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on
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Prepared by:

Sherman W. Rabideau, Contract Employee

G. W. Work, Contract Employee

F. S. Thomas, Chemist

Reviewed by:

J. C. White, Chief of Electrochemistry Section

P. Borgstrom, Superintendent Chemistry Division

Approved by:

A. H. Van Keuren, Rear Admiral USN, Director

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ABSTRACT

The unsatisfactory operation of the one Mark I hydrogen detector removed from service due to faulty operation was verified in the laboratory. The direct cause of the change of calibration was found to be alteration of the catalyst cell. The underlying condition giving rise to this cause appears to have been inadequate repair facilities. A suggested system for repair and recalibration of these instruments is discussed. The calibration of the instrument after repair and general overhaul leads to the recommendation that other units which have been in service use should be studied for possible irreversible change of calibration. Reasons are given for a recommendation that the present test and recalibration methods be critically examined for needed changes.

The MSA and Davis installed hydrogen detectors were operated for considerable periods of time in the laboratory under various catalyst poisoning and non-poisoning conditions. The effect of the various variables in operating conditions was also studied. The results of these studies indicated that alterations to both instruments would appear to be necessary before satisfactory operation could be expected. Both instruments require rather extensive changes or additions to the gas flow system to ensure removal of gas impurities and to prevent leakage. The major fault in both electrical systems lies in the balance rheostat. Other parts of the electrical systems, however, require change either to attain stability or to compensate for the variables in operating conditions. Recommendations for the alteration of test instruments and for further study of those altered instruments are presented.

The calibrations of the MSA and Davis portable combustible gas indicators were determined with hydrogen-air mixtures of known composition. The indications with one MSA unit and the Davis instrument were low. The other MSA instrument was seriously in error. The battery life of one MSA unit was determined under two arbitrary sets of operating conditions. Both makes of instruments were subjected to a preliminary study of the effect of gas impurities on the indication which showed that only the Davis indicator was poisoned under the conditions employed. Recommendations for further study are presented

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INTRODUCTION

A. Authorization

1. This problem was authorized by references (a), (b) and (c). Other pertinent references are (d) through (l).

(a) BuShips ltr C-SS/S62 (1-29-Mz and Dys) of 31 January 1941.
(b) BuShips ltr S65-4(350) of 22 September 1942.
(c) BuShips ltr S65-4(350) of 2 October 1942.
(d) BuC&R ltr S87-(6) (DS) SS/S87 of 19 February 1929.
(e) Submarine Board ltr of 3 January 1929, no number.
(f) Lamb, A.B., and Larson, A.T., J. Am. Chem. Soc. 41, 1908-21(1919).
(g) NRL ltr C-S62-4 of 16 January 1941.
(h) NRL ltr S62-4 (454-FST) of 23 December 1942.
(i) NRL conf. report P-2130 of 3 August 1943.
(j) NRL, Instructions for Testing and Recalibrating Mark I Submarine Hydrogen Detectors, 26 May 1933, in file SS/S87-(20).
(k) NYd. Portsmouth, N.H. Instructions for Testing, Hydrogen Detector, Mark I, Model 1, file S 4822 of 25 March 1941.
(l) NYd.NYk. Report 4517-1 of 3 August 1942.

B. Statement of the Problem

2. The problem is a general study of hydrogen detectors for submarine use and especially of certain commercial instruments in service use or proposed for service use with respect both to suitability of these instruments and to revision of specifications and test procedures for such instruments.

C. Known Facts Bearing on the Problem

3. The need for a hydrogen detector aboard submarines results from the fact that hydrogen is normally produced by lead-acid storage batteries under certain conditions and that the concentration of this gas in all parts of the

submarine atmosphere must be kept below the inflammable and explosive regions at all times. When the submarine is on the surface the hydrogen produced is usually disposed of by dilution with a forced ventilation air stream which is then emptied outboard. When the boat is closed the hydrogen cannot be disposed of outboard so it is mixed, by forced ventilation, through the atmosphere of the submarine to keep the concentration low enough in all parts of the boat to ensure safety.

4. As reported in enclosure (A) of reference (d) the Bureau of Construction and Repair investigated, throughout the early history of the submarine service, numerous devices for hydrogen detection. The National Bureau of Standards investigated some 18 types and finally developed a delicate platinum wire bridge which proved to be too fragile for submarine use. The Burrell combustible gas detector, originally intended for mine use, was finally taken as the standard means for indicating hydrogen in submarines.

5. This instrument operated by measurement of the volume change resulting from the catalytic combustion of the hydrogen in a trapped sample of the gas to be analyzed.

6. The Burrell device remained as the standard until about 1930. Somewhat before this date the Submarine Board recommended in reference (e) that the development of a hydrogen detector suitable for submarine use be carried on at the Naval Research Laboratory. The problem of development of such an instrument was sent to this Laboratory by reference (d).

7. The fundamental principle of the Mark I detector, which was developed through experimentation at this Laboratory, is to pass a continuous stream of the gas to be analyzed through an essentially thermally isolated catalyst bed and to measure the temperature rise resulting in the gas stream from the combustion. This method had been employed for the detection of carbon monoxide and other combustible gases in various laboratories for a number of years. The method had been reported in reference (f).

8. Service tests were carried out aboard submarines of the NRL instrument employing the temperature rise of the gas stream, a commercial instrument employing catalytic combustion on a heated wire and a commercial instrument employing the thermal conductivity of the gas sample as methods of hydrogen detection.

9. The Mark I hydrogen detector was accepted then for general use and a number of units of the detector were built and installed aboard the submarines.

10. As part of the conversion a few years ago of the submarine service to a war basis, the specific gravity of the storage battery electrolyte was raised. This being one of the variables effecting the rate of self-discharge of storage batteries and hence of hydrogen evolution on stand, tests were carried out to determine the rate of hydrogen evolution of the batteries of the several boats under the new conditions, reference (g).

