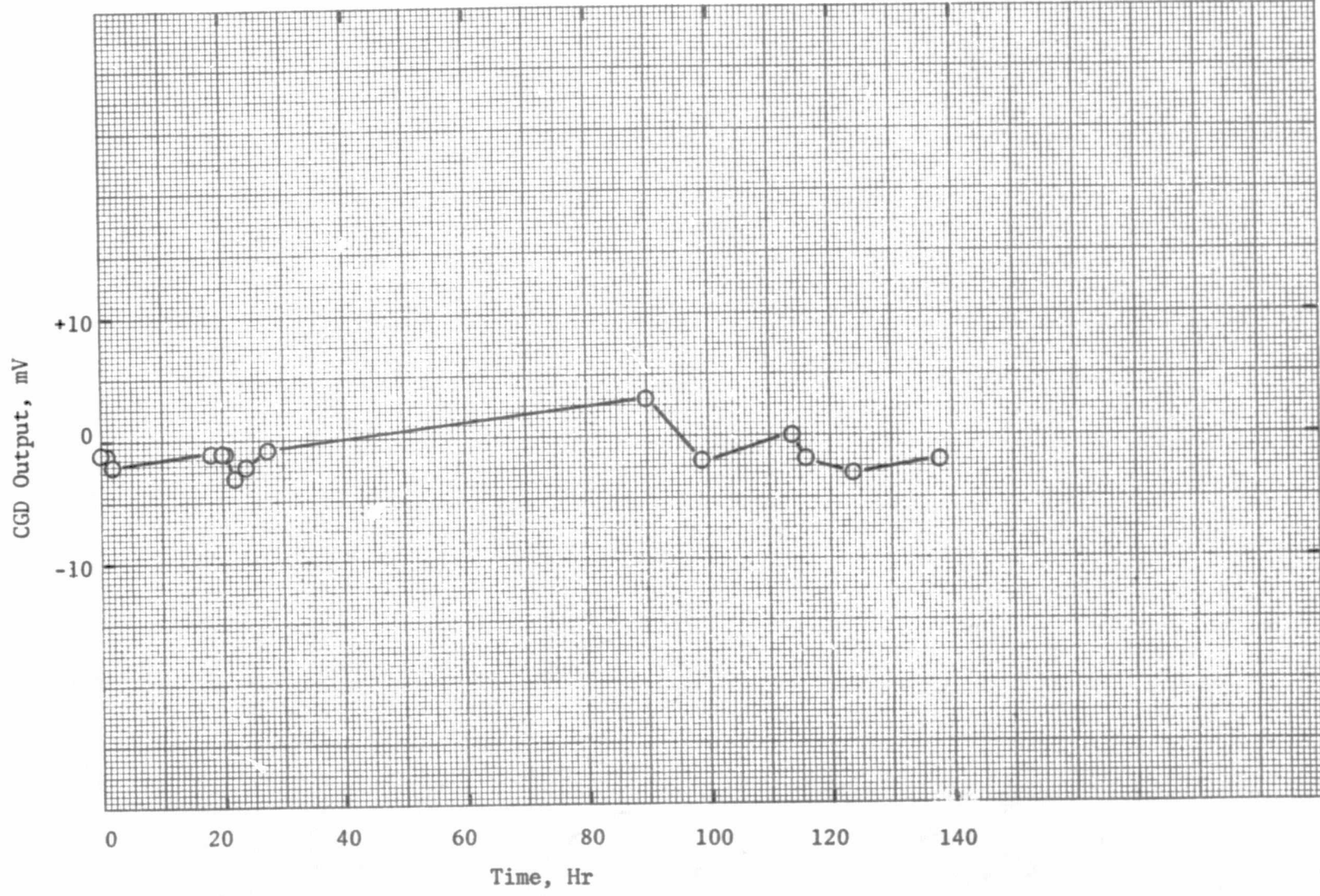


FIGURE 18 CGD BASELINE STABILITY

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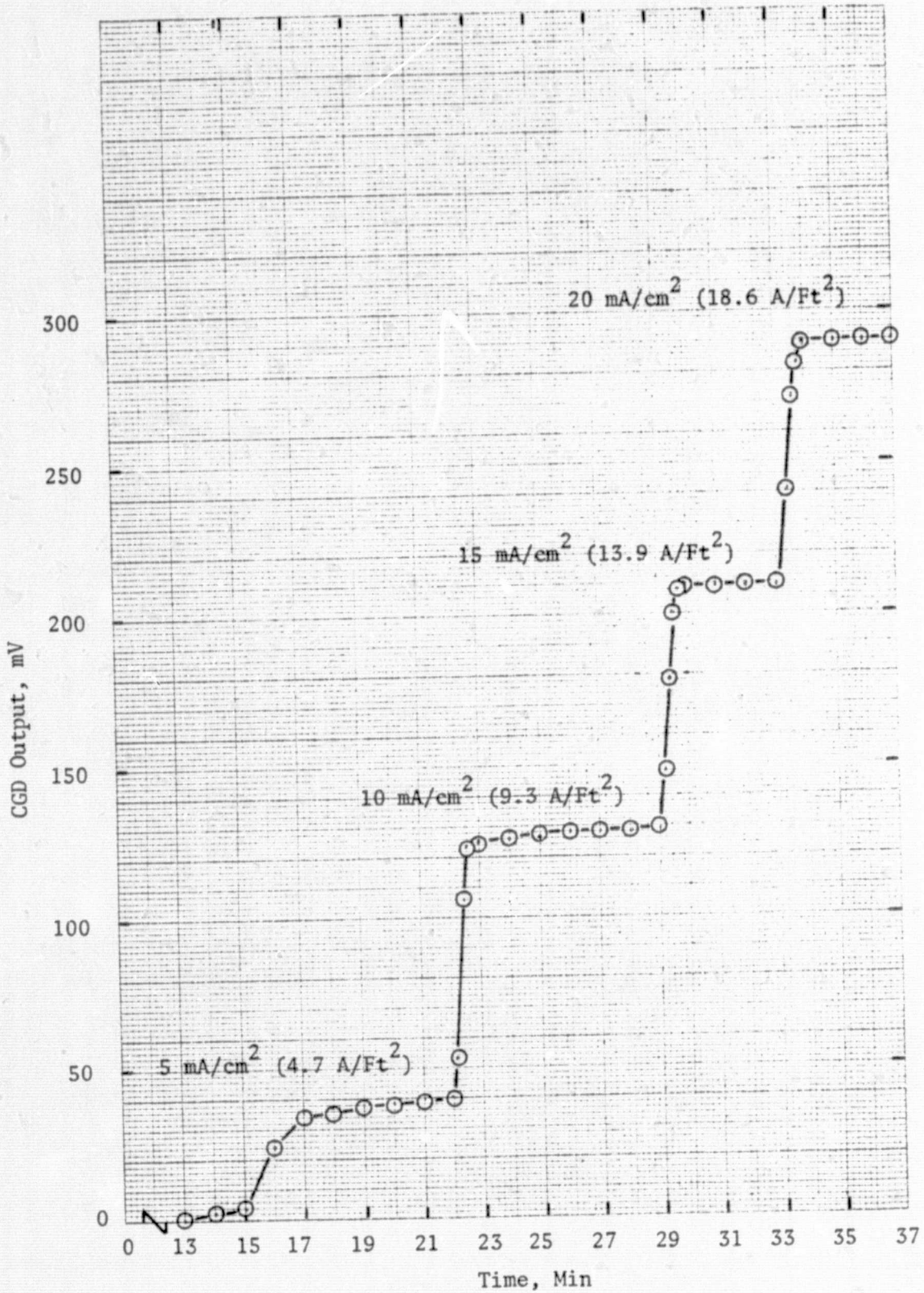


FIGURE 19 CGD/WVE PLATEAUS FOR VARIOUS CURRENTS

equals the H_2 production rate of the WVE. The plateaus represent this steady-state equilibrium. When the current density of the WVE is increased the H_2 evolution rate is increased and results in the attainment of an equilibrium at a higher H_2 -in-air concentration.