11. It appeared as one result of these tests that, as reported in paragraph 4 (a) of reference (a), certain of these detectors were not operating in a satisfactory manner and the operation of others was at least questionable.

12. As a result of these findings the Mark I unit referred to in reference (g) and one new unit were supplied to this Laboratory with the request, reference (a), that the unsatisfactory operation of the one unit be verified and the underlying causes be found. This letter further authorized a general study of the hydrogen detectors both as to installed and portable models. Units of the MSA installed hydrogen detector, the MSA portable combustible gas detector, the Davis portable combustible gas detector and the experimental model of the Davis installed hydrogen detector were later supplied and study of these specific units further authorized by references (b) and (c).

13. The results of a preliminary study of the MSA installed hydrogen detector were reported in reference (h).

D. Theoretical Considerations

(1) General

14. Any method of analysis for one constituent in a mixture must be based on some characteristic which is descriminate between the material to be determined and all the various other materials present. In the case of the determination of the hydrogen concentration of a hydrogen-air mixture, the method of analysis for the highest accuracy should be based on a physical or chemical characteristic which is possessed by hydrogen only. Where a lesser degree of accuracy can be used satisfactorily, the method may be based on a characteristic which is specific for a group of materials and where the other members of this group may reasonably be expected to be absent or present in only small amounts. Where an even lesser degree of accuracy than that immediately above is permissable, the characteristic employed may also be possessed by other materials expected to be present but where a sufficiently appreciable degree of difference exists in respect to that characteristic to permit segregation.

15. There are a number of physical and chemical characteristics of hydrogen in hydrogen-air mixtures which have been used for the determination of hydrogen concentrations. The only property used which is highly specific for hydrogen is the absorption of it by palladium metal. The other methods employed have been of the less specific types above. These include such methods as the determination of the density either by direct measurement or by comparison to a standard gas, measurement of optical refractivity, determination of the rate of effusion of the gas mixture through a small opening, comparison of the thermal conductivity of the gas mixture to that of a standard gas, combustion of the hydrogen with oxygen and measurement of the volume change or other characteristic effect of that combustion, and other methods.

16. For submarine use the hydrogen detector needed is a reliable, continuous, automatic, hydrogen-air mixture analyzer suitable for operation either in an atmosphere of the gas to be analyzed or in a different atmosphere. The instrument must also be rugged and

easily built and maintained. A further complication enters due to the variable amounts of various impurities in the mixture which are characteristic of submarine atmospheres and ventilation gases and which must not affect the instrument or the analysis obtained with it. It is preferable to avoid the use of chemical reagents as far as possible, especially those which are highly corrosive and those which require frequent replenishment or replacement.

17. These conditions remove immediately most of the common laboratory methods of analyzing such a gas mixture. In fact, of the characteristics of hydrogen-air mixtures only those of combustion and thermal conductivity appear to be capable of being adapted with any degree of facility to yield a continuous indication of hydrogen concentration.

18. All analytic methods employing the combustion characteristics of this mixture are based on the reaction:

$$H_2 + 1/2O_2 \longrightarrow H_2O_{(g)} + 58.3 \text{ kg-cal.}$$

The method of employing this reaction depends to a large extent on the range of hydrogen to be encountered and the nature and concentrations of the other constituents present in the gas mixture. The storage battery ventilation gases aboard submarines comprise normally a mixture of gases with about the range of concentrations shown in Table 1. It is apparent that there is more oxygen than an amount equivalent to the amount of hydrogen present, that no other combustible gas is present, and that the hydrogen concentration is well below the explosive region.

(2) Mark I Hydrogen Detector

19. In the Mark I hydrogen detector the above reaction is utilized by drawing a stream of the storage battery ventilation gas through a catalyst bed. The gas stream before reaching the catalyst is heated to a temperature slightly above the boiling point of water. This hot gas heats the catalyst bed which is, in all other respects, essentially thermally isolated. The temperature which the catalyst bed attains in this way is sufficient to permit the catalyst used, palladium on pumice stone, to bring about almost complete combustion of the hydrogen.

Since, as previously mentioned, the catalyst is essentially thermally isolated, the heat evolved by the combustion of the hydrogen can only leave the reaction zone in the exhaust gas. This heat appears as a temperature rise of the gas stream. The approximate elevation of the temperature to be expected may be calculated as shown in Appendix A. It is evident from this calculation that under the conditions stated the temperature rise occurring across the catalyst bed should be a reasonably accurate, linear function of the hydrogen concentration and approach a value of about 83 degrees C per percent of hydrogen present in the sample.

20. Since this gas stream actually contains very little heat, the temperature measuring system must be designed so that it will contain a minimum amount of heat capacity and heat conduction. The limitation of heat capacity is required to keep the time of response short. The limitation on heat conductivity is required to give a minimum conduction of the heat away from the active measuring element since this would result in the measurement of a temperature less than the actual exhaust temperature. These results are achieved by using a multijunction thermocouple made of fine wires. The cold junctions are so placed that they assume the temperature of the input gas stream by contact, through electrical insulation, with the furnace wall. The hot junctions are grouped near the exhaust side of the catalyst bed so that the gas stream passes directly over them. Each wire in this thermopile is long in relation to the size of the wire. This gives a measuring arrangement in which the active element approaches the gas stream temperature as nearly as possible.

21. It is necessary still to convert the emf generated by these couples into a visual or other indication. For this use, the indicating unit of the temperature measurement system must be sensitive to millivoltage, of rugged construction, and readily obtainable. To fulfill these requirements a sensitive millivoltmeter was used. However, since this meter was of low resistance, at least in comparison to the resistance of the thermopile, a large part of the emf generated is lost in the resistance of the thermopile itself instead of being used to activate the meter.