The CGD output plateaus obtained for various WVE H_2 generation current densities appeared to furnish promising points for calibration. The CGD output varies only slightly with WVE generation time at a fixed current after the plateau is reached.

The CGD plateau versus the corresponding WVE cell current densities are plotted in Figure 20. This curve indicates an essentially linear relationship between WVE cell current density and CGD output. Thus, a WVE current density can be chosen to generate a plateau corresponding to any desired percent H_2 calibration point.

WVE Calibration Plateau Repeatability

In order to establish if the H_2 -in-air mixture produced by the WVE would be constant from one time to another, the repeatability of the plateau level for a specific WVE current density and WVE H_2 generation time had to be demonstrated. Twenty plateaus were generated at 9.4 mA/cm^2 (8.7 ASF) over a period of three days with at least one hour between generation cycles. Figure 21 is a chart recorder trace of a typical plateau. The CGD outputs at these plateaus after 6, 8 and 10 minutes of H_2 generation are plotted versus total elapsed time in Section A of Figure 22. The output after 8 and 10 minutes of H_2 generation are quite reproducible. Either can be chosen for in situ calibration. The six-minute output was not considered reproducible enough. This data is further illustrated in the statistical analysis of the 6, 8 and 10 minute data which is presented in Table 5. Note that three times the standard deviation (3σ) for the 20 outputs at 8 and 10 minutes is 1.7 and 1.6 mV, respectively, which corresponds to approximately 1/2% of full scale CGD output, or $\pm 0.02\% H_2$. Statistically this means that greater than 99% of all measurements will have variations from the mean no larger than $\pm 0.02\% H_2$. This error limit is well within the accuracy of the off-the-shelf CGD used in these experiments, demonstrating the excellent reproducibility of this calibration technique.

In Situ Calibration of Simulated Degraded CGD

To demonstrate that this calibration procedure can correct for actual CGD variations, a large characteristic change was introduced into the commercial CGD. The CGD was then calibrated utilizing the in situ calibration procedure.

The CGD sensing bead self-heat power was reduced (from $300 \text{ mA} \times 2.5\text{V}$ to $230 \text{ mA} \times 1.4\text{V}$), thus drastically lowering its operating temperature.

A calibration curve for the CGD had been obtained prior to the multiplateau reproducibility experiments using 0% H_2 , 0.55% H_2 and 2.10% H_2 -in-air gas mixtures (curve 1 in Figure 23). Without span or zero adjustments after