(3) MSA and Davis Detectors

22. In the types of MSA and Davis hydrogen detectors considered here, the reaction employed is the same as that of the Mark I. The method of using this reaction, however, differs in that the catalyst and the measuring element are combined in the form of a heated platinum filament or element. This filament is, in each case, one arm of a Wheatstone bridge circuit. When this filament is exposed to a gas mixture containing oxygen and a combustible component, reaction takes place on the surface of the filament resulting in an increased temperature of the filament. Since the resistance of platinum varies with the temperature this results in a change of resistance of this arm of the bridge. A meter across the bridge indicates the extent of unbalance which is, therefore, an indirect function of the concentration of the combustibles present.

23. The various instruments in this group differ only to the extent of the secondary parts of the set-up; that is, such things as the type of power supply, the method of exposing the filament to the gas stream, and the compensation for variables such as temperature.

24. The temperature rise of the filament cannot be calculated as was done for the Mark I. It must suffice here to state that when other variables are held constant, the extent of bridge unbalance indicated by the meter is a function of the concentration of combustibles in the gas stream.

NARRATIVE OF ORIGINAL WORK DONE AT THIS LABORATORY

A. Mark I Hydrogen Detector

25. Two units were supplied for the tests requested by reference (a). One of these units, serial number 46, was the unsatisfactory detector reported in reference (g). This instrument was removed from the after battery ventilation system of the S-26. The other unit, serial number 249, was a new detector ready for delivery to the service.

26. These instruments were set up as received and the calibration checked at several points in their

operating range with a stream of hydrogen-air mixture of known composition. Of course, some preparative steps were required due to the fact that the instruments had been shipped, but only those due to that cause were performed before the first attempted calibration check. The unsatisfactory operation of unit 46 was verified by that first calibration check. The various apparent possible causes of the unsatisfactory operation of unit 46 were then removed one at a time. After each alteration or group of related alterations a calibration check was performed so that the effect of each individual or group of causes could be isolated. The new instrument, unit 249, was used for checking the mixture being admitted to the other instrument, the presence of hydrogen in the exhaust, and as a source of parts for temporary use on unit 46. This study was pursued to the point where further work would entail the replacement of parts which were not obviously defective or the change of adjustments for which there was no apparent need.

27. A preliminary study was made of certain parts of the method employed in the original calibration of these instruments. In these tests several methods of calibration were tried. The results obtained were not complete as to a study of the calibration methods as a whole but only as to certain points in the methods.

B. MSA Installed Hydrogen Detector

28. This instrument was operated for a long period of time using different arrangements of the auxiliary equipment in an attempt to separate, without fundamentally altering the instrument, the various possible variables which might affect its operating characteristics.

29. The calibration of the instrument in its original condition was, of course, checked first. The system was then revised to test for the effect of leakage on the indication of the instrument. In order to obtain a rough idea of the results to be expected in operation on an actual battery ventilation gas stream such a system was set up and the instrument was operated on an actual battery ventilation gas stream in the laboratory.

In order to separate the variables of this type of operation the system was completely changed and the instrument was put onto a hydrogen-air stream which contained none of the impurities which may be present in the battery ventilation gas stream. The instrument was operated for a long period of time under this condition to permit observation of the effects of the normal variables of operation as distinct from effects due to impurities in the gas stream.

30. During the period of the preceeding tests, an investigation had been carried out to develop a method of preparation and a method of analysis of stibine suitable for use in this problem and other similar problems, reference (1). Using these methods a study of the effect of this impurity on the operation of the instrument was carried out. This test was first performed on the instrument in such a way as to ensure that the stibine actually reached the active element so the effect of the known presence of this material would be evident. The instrument was then operated with its normal protective devices against such impurities (stibine scrubber cartridges) on a stream of the hydrogen-air mixture to which was added stibine in known amount. The instrument was operated under this condition for a long enough time to indicate the useful life of the stibine scrubber under the given conditions and the effect on the indication of the instrument of use of a stibine scrubber cartridge beyond that time.

31. In order to better evaluate the effectiveness of the stibine scrubbers furnished with the instrument, tests were performed on this part alone. In a system separate from the instrument the scrubber was placed in a stibine containing gas stream and the efficiency of the scrubber for removal of the stibine was determined over a period of time by analysis for stibine passed in and passed through. Two materials, referred to here as "A" and "B", developed for other use were also studied in this manner for possible use for this purpose.

32. A number of tests of controllable isolated variables were carried out which were of short duration.

The instrument was exposed to ambient atmospheric temperatures covering the range which might be encountered on submarines and the effect of this change of temperature on the indication of the instrument within its useful hydrogen concentration range was determined. The ambient atmospheric pressure was changed in another experiment from atmospheric to about 80% of that pressure to determine the effect of the pressure variable. Since the battery ventilation gas mixture varies in composition as shown in Table 1, the effect of such variation on the indication of the instrument was determined. The oxygen content of the input mixture was changed from its normal value to its minimum expected value, the carbon dioxide content was changed between its limits, and the water vapor content was changed from dry to saturated at a normal temperature (25°C). The effect of change in these variables was determined both singly and in combination through the useful hydrogen concentration range of the instrument. The effect of the change of input voltage to the instrument was also determined over the concentration range.

33. Since the instrument can only operate on the gas sample which is brought to it from the ventilation duct, a set of flow-head-voltage curves were determined for the pump and the flow-head relation of the instrument was determined under several conditions.

34. There were provided, as a means for checking the accuracy of the instrument under any conditions of operation, cylinders containing compressed hydrogen-air mixtures with the concentration of the hydrogen in the contained gas marked on each cylinder. These gas mixtures were analyzed for hydrogen concentration and the pressure measured to determine the amount of gas contained when received.

C. Davis Installed Hydrogen Detector

35. In general, the tests carried out on the Davis Installed Detector were the same as those performed on the analogous MSA instrument. Certain of these tests, however, were not applicable to the present instrument and hence were omitted.

36. The instrument was operated for a long period of time on a hydrogen-air mixture saturated with water vapor. This test was intended to determine the characteristics of operation of the instrument when none of the impurities are present which may be part of the battery ventilation gas stream. The gas mixture employed in this test was the same as that in the similar MSA test.

37. To determine the effect of what is thought to be the most common impurity in the battery ventilation gas stream, stibine was added to the input gas stream. Since there was no part of the instrument apparently specifically intended to remove this constituent from the gas stream, the test was much simpler than the analagous test on the MSA hydrogen detector. One part of this test was carried out so that the presence of stibine in the active element chamber was ensured by determining its presence by analysis.

38. The same tests covering the effects of the temperature, pressure, and gas mixture composition variables were performed on this instrument as on the MSA Installed Hydrogen Detector.

D. Portable Combustible Gas Indicators

39. It is much more difficult to arrange tests for the portable instruments which will have significance toward their normal mode of use than is the case with the continuous installed detectors.

40. All of the portable combustibles indicators available were carried through a calibration check.

41. A test of the life of the batteries was performed under a set of arbitrary conditions of operation designed to permit automatic operation in the laboratory and to approach, even though remotely, severe service use.

42. A test of the effect of stibine on the indication of the MSA Explosimeter, Model 2, and the Davis Combustible Gas Indicator, Model M-1, was carried out by operating these instruments on a stream of hydrogen-air mixture containing that gas.

METHODS

A. Mark I Hydrogen Detector Tests

43. The electric power needed to operate these instruments was drawn from the 110 volt d.c. circuit available in the laboratory. Electrolysis current was obtained from storage batteries and measured by a Weston ammeter, Model 45.

44. The hydrogen-air mixtures needed for checking the calibration of the Mark I hydrogen detectors were prepared most of the time by using essentially the same method as that employed in the original NRL method of calibration, reference (j). The hydrogen needed to give the desired hydrogen-air mixture was obtained by the electrolysis of water in small electrolytic cells such as those used in the Mark I detectors. The amount of current passed and the number of cells in the series arrangement permits calculation of the weight and hence of the volume of hydrogen produced. The gas stream was drawn through the instruments by the pump built into each detector. The flow rate of the air which makes up the main part of this stream was measured in the original NRL calibration check method by use of a capillary, pressure-drop meter. In this work the air flow rate was measured by use of a wet test meter.

45. From time to time it was necessary to check the instrument for leakage. This was done by first drawing a gas stream containing about 3% hydrogen through the instrument using the method described above except that a restriction was put into the input gas stream just ahead of the instrument so that the gas in the instrument was under a vacuum of a few inches of water. The system was then changed so that the air was taken from the compressed air line in the laboratory. A pressure reducer and needle valve gave a constant air flow rate which was measured by the wet test meter. The pump was disconnected from the output side of the combustion furnace and a restriction installed in the output line to give a slight pressure on the system. The difference in the readings, when the hydrogen concentration was known to be identical, was then a measure of the leakage of the system.

B. MSA and Davis Installed Hydrogen Detector Tests

(1) Power Supply

46. The 110 volt d.c. needed to operate the MSA instrument was obtained originally by connection to a circuit of that rating available in the laboratory. In order to operate the instrument overnight it was later necessary to supply this power by use of a motor generator set. This system of power supply had the added advantage of permitting variation, when desired, of the supply voltage to allow the study of the effect of this variable on the operation of the instrument.

47. The Davis Instrument was operated at all times either directly on the 110 volt a.c. line or through a Variac from the 220 volt a.c. line available in the laboratory.

(2) Indication Recorder Arrangement

48. The study of the operation of this type of instrument normally would require continual observation of the indicating meters over a considerable period of time. A much more satisfactory arrangement is attained if the indication of the meters can be automatically recorded. This was readily attained with these instruments by using a voltage divider in place of the remote indicating meter. Each of these voltage dividers had a total resistance equal to the meter circuit which it replaced and the voltage taps to the potentiometer recorder were adjusted to give full scale deflection on the recorder for a full scale deflection on the instrument panel meter. In the MSA, the leads to the recorder from each side were carried through the normally closed contacts of a relay whose coil was attached to the remote alarm signal pilot terminals of the same side. This was advisable to protect the recorder from the high voltage which results in the indicating circuit when a filament burns out or other similar malarrangement occurs. Since the Davis instrument had no provision for remote signal lights, this protective system could not be used on it. The potentiometer used in this work was a six point Tag Celectray, Model B, having a full scale range of ten millivolts.

(3) Air Supply

49. The operation of this equipment requires that a stream of the gas to be analyzed be moved through the instrument continuously. For the MSA the amount required, according to the instruction book, is about 425 cubic centimeters, (cc), per minute for each analyzer circuit. The Davis instrument has a flow requirement which is less well defined but, by measurement in this Laboratory, 1500 cc per minute for each analyzer circuit appears to satisfy the flow requirements stated in the instruction manual.

50. Three different arrangements of equipment were employed to produce the gas flow stream.

(3-a) MSA Pump

51. The design of this pump is such that it can only be used to produce a reduced pressure. Therefore it was usable only to draw the gas stream through the instrument.

(3-b) Vibrator Pump

52. There were available, in this Laboratory, several small 110 volt, 60 cycle, a.c. vibrator pumps of standard design and commercial manufacture. These were capable of delivering about 400 cc per minute each against nominal back pressure. Three of these pumps were used in parallel for the first tests in which the gas stream was forced through the MSA instrument. By keeping the voltage supply to the pumps constant by use of a voltage regulator transformer, it was found by measurement, that a constant flow rate was obtained. The air stream input to the pumps was filtered through a sintered glass plate so that dust was excluded which avoided failure of the check valves to seat.