WVE Current Density, ASF

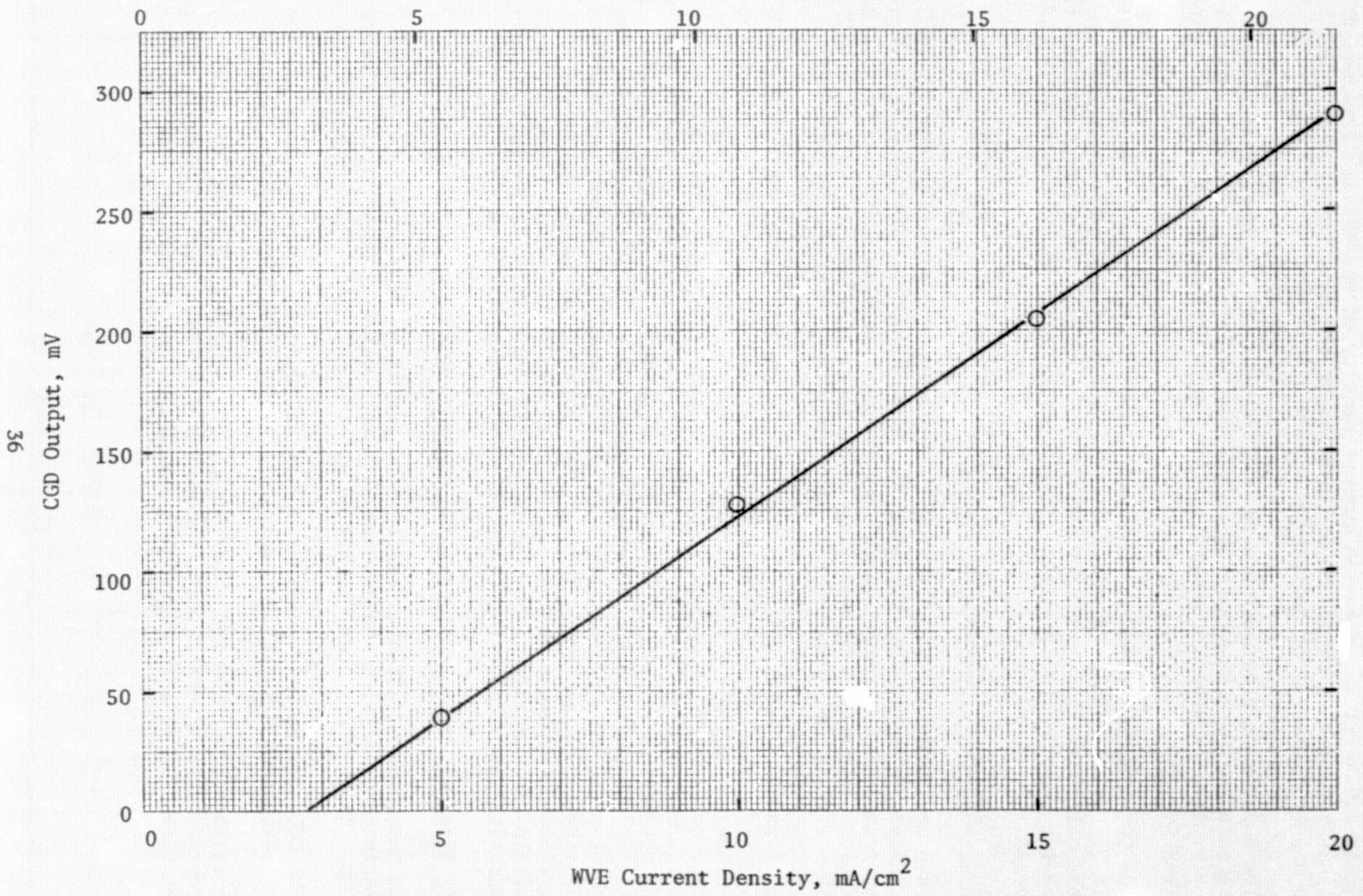


FIGURE 20 CGD/WVE PLATEAUS VERSUS WVE CURRENT DENSITY

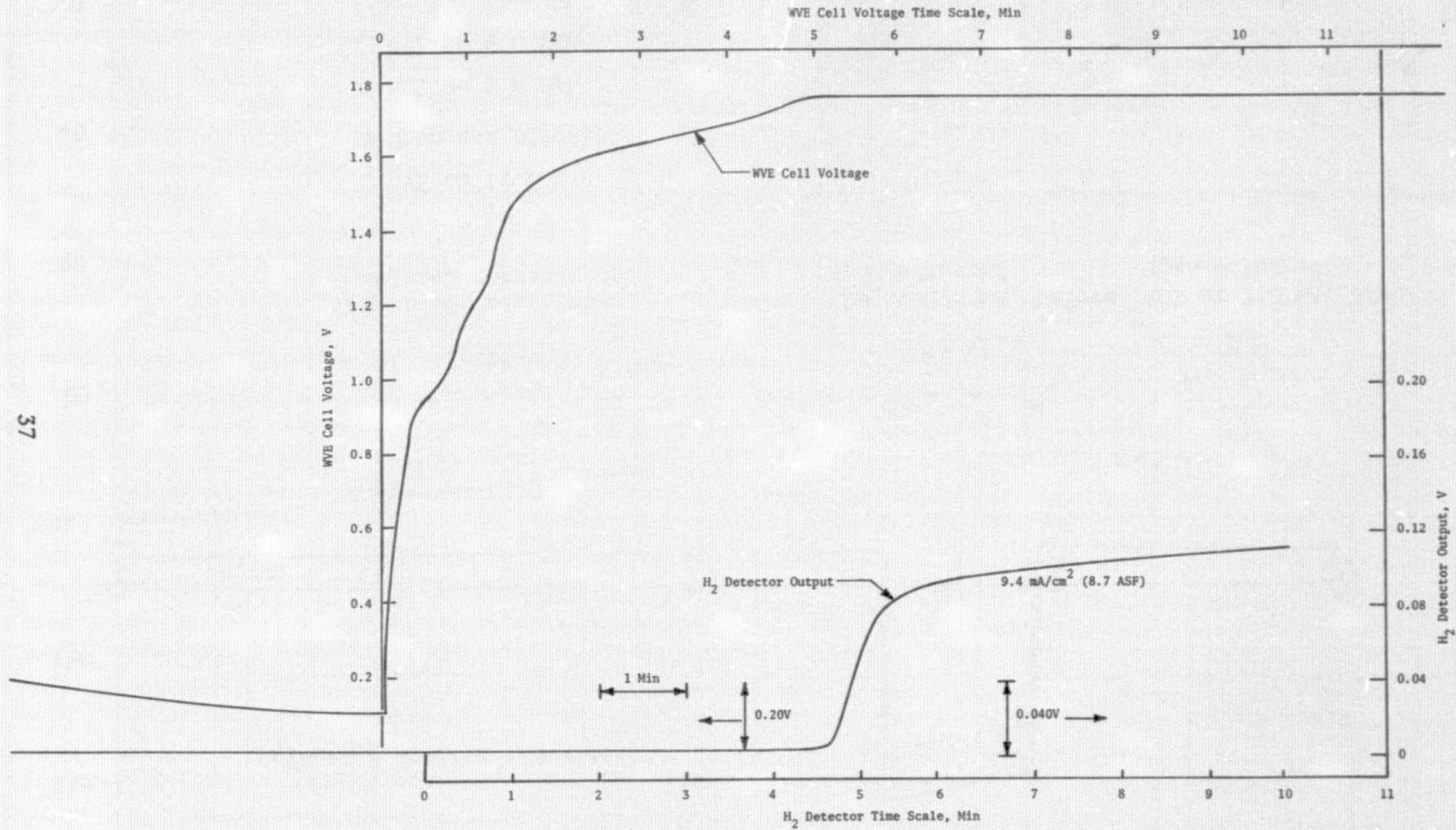


FIGURE 21 RECORDER TRACE OF TYPICAL IN SITU CALIBRATION PLATEAU

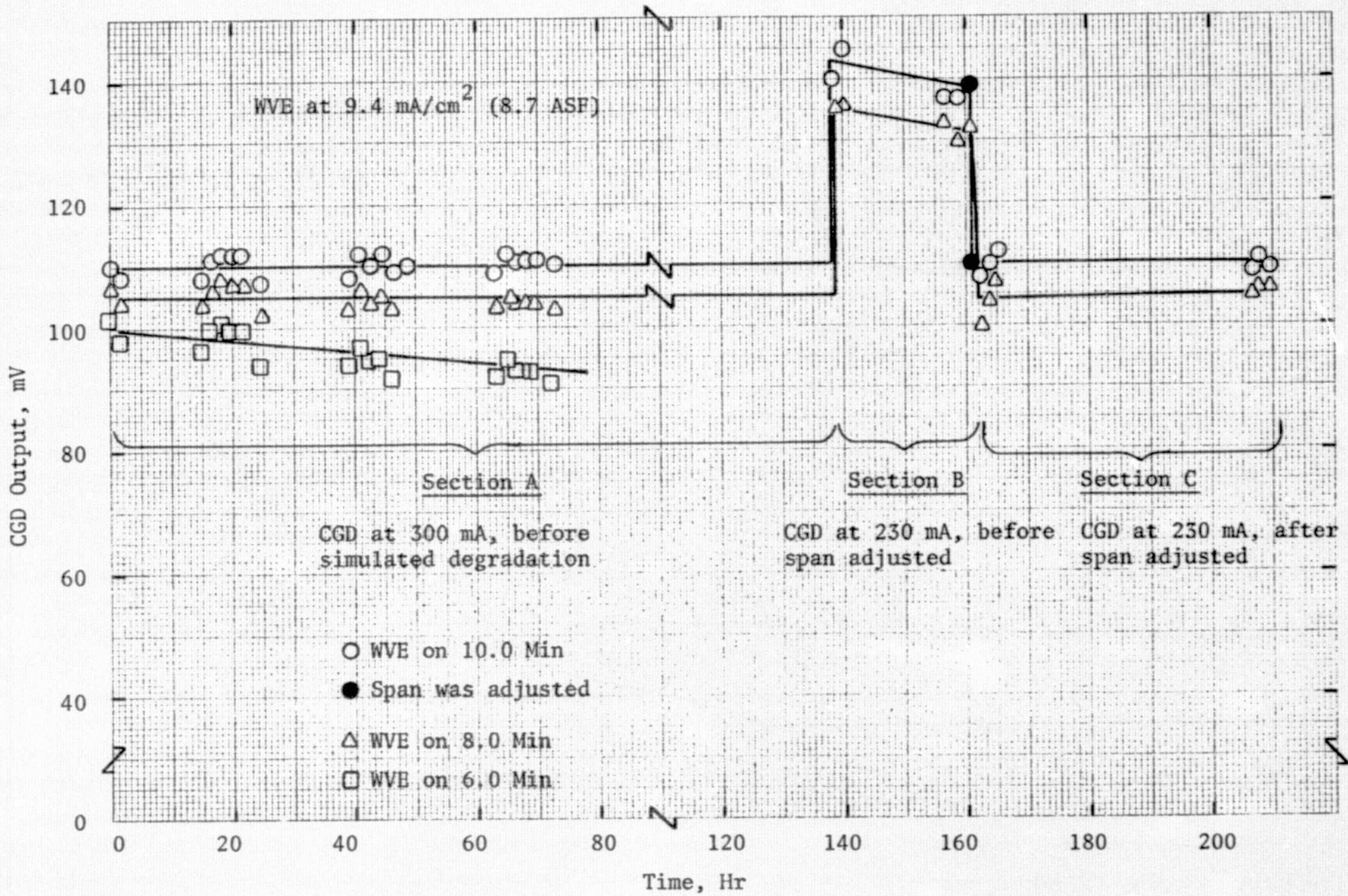


FIGURE 22 CALIBRATION PLATEAU REPEATABILITY AND CGD IN SITU CALIBRATION

TABLE 5 ANALYSIS OF
9.4 mA/cm² (8.7 ASF) PLATEAU DATA

| | <u>At 6 Min</u> | <u>At 8 Min</u> | <u>At 10 Min</u> |
|-----------|----------------------|-----------------|------------------|
| \bar{X} | 95.9 mV | 104.7 mV | 110.3 mV |
| σ | 3.4 mV | 1.7 mV | 1.6 mV |
| Range | 91-102 mV | 102-108 mV | 107-112 mV |
| 3σ | 1% FS ^(a) | 1/2% FS | 1/2% FS |