(3-c) Rotary Vane Pump

53. In order to add the Davis detector to the same system on which the MSA instrument was operating, it was necessary to increase the quantity of the gas stream beyond the amount available with a reasonable number of units of the vibrator pump. A rotary vane pump, Gast type INF10, of suitable capacity, which had been furnished as part of the Davis equipment, was available and was, therefore, installed as the pump in this system. A pressure gauge, pressure maintained switch and a needle valve were installed in that order beyond the pressure

relief valve on the output side of the pump. The input air was drawn through a dust filter of absorbent cotton to avoid any possible damage to the pump from dust. The electric lead to the pump motor was wired through the pressure maintained switch so that if the outlet pressure dropped below the set value the motor was removed from the line and would not again operate until the manual switch which by-passed the pressure maintained switch was thrown. This served the double purpose of protecting the pump and motor from damage due to excessive friction in the apparatus and keeping the pump shut down if it stopped for any reason when unattended.

(4) Hydrogen Supply

54. Two different sources of the hydrogen necessary to give the hydrogen-air mixture gas stream were employed.

(4-a) Battery Overcharge

55. In most of the early work on the MSA detector the hydrogen needed was obtained by continuously overcharging a small, 35-ampere hour, 6 volt, lead-acid storage battery. The top of this battery was carefully sealed and the gases allowed to escape only through glass tubes sealed in the filling openings. These three tubes were brought together and joined to a tee in the air supply tube so that all the gases generated in the battery were forced into that gas stream. The amount of hydrogen was controlled by adjustment of the electric current through the battery.

(4-b) Cylinder Hydrogen

56. When it became necessary to increase the gas flow rate in order to add the Davis detector to the system it appeared to be no longer feasible to obtain the hydrogen by overcharge of a storage battery. The required hydrogen was then obtained by using a pressure reducer and a needle valve on a cylinder of compressed hydrogen. A solenoid valve was installed between the pressure reducer and the needle valve and so wired into the system that any forseeable dangerous condition would shut off the flow of hydrogen. The power for this solenoid was taken from the pump side of the pressure maintained switch and was carried through the normally open contacts of a relay whose coil was energized from the remote

normal operation pilot terminals of one side of the MSA detector. Thus a turn-off of the pump due to pressure drop, failure of the current supply to the pump or to the detector, or an alarm indication would cause the hydrogen flow to be cut off. Due to the non-reversible character of the pressure maintained switch and the alarm system the hydrogen would not be again admitted to the system after any of the above occurrences until the system was manually reset.

(5) Humidification

57. The submarine storage battery ventilation gas stream has a possible wide range of humidity as indicated in Table 1. No attempt was made to study the operation of the instruments at conditions other than those near complete dryness and near saturation at room temperature. All tests involving extended periods of operation were carried out with a saturated gas stream since it is known that corrosion is normally accelerated by that condition. This saturation was attained by passing the gas stream through a packed water column. In the tests in which the overcharge of the storage battery was used as a source of hydrogen, only the air stream was passed through the saturator since impurities in the battery might be lost by solution or decomposition in the saturator. In the tests using cylinder hydrogen, the hydrogen-air mixture was passed through the saturator since no such impurities would be present. For the test at low humidity, the gas stream was passed through a column packed with broken sticks of potassium hydroxide.

(6) Low Oxygen and High Carbon Dioxide Concentration Mixtures

58. In order to obtain a gas stream with the lowest oxygen concentration expected to be encountered in the submarine battery ventilation, a suitable amount of nitrogen was added to the input air to give the desired dilution of the oxygen. This nitrogen was drawn from a cylinder of that compressed gas by use of a pressure reducer and needle valve. The carbon dioxide was obtained in a similar manner. The flows of both gases were held constant by manual control from the flow indications on capillary, pressure-drop, flow meters.

(7) Stibine

59. The stibine used in these tests was generated in the electrolytic cell described in reference (i). For the experiments in which the stibine was passed into the hydrogen detector the external fittings of the instrument's gas supply system were removed, in so far as possible, and glass tubing substituted. It was necessary to equalize the pressure on the two sides of the electrolytic cell and still avoid decomposition of the stibine which would result from the ozone which is present in the oxygen evolved by the anode. This was achieved by passing the anodic oxygen through a glass tube containing MSA stibine scrubber catalyst before the anodic and cathodic gases were combined and passed into the hydrogen-air gas stream. This catalyst served to decompose the ozone. On the Davis detector the gas sample stream was carried in glass tubing to the filament chamber input port proper. On each instrument, for further test, one active filament was brought outside the case by using extension wires and installed in a suitable glass tube for visual observation during poisoning by stibine. In the case of the MSA filament a small opening was cut in the shield and a thin glass window was cemented on. This arrangement also permitted visual observation of the temperature of the filament during normal operation.

(8) Analysis System

(8-a) Hydrogen

60. All analyses of the concentration of this material in this study were based on analysis by slow combustion in a mercury sealed Orsat gas analysis apparatus. To provide continuous indication of the gas concentration input two thermal conductivity gas analysis cells were operated on small side streams of the input gas taken from the main stream just before it passed into the detector. These streams were dried over solid potassium hydroxide and compared to a stream of room air which was also dried. The indication of these cells was recorded on the other two points of the recorder previously mentioned. This apparatus was calibrated in place a number of times during the test by use of the Orsat apparatus.

(8-b) Carbon Dioxide

61. In the tests involving added carbon dioxide, (CO_2), the concentration of this gas was determined continuously by use of a thermal conductivity gas analysis cell which had been calibrated by the use of gas samples in which the CO_2 content was determined by absorption of that constituent in a potassium hydroxide solution in the Orsat apparatus.

(8-c) Oxygen

62. The oxygen analyses in tests which included variation of the concentration of that constituent were made by use of an apparatus of known accuracy which had previously been calibrated in this Laboratory.

(8-d) Stibine

63. The two methods of analysis given in reference (i) were employed. Where the gas was to be sampled over a period of time a small portion of the gas stream was passed through the silver nitrate scrubber and then through a small wet test meter. Where concentrations were small it was necessary to pass the largest sample possible to obtain sufficient material for analysis in a reasonable time. The field method was utilized where short period analyses of reasonable concentrations were desired.

(9) Ambient Conditions

64. In order to study the effect of the change of ambient conditions on the operation of the detectors it was necessary to remove the instruments from the laboratory surroundings where these conditions are not readily alterable. A compartment with inside dimensions about 2 by 2 by 1 1/2 feet was available which contained means of maintaining any desired temperature within a range extending both above and below normal room temperature. This compartment was also essentially gas tight and the pressure within the compartment could be readily reduced below atmospheric pressure. The detectors were installed in this compartment one at a time. Since the door of the compartment contained a full-sized window no leads were brought out to the recorder and all observations of the indication under the various conditions were made visually on the panel meters.

Electric power was supplied by way of electric leads built into the box. The gas flow stream for analysis was made up as previously described and supplied under pressure to a needle valve and capillary, pressure-drop, flow meter to permit control of the flow rate. From the needle valve the gas stream passed through a tube sealed through the side of the box, through a saturator inside the box, and finally into the detector. The exhaust from the detector emptied into the compartment. For tests at atmospheric pressure the gas merely passed out another of the through-tubes extended to suitably dispose of the hydrogen containing gas. For tests under reduced pressure the gas was drawn out of the compartment by use of a vacuum pump and a cartesian manostat to maintain the desired pressure.

(10) Stibine Scrubber Cartridge Test

65. This test work was mostly carried on in an independent set of apparatus to avoid unncessary tie-up of the detector. The apparatus comprised essentially a rotary vane pump supplying a constant rate stream of air by means of a suitable pressure relief valve, needle valve and capillary flow meter. This air stream was humidified and stibine containing hydrogen obtained from the generator of reference (i) was added. A small sample of this stream was continuously bled off for analysis by bubbling through silver nitrate solution and the remainder of the stream was passed through the cartridge. All of the output gas from the cartridge was passed through a second silver nitrate bubbler. The ratio of rates of the two streams was maintained by valves and measured by small wet test meters on the output of the bubblers. The system was made up, in so far as possible, of glass since it is reported to be less catalytic toward the deomposition of stibine than other suitable materials. The gas stream put through the cartridge contained about three percent of hydrogen and approximated in volume that required for the operation of one analyzer circuit of the MSA detector.

66. It appeared that the time required for break down of material "B" might be excessive if an amount of that material sufficient to fill the regular cartridge were used. Therefore, the test of this material and a further test on each of the other materials was carried out in which only a thin layer of material in a small tube was used. The flow rates and gas concentrations used were very high.

C. Portable Combustible Gas Indicator Tests

(1) Calibration Check

67. In order to check the calibration of the portable combustibles indicators it appeared best to accumulate a quantity of the desired concentration hydrogen-air mixture in a gas holder. This sample could then be analyzed any number of times necessary to give satisfactory checks and the gas could be withdrawn at a rate which would be fixed by the instrument being checked. The gas needed for these tests was prepared by withdrawing part of the hydrogen-air stream prepared for the MSA and Davis installed detectors into a water sealed gas holder of two cubic feet capacity. This gas having been mixed in the process of preparation should, therefore, be ready for immediate use. It was shown by analysis that this was the case. The hydrogen concentration of the trapped gas was determined by slow combustion in the Orsat gas analysis apparatus, sufficient analyses being performed to ensure a knowledge of the concentration. This gas was then drawn from the gas holder through a short length of rubber tubing directly into the portable detector being checked. The exhaust gas from the detector passed to the surrounding atmosphere. After each of the detectors had been operated on this sample of gas, the remaining gas was again analyzed by the Orsat apparatus as a further check on the original analysis. It was found in this respect that the hydrogen concentration of a trapped sample in the gas holder remained constant within the limits of accuracy of the analysis method over a period of a number of days.

(2) Battery Life Test

68. The battery life test apparatus comprised essentially a small, 1 r.p.m. motor driving a rheostat and switch. A bakelite disc was fastened onto the motor shaft and around part of the rim of this disc a copper strip was fastened. At the leading end of the strip an insulated manganin wire with the adjacent end fastened to the copper strip was looped back and forth across the rim between pegs on the sides of the disc. This wire was fastened in place by varnish and the insulation was removed from the face of the winding. Two brushes were arranged to bear on the rim of the disc so that as the disc revolved these brushes were joined first by the entire length of manganin wire and, as the disc turned, by less and less of the wire until finally the brushes were shorted by

the copper strip. For a second test an auxiliary switch was operated by a cam geared to the motor shaft. In this case the switch was off for four motor revolutions in each five. The lead from one side of the battery to the detector was broken and the auxiliary switch and the two brushes were inserted in series. While both of these switches were closed the filament current and the balance of the detector were brought to their prescribed values. The net effect, therefore, of the apparatus was to turn on the electrical system of the detector gradually over a period of a few seconds, as is the case in manual operation, and to hold it full on for a few seconds before turning it off for the remainder of the cycle period. Several times each day the filament current and balance were checked and brought back to the normal values by means of the manual controls. When the filament current or balance had changed beyond the limits of the controls the test was ended.

69. The minimum operating voltages and currents were determined by measurement with a Sensitive Research meter, (Model S). An external rheostat was inserted in one lead between the battery and the detector and the meter was inserted between the external rheostat and the detector. For each measurement the internal rheostat was set to give a minimum resistance to simulate operation with a discharged battery and the resistance needed to attain the operating condition was obtained in the external rheostat.

(3) Stibine

70. For the stibine test on the MSA and Davis portable detectors the aspirating bulbs were removed. Stibine containing hydrogen from an electrolytic generator was added to a stream of air supplied under pressure by a small pump. This stream was then split and part of it passed through each of the instruments. These streams of gas were not as great as those normally drawn by the instruments but sufficed for this test since only the change of indication was of interest. In order to ensure the presence of the stibine in the filament chamber the flame arrestor and other equipment on the input side of the detectors was removed and replaced by glass tubing.