(a) FS = 900 mV

subsequently lowering the bead temperature, a new CGD calibration curve was obtained with the gas mixture (curve 2 in Figure 23). Then an in situ calibration plateau was generated at 9.4 mA/cm² (8.7 ASF) and at 10.0 minutes the CGD output was rapidly adjusted with the span control back to the plateau voltage obtained before the detector "degraded," 110 mV. Thus, the CGD output was restored to its proper value at a specific percent H₂, a true in situ calibration.

A comparison of calibration curves 1 and 2 of Figure 23 obtained before and after simulated CGD degradation, respectively, shows that a significant change had been effected by lowering the bead temperature. Curve 3, obtained after the in situ span calibration, nearly matches curve 1 for the nondegraded CGD. These curves match within 0.04% at the 0.55% H₂ point and within 0.06% maximum over the entire 0 to 2.1% H₂ range. Since the repeatability specification for the CGD is ±2% full scale or 0.08% H₂, it was concluded that the in situ calibration was quite effective.

Section A, B and C of Figure 22 are plots of output plateaus obtained before simulated degradation, after degradation, but before in situ span calibration, and after degradation and in situ span calibration, respectively. The span was adjusted during the plateau represented by the blackened circles. The several plateaus for each CGD state were generated to check for repeatability.

Second In Situ Calibration

The CGD was restored to its operating condition and again in situ calibrated to further demonstrate technique feasibility.

The bead current and voltage were returned to 300 mA and 2.5V, respectively, and a calibration curve was again determined with 0.0% H₂, 0.55% H₂, and 2.1% H₂-in-air gas mixtures (curve 1 in Figure 24). Plateaus were again generated, and on the second plateau the CGD output was restored to 110 mV at the 10 minute point as in the previous in situ calibration. This operation was followed by another gas mixture calibration (curve 2 in Figure 24). Curve 3 is the calibration curve for the detector in its original, nondegraded state. Note that the original calibration was restored rather well. Curves 2 and 3 coincide again within 0.04% at the 0.55% H₂ point and within 0.07% over the entire 0 to 2.1% H₂ range.

Testing to Reduce In Situ Calibration Time

The previous data has indicated that a CGD can be calibrated by in situ generation of H₂ in 8 or 10 minutes. Such times are somewhat long for spacecraft use, however, considering that the sensor is not in service during in situ calibration and a leak that occurs at that time would go undetected until calibration is completed.

Oxygen adsorbed on the WVE cathode must be consumed before the H₂ concentration within the flame arrestor of the CGD begins to increase, causing a substantial delay in reaching the desired H₂ concentration calibration point. This