71. To determine the amount of any effect obtained with the use of this mixture which was due to the presence of the stibine, a stibine scrubber was alternately inserted into and removed from the gas stream ahead of the instrument when an effect was obtained.

DATA OBTAINED AND DISCUSSION OF DATA

72. The major part of the data obtained in these tests is contained in the Plates and Tables contained in this report. Reference to these and discussion of this data is contained in the following section.

A. Mark I Hydrogen Detector Tests

73. Plate 1 shows the effect on the indication of the instrument of the various steps in the rehabilitation of unit 46. The curve 1 was for the instrument essentially as received. The change from curve 1 to curve 2 was the result of the introduction of a new charge of catalyst. If the instrument had been received with no catalyst in the catalyst cell the "as-received" values would have been curve 2. However, the instrument when received actually contained about one-seventh of a normal charge of catalyst which may, therefore, be assumed to be the catalyst employed in the detector at the time of removal from service. The shift from curve 2 to curve 3 was the result of a complete clean-up of the instrument, tightening of connections, and realignment of the thermocouples. This would have been expected to result in an increased indication instead of the decrease found. The explanation probably lies in the positioning of the thermocouples. The change from curve 3 to curve 4 was the result of removal of the direct, immediate cause of the unsatisfactory operation; namely, the replacement of the iron screen on the catalyst cell by the platinum screen which is normal for this part. This iron screen in its own right might have made no more than a small effect on the indications if it had been applied by the welding or spinning process originally employed to attach the platinum screen or by any other equal process. The attempted repair had been, however, to soft solder the screen to the cell tube. In this process part of the mesh of the screen had been filled with solder so that the gas stream was deflected away from part of the

thermocouples and a necessarily low reading was obtained. It appears possible that if this repair of the catalyst cell had been made before the general overhaul instead of afterward the final indications obtained might have more closely approached the theoretical values. The shift from the values of curve 4 to curve 5 are of interest because the only cause for this increase was an increased gas flow rate. The flow rate used in obtaining curve 4 was supposed to be of such size that further increase would not give increased indications. This is obviously not true in this case.

74. Plate 2 shows the indications obtained using the catalyst cell from unit 249 in unit 46. The three curves of this plate being so closely grouped indicates that the instrument was probably not fundamentally changed in the overhaul process. It is of interest to note here that the increased indications found with the increased flow rate when using the catalyst cell from unit 46 were not obtained when using this catalyst cell.

75. Plate 3 shows the indication of unit 249 when using its own catalyst cell, curve 1, and the catalyst cell from unit 46 before replacing the iron screen, curve 2. Note that curve 1 is a calibration check for instrument 249. The agreement between the indications with the catalyst cell from unit 46 when used in units 46 and 249 respectively as shown in curve 2, Plate 1 and curve 2, Plate 3 is of interest.

76. Plate 4 is included to show the effect of use of a third catalyst cell. This cell is from unit 1 (NRL) and demonstrates that only results obtained with the catalyst cell intended for a particular instrument are necessarily valid. Note the change in indications obtained here between curves 1 and 2 as a result of the thermocouple readjustment and between 2 and 3 as a result of the overhaul. These should be compared to the small changes resulting from the sum of these two operations in the use of catalyst cell 46 and 249 in Plates 1 and 2.

77. The compilation contained in Table 2 of the various malarrangements of unit 46 contains what is undoubtedly the major point of interest in this work. Most of the items listed are without significance directly toward the unsatisfactory operation of this instrument. The list as a whole does show, however, that the care and repair of the instrument had been

unsatisfactory from the angle of achieving continued satisfactory operation. The individual items within this list are thought to be self-explanatory.

78. The only remedial measure which can be recommended on the basis of this work is to set up some system whereby the repair and recalibration of these instruments would be placed under the supervision of persons trained in the theory and operation of this instrument. Unless some person on each boat were trained this would entail removal of any unit from service which had been repaired by operating personnel or which was reported as appearing to operate unsatisfactorily. The unit would be replaced by a unit which was known to have been restored to serviceable condition. This should include also that all units be periodically withdrawn from service a few units at a time for a general clean-up, tightening and calibration check to avoid the accumulation of minor malarrangements such as was found in unit 46.

79. It is realized in this connection that some cases of failure during service use will occur at times when it is impossible to replace the faulty instrument immediately and which will then necessitate that the operating personnel undertake repairs. Under these conditions it would be of value, since there are two of these instruments aboard each submarine, to arrange a connection of the two instruments to the same source of gas supply so that the calibration of the repaired instrument could be checked by parallel operation with the other instrument. This might preferably be carried out by a cross connection tube between the two instruments or in the absence of that by removing the repaired instrument to the location of the other instrument. A third method might be the use of a small cylinder of compressed gas mixture of hydrogen and air of known composition such as is used with the MSA detector.

80. The cause of the remaining difference between the indication of unit 46 and the theoretical values remains open to question. The black coating on the thermocouples and their mounting may account, at least in part, for this change of calibration and also for the increased flow required to obtain a state of flow independence. Examination and testing of other used instruments would be required to arrive at any conclusion on this subject.

81. The method of calibrating and testing these instruments has passed through several modifications. Preliminary experiments on certain points relative to these methods indicate that several changes should be made in the present method. For example, first, reference (k) provides for a one hour period of operation of the instrument to allow the instrument to become thoroughly heated before starting the test procedure. This should be increased to three hours of preheating since temperature measurements have shown that the temperature is changing rapidly at one hour and that three hours is required before equilibrium values are approached. Second, the flow meter indication obtained with an air stream containing hydrogen is not the same as that for air alone at the same rate of flow so that the concentrations obtained by using the built-in flow meter cannot be calculated from the flow rate for the flow meter on air alone and the known amounts of hydrogen added.