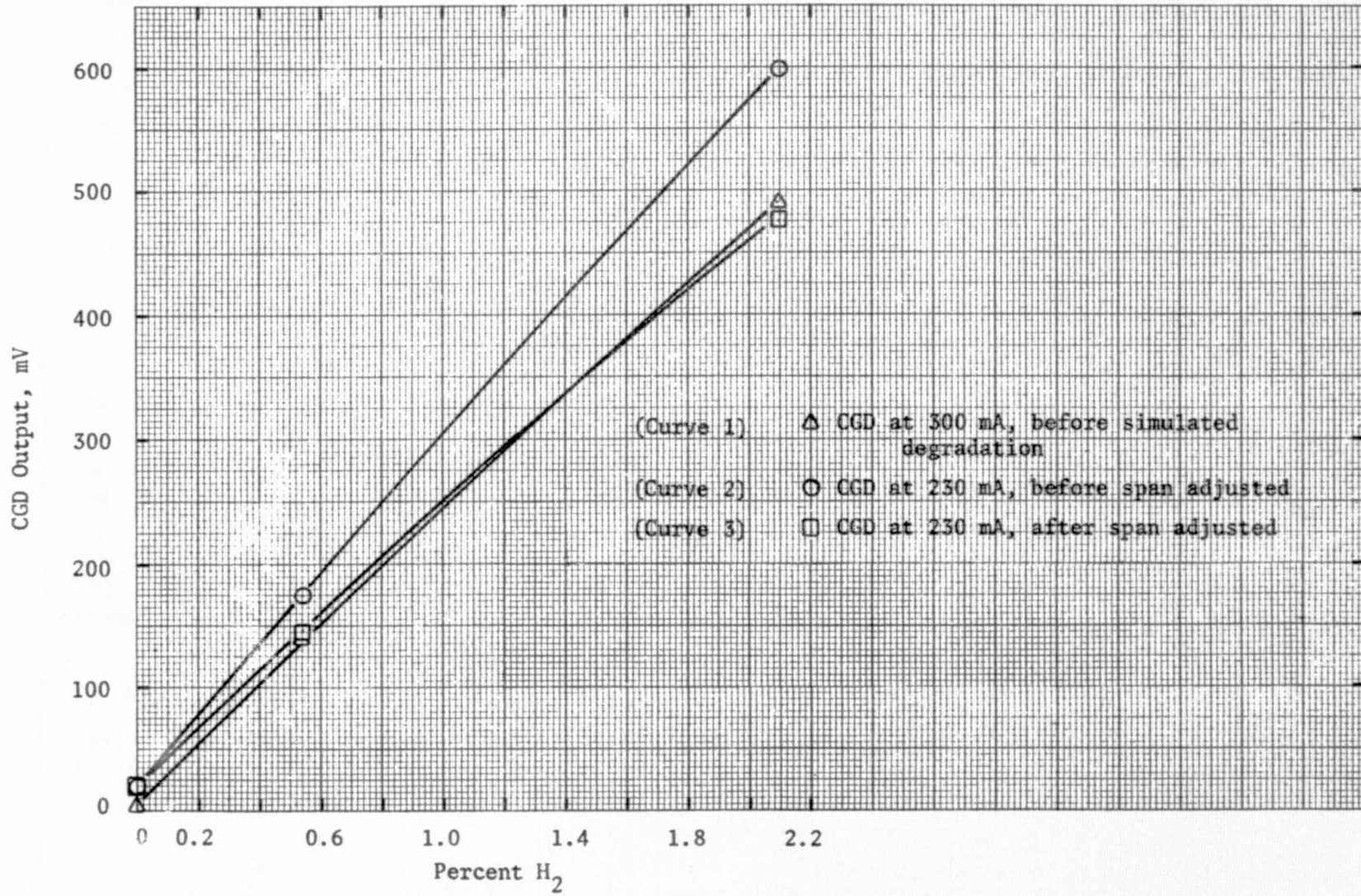


FIGURE 23 CGD CALIBRATION PLOTS, BEFORE AND AFTER FIRST IN SITU SPAN CALIBRATION

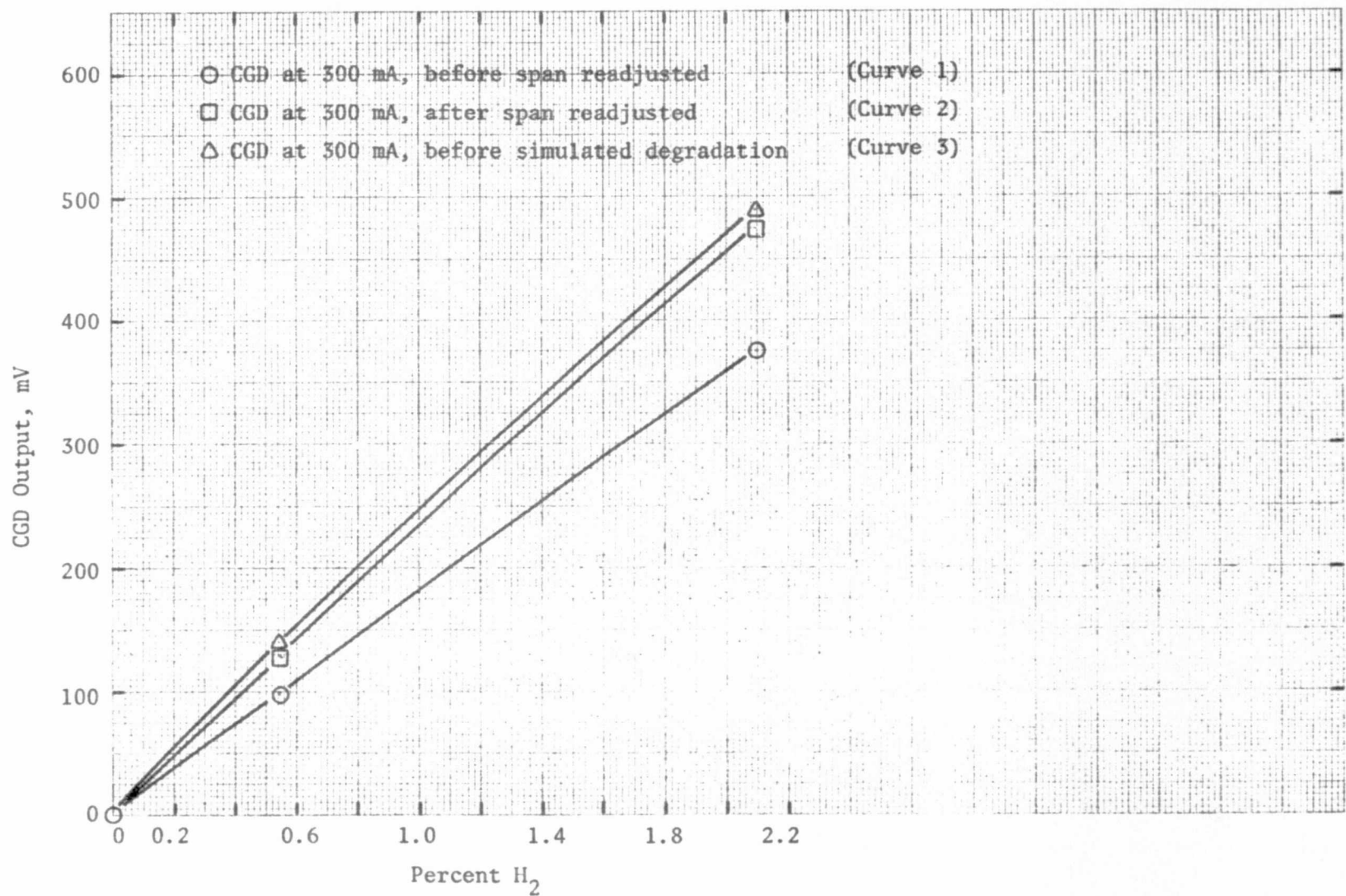


FIGURE 24 CGD CALIBRATION PLOTS, BEFORE AND AFTER SECOND IN SITU SPAN CALIBRATION

delay can be minimized by preconditioning the cathode to reduce the amount of O_2 adsorbed there prior to actual in situ calibration plateau generation. The methods discussed below demonstrate how this has been successfully accomplished.

These methods include, followed by plateau generation at the normal selected current density:

1. Initiating the calibration sequence with a short application of a higher current density than used for the plateau generation (preplateau method).
2. Maintaining a small signal, constant current or constant voltage, through the WVE during idle periods (idle signal method).
3. Combining the two previous methods (idle signal plus preplateau method).

Preplateau Method

Adsorbed O_2 on the cathode of the WVE is removed more quickly at current densities higher than those used during calibration plateau generation. Thus, preceding the actual plateau with a higher current density step, followed by plateau generation, was expected to reduce the total calibration time. This technique was tried and has been shown to indeed reduce the calibration time, as indicated in Columns A to C in Table 6. A current profile diagram above these columns illustrates the nature of the applied current during the calibration. Note that the calibration times have been cut in half from a previous 10 or 8 minutes to 5 or 4 minutes. Further experiments with this method were discontinued, however, because still lower calibration times were desirable. The reduction of calibration current density was also desirable to minimize the power supply size and required power.

Idle Signal Method

Another way to minimize the amount of adsorbed O_2 on the cathode is to apply a small current continually during idle periods to electrolyze the O_2 it attempts to adsorb. This current must be small enough, of course, that no H_2 is transmitted to the CGD.

The applied idle signal can be either a constant voltage or constant current. Constant voltage was initially selected, however, because H_2 evolution, and consequent CGD baseline shift can occur if the net WVE cell voltage reaches a sufficient level. Controlling cell voltage avoids this, whereas the cell voltage may vary unpredictably when operated at constant current.

Initially, 1.2V was maintained across the WVE during idle periods, followed by the usual WVE plateau generations. The total calibration time to reach the plateau was eight minutes. This calibration interval was essentially identical to that obtained when no idle signal was applied to the WVE, and thus 1.2V was an inadequate preconditioning signal. The idle voltage was increased to 1.5V

TABLE 6 IN SITU CALIBRATION TIME REDUCTION PROFILES

| WVE Preconditioning Technique In Situ Calibration Current Profile | Preplateau | | | Idle Signal | | Idle Signal plus Preplateau | | | | | |
|--|--------------|--------------|--------------|--------------|--------------|---|--------------|--------------|--------------|--------------|--------------|
| | Time | | | Time | | Time | | | | | |
| Column Reference | A | B | C | D | E | F | G | H | I | J | K |
| Idle Signal | None | None | None | 1.2 Volts | 1.5 Volts | 2.3 mA/cm ² (2.1 ASF) | 1.5 Volts | 1.5 Volts | 1.5 Volts | 1.5 Volts | 1.5 Volts |
| Preplateau Step Current Density, mA/cm ² (ASF) | 40 (37.2) | 40 (37.2) | 35 (32.5) | None | None | 30 (27.9) | 35 (32.5) | 35 (32.5) | 19 (17.7) | 19 (17.7) | 15 (13.9) |
| Preplateau Step Duration, Min | 1.0 | 1.5 | 1.5 | - | - | 1.5 | 1.0 | 0.75 | 1.2 | 1.0 | 1.0 |
| Plateau Current Density, mA/cm ² (ASF) | 9.4 (8.7) | 9.4 (8.7) | 9.4 (8.7) | 9.4 (8.7) | 9.4 (8.7) | 9.4 (8.7) | 9.4 (8.7) | 9.4 (8.7) | 9.4 (8.7) | 9.4 (8.7) | 9.4 (8.7) |
| Total Calibration Time To Reach Plateau, Min | 5.0 | 4.0 | 4.0 | 8.0 | 3.0 | 3.0 | 3.0 | 2.0 | 2.0 | 2.0 | 3.0 |
| Mean Detector Output at 2 Min | - | - | - | - | - | - | - | 113 | 112 | 108.4 | - |

and at this condition only three minutes were required to reach the plateau. These results and an illustration of the calibration current profile are listed in Columns D and E of Table 6.

Because this latter technique showed promise for reducing in situ calibration times, a series of calibration plateaus were generated by this method. In Figure 25 the detector outputs, after three minutes of calibration time, are plotted versus the elapsed time between calibrations to demonstrate the repeatability of the technique. Statistical data for these points is listed in Table 7.

These plateaus appear to be reproducible enough for use as in situ calibration points. Three times the standard deviation (3σ) for the series of points (99% confidence) falls well within the 2% full scale repeatability specified for the commercial CGD. But comparing the range in data for this technique (101 to 113 mV) to that obtained with no WVE preconditioning (102 to 108 mV, eight-minute point in Table 5) reveals that the idle signal technique using 1.5V idle voltage yielded about twice the scatter in data. A desire for more reproducible plateau generation and even a shorter calibration interval led to the combination of the idle signal and preplateau methods, as discussed below.

An attempt was also made to idle with a small constant current rather than a constant voltage. This try was worthwhile because, for a practical CGD in situ calibration combination, both idle and plateau signals could be generated by simply switching a reference voltage within a single constant current power supply. Constant voltage idling will require an extra integrated circuit. The cell was idled at 2.8 mA/cm^2 (2.6 ASF) until, at about 1.58V the H_2 detector baseline shifted upward, indicating that H_2 was being generated. Control of the cathode voltage may be required to minimize generation of H_2 as a secondary action during the idle periods.

Idle Signal Plus Preplateau Method

Because the idle signal and the preplateau methods independently were shown to reduce calibration times, a combination of these two methods seemed a logical next step to reduce the in situ calibration interval still further. Also, greater reproducibility was expected. Expectedly the CGD output could be made to decay from the preplateau level into the desired calibration plateau level rather than rising into the desired calibration plateau, thereby reducing the effect of WVE prehistory.

In initial idle signal plus preplateau experiments, the idle signal was a constant current, as discussed in the previous section, but only at 2.3 mA/cm^2 (2.1 ASF). The preplateau current step was at 30 mA/cm^2 (27.9 ASF). The total calibration time, as shown in Column F of Table 6 was still three minutes. Also, the CGD baseline rose during the idle period in a second attempt, as observed during the previous testing where the idle signal was a constant current. Subsequent experiments, therefore, were carried out with a constant voltage idle.

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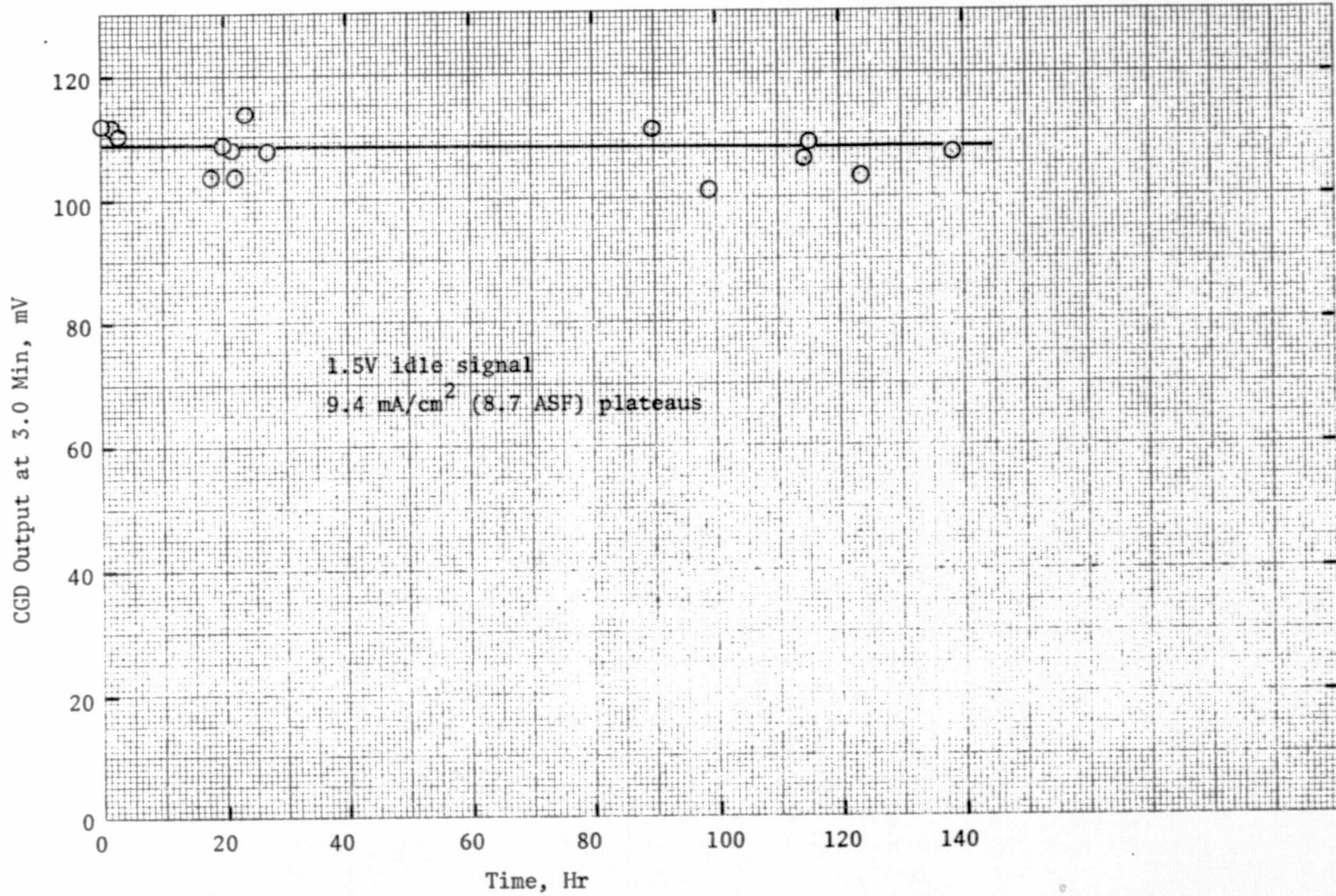


FIGURE 25 CALIBRATION PLATEAUS, IDLE SIGNAL METHOD

TABLE 7 ANALYSIS OF PLATEAU DATA
FOR IDLE SIGNAL METHOD

Conditions

1.5 Volt Idle before Plateau at 9.4 mA/cm²

Total Calibration Time: 3.0 Min

Analysis

| | |
|---------------------------|------------|
| N | 15 |
| \bar{x} | 107.9 mV |
| σ | 3.7 mV |
| Range | 101-113 mV |
| $3\sigma/\text{FS}^{(a)}$ | 1.2% |

(a) FS = 900 mV

The WVE was idled at 1.5V and calibration plateaus were generated using various combinations of preplateau current densities and durations. The results of these experiments are summarized in Columns G to K of Table 6. Use of preplateaus at 35 mA/cm² (32.5 ASF) and 19 mA/cm² (17.7 ASF) resulted in satisfactory calibration times of two minutes. Preplateau generation at 15 mA/cm² (13.9 ASF), however, caused insufficient preconditioning to shorten the calibration time to better than three minutes, as was the case for the application of the 35 mA/cm² (32.5 ASF) preplateau for one minute.

If at least 19 mA/cm² (17.7 ASF) are used for the preplateau, the current density and the timing of the preplateau are apparently not critical, as evidenced by the mean CGD outputs for the data collected using the profiles described in Columns H, I and J of Table 6. Generation of plateaus utilizing preplateau steps of 35 mA/cm² (32.5 ASF) for 0.75 minutes, 19 mA/cm² (17.7 ASF) for one minute agreed within 3% of each other.

To satisfy the objective of minimizing the time required for in situ calibration and minimizing the WVE operating current density, the following calibration sequence was chosen for further repeatability studies: idling at 1.5V, followed by a preplateau of 19 mA/cm² (17.7 ASF) for one minute, followed by plateau generation at the usual current density of 9.4 mA/cm² (8.7 ASF) for an additional minute. Figure 26 is an actual recorder trace for this calibration sequence. Figure 27 is a repeatability plot of the two-minute plateau for this calibration sequence versus elapsed time between plateau generations. The data is very reproducible.

Table 8 is a statistical treatment of the data presented in Figure 27. Note that (3 σ) deviation (99% confidence) is 1.5 mV, corresponding to 0.2% of the full scale CGD output, or $\pm 0.008\%$ H₂. This is the best reproducibility obtained by far for any of the calibration sequences used. A similar sequence is recommended for further development of the in situ calibration spanning of CGDs.

CONCLUSIONS

From the results of the program the following conclusions are drawn:

1. Using a WVE cell for the in situ generation of H₂ calibration gas is a viable technique for automatically calibrating CGDs.
2. A constant H₂-in-air concentration is achieved within the volume of the flame arrestor of a CGD when the WVE cell is operated at a given current density. Water vapor electrolysis cell current density and operating time are a function of the configuration of the CGD and the desired H₂ calibration point. The equilibrium concentration of H₂ within the flame arrestor of the CGD is directly proportional to the current density of the WVE cell. For each WVE cell current density a H₂-in-air concentration calibration point is achieved due to the equilibrium attained between the H₂ being generated by the WVE and the H₂ being consumed by the sensing beads of the CGD and the H₂ exiting through the flame arrestor of the CGD.

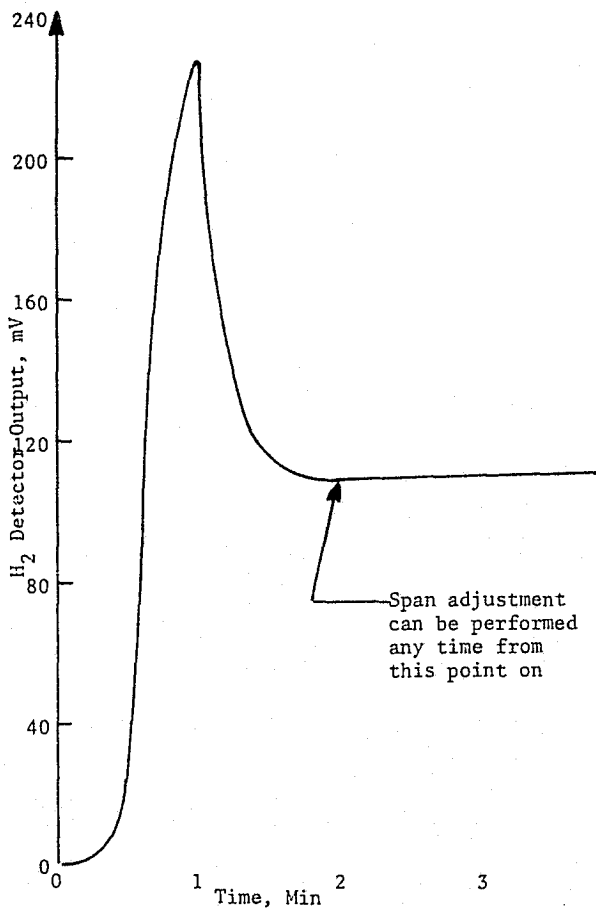
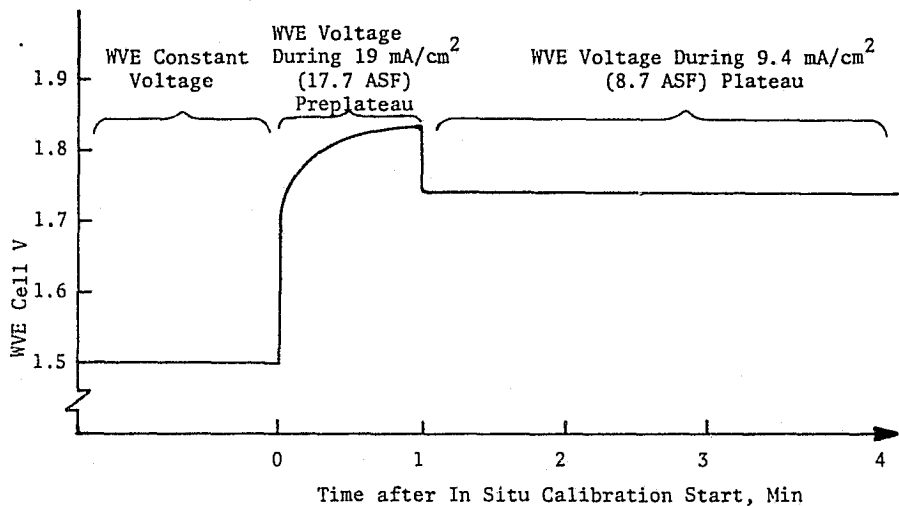


FIGURE 26 RECORDER TRACE OF TYPICAL IDLE SIGNAL AND PREPLATEAU CALIBRATION PROFILE

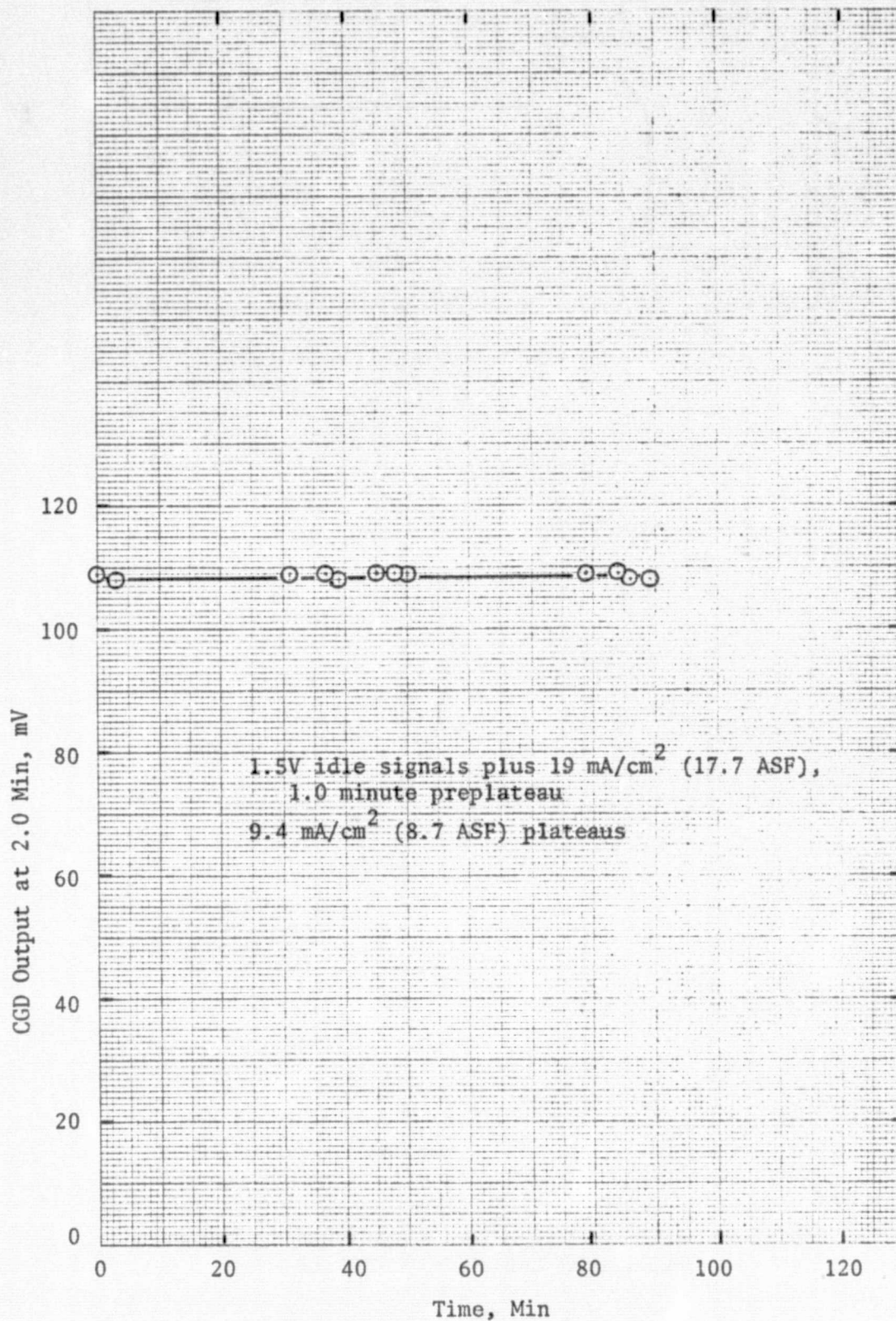


FIGURE 27 CALIBRATION PLATEAUS, IDLE SIGNAL PLUS PREPLATEAU METHOD

TABLE 8 ANALYSIS OF PLATEAU DATA
FOR IDLE SIGNAL PLUS PREPLATEAU METHOD

Conditions

1.5 Volt Idle, 19 mA/cm² Preplateau for 1 Min,
9.4 mA/cm² Plateau

Total Calibration Time: 2.0 Min

Analysis (Circles in Figure 3)

| | |
|---------------------------|------------|
| N | 13 |
| \bar{x} | 108.4 mV |
| σ | 0.5 mV |
| Range | 108-109 mV |
| $3\sigma/\text{FS}^{(a)}$ | 0.2% FS |

(a) FS = 900 mV

3. Tests performed with the WVE/CGD configuration derived under this program indicated that the time required for generating the H₂ gas needed to perform an in situ calibration at 0.5 % H₂ can be reduced from an initial eight minutes to as low as two minutes. This was done by maintaining a constant voltage of 1.5V on the WVE cell followed by a preplateau step of 19 mA/cm² (17.7 ASF) for one minute. This sequence was designed to decrease the time required to remove absorbed O₂ from the cathode of the WVE cell and to speed up the initial generation of H₂, thereby reducing the time required to reach the desired H₂ concentration within the flame arrestor.
4. Analysis of the in situ calibration concept revealed that the procedure must be expanded to include provisions for zero calibration. This is required to avoid errors in the span calibration due to a background combustible gas concentration.
5. The commercial CGD used for this program was position sensitive. Its output in H₂-free air varied by as much as 100 mV out of a 0 to 1V scale (equivalent to 0.4% H₂-in-air) when rotated 3.1 radians (180 degrees) about the axis of the sensor head.
6. Testing verified that the repeatability of the CGD was within the ±0.08% H₂ repeatability specified for the instrument. The output of the CGD was linear over the range tested in this program (0 to 2% H₂).
7. The CGDs were unaffected by exposure to a 2% H₂-in-air environment for up to 24 hours. The output of the CGD during the 24 hour period varied by only ±5 mV or ±0.04% H₂.
8. The CGD was not significantly affected by variations in line voltage. The total fluctuation in the CGD output for line voltage changes from 105 to 120V was only 4 mV, corresponding to 0.04% H₂.

RECOMMENDATIONS

Based on the results of this investigation, the following recommendations for advancing the CGD in situ calibration technology are made:

1. Perform the design, development and fabrication activities required to expand the in situ calibration procedure to include zeroing the CGD. This is required to avoid possible errors that could be introduced during in situ calibration due to the effect of a combustible gas background.
2. Develop the required instrumentation that will enable the automatic initiation of the in situ calibration sequence.
3. Develop the instrumentation required for automatic span and zero adjustment during the in situ calibration sequence.

4. Upgrade and repackage the electronics of the current breadboard. In addition, expand the preprototype instrumentation package to include the circuits required for automatic calibration initiation, automatic span and zero adjustment and zero calibration.
5. Perform the design and fabrication activities required to develop a preprototype Triple Redundant Hydrogen Monitor by integrating LSI's Triple Redundant H₂ Sensing Subassembly with the in situ calibration hardware established under this contract.
6. Characterize the preprototype Triple Redundant Hydrogen Monitor, including in situ calibration. Testing performed should consist of verifying the use of the WVE cell for zeroing the Triple Redundant Hydrogen Monitor, testing the WVE cell in the O₂ generation mode followed by the H₂ generation mode, which simulates zeroing and spanning of the sensor, and testing to determine the accuracy and repeatability of the in situ calibration procedure for both zero and span calibration.
7. Perform design, development and testing activities to improve the repeatability of the Triple Redundant Hydrogen Monitor and the repeatability of the in situ calibration procedure.
8. Perform a testing evaluation of the in situ calibration procedure to determine the effect of variations in atmospheric relative humidity on the accuracy of the in situ calibration.
9. Perform the design, development and testing required to improve the Triple Redundant Hydrogen Monitor with regard to speed of response and sensitivity and to determine the ability of the Triple Redundant Hydrogen Monitor to detect CH₄/air mixtures.
10. Perform additional testing of the Triple Redundant Hydrogen Monitor to include (1) a 120-day endurance test, (2) determining the maximum number of exposures to 4.0% H₂ the catalyzed sensing beads can withstand before deterioration is noted, (3) determining the effects of expected cabin contaminants on the performance of the catalyzed sensing elements, (4) testing associated with verifying speed of response and sensitivity of the Triple Redundant Hydrogen Monitor, and (5) testing necessary to determine the position sensitivity of the Triple Redundant Hydrogen Monitor.
11. Perform additional supporting studies associated with the evaluation of existing combustible gas detection concepts for manned spacecraft and the recommendation of advanced concepts for the detection of combustible gases for future manned space vehicles.

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