B. MSA Installed Hydrogen Detector Tests

(1) Normal Operation

(1-a) Filament Deterioration

82. From the information contained in Table 3 it is apparent that the filaments deteriorate only very slowly when operated under the conditions existing in this part of the test. Note, for example, filament pairs 5 and 6 which were used for 1371 hours on an average of 2.3% hydrogen input and which were still operating satisfactorily when removed to use the equipment for other tests. Also filament pair 10 was used for 2132 hours at an average of 2.3% hydrogen input. The gas stream employed during part of this time contained stibine and the filament was protected by a regular MSA stibine scrubber cartridge. This filament was actually poisoned by the stibine a number of times but at the end of the test, when it had been running on hydrogen-air mixture for some time after the end of the stibine test, it could be brought to zero and would read 1-1/2 and 3% hydrogen correctly.

83. A point which must be kept in mind on the results of this test is the fact that the instrument was set up in the laboratory with a recorder to give a complete

history of its operation and no other result than information on the operational characteristics of the instruments was required. Therefore, it was possible to carry the test on through minor mal-arrangements which in service use would have been sufficient to cause replacement of the filaments and scrubbers since this is the most obvious repair operation.

84. It appears that the filament life resulting from normal filament deterioration only can be expected to be considerably greater than 1000 hours and probably will actually be of the order of several thousand hours.

(1-b) Zero Change

85. It is apparent from the data contained in Plate 5 that the zero change for this instrument is not a regular function of the time of use. As a matter of fact, several factors appear to enter into the values shown as zero change. First, there is a zero drift due to deterioration of the filament. This deterioration results from evaporation and transportation of the platinum of the filament. This phenomena causes an increased resistance of the filament which would show as an essentially continuous and constant rate drift of the zero point to positive values. This factor is undoubtedly the cause of the general upward trend of the zero point as shown in the plate. Second, a source of change lies in the balance rheostat. Since this rheostat is put into the circuit to change the balance of the bridge it follows that any spontaneous change in the rheostat which in effect alters the various resistances of this part of the circuit results in a change of the zero point. The fact that this balance rheostat introduces discontinuities into the operation is recognized in the instruction manual furnished with the instrument. This states that trouble due to this cause may arise due to corrosion in the rheostat and may be removed by wearing-in the rheostat by several movements of the rheostat arm between its extreme positions. This can only be done when fresh air or some other standard for resetting the instrument is available. Hence this method can only be considered to be a partial solution. In fact, the wearing-in remedy appears usually to bring the instrument to a satisfactory condition for

a period of time which may extend for from a few hours to several weeks. The discontinuities which result from this cause appear sometimes as sudden changes to a new stable position which, without a recorded history of the immediately previous history of operation, might escape detection. A third factor entering here is a variable resistance which exists in the system outside of the balance rheostat. It was found that the correlation existing between the panel meter and remote meter was not constant. This variability probably arises in the separable plug connector which, in any case, should not be in the circuit since meter indications are very dependent on small changes in resistance. Other points which introduce variable resistance into the system may be present but are not evident as long as these known sources are also present.

(1-c) Calibration Change

86. The three calibrations shown in Plate 6 were taken after the hours of use of the filament as shown on the several curves. It is known that the differences between the curves are not due to change of ambient temperature or input voltage since these were essentially constant during each calibration and the same for the three calibrations. The cause of the break in the calibration curve for 25 hours on pair 5 is unknown. The high percentage points were run first and followed by the points at lower percentage. It is known that during the time of this calibration the zero change was proceeding in a negative direction which is not normal for this instrument. On the other hand, the two later calibrations appear to be perfectly normal and to indicate the change in the calibration which may be expected to take place with use of the filament under normal conditions.

(2) Stibine Effect

(2-a) Effect on the Indication

87. It was found that with about 3% hydrogen and 0.1 part per million (ppm) of stibine in the input gas to the filament the indications obtained with the instrument were low and erratic. The indication centered around a value which was about two-thirds of the actual

hydrogen concentration input. The erratic behavior, which was usually but not always present, took the form of a more or less continuous oscillation between two points on the scale about 0.5 to 1% apart. This was rapid enough that the potentiometer recorder could not keep up with the change. At this time the stibine had been passed into the scrubber for about 225 hours. After the stibine was shut off for the night several hours were required for complete recovery of the indication.

88. It is of interest to note that after only about 140 hours of passage the reading dropped slightly when the stibine was being passed in. No analysis was possible at that time due to the low concentration involved but the work in paragraph 94 indicates a probable concentration of stibine of the order of 0.03 ppm.

89. When the concentration input to the filament had reached 0.14 ppm. the oscillation had increased in amplitude and recovery time had become somewhat longer.

90. At 0.5 ppm. the indication became negative and the reversal was maintained as long as the stibine was passed in. Recovery required from 3 to 18 hours.

91. It was apparent in this work, although the point was not pursued sufficiently to give any numerical data, that for a given low concentration of stibine in the input gas the poisoning effect is greater the less the hydrogen concentration which accompanies it.

92. While there was 0.5 ppm. of the stibine reaching the filaments, which had caused the indication to reverse, the one set of filaments were removed and replaced by a new pair. This new pair of filaments indicated for the first few moments a positive indication of hydrogen, about one-third of actual value, and then reversed. This indicated that the filament is poisoned almost immediately even at this low concentration and that the effect does not need to result fromaccumulation.

93. As shown in Table 3 the active filament of pair No. 7 was opened in an attempt to find the cause of the erratic indication by visual inspection. This filament was operating on a stibine-hydrogen-air mixture gas stream and giving a low and oscillating indication

up to the moment of removal. It was immediately, on removal, opened by cutting the shield with a knife. Examination with a seven power magnifying glass showed no apparent cause of the oscillating nature of the indication obtained. It is of interest that this filament assembly did show a white deposit on one of the brass support posts and on the filament leads near the point of attachment of the filament. Most of the other filaments operated on stibine showed more or less of such a deposit. A sample of the material making up the deposit was shown by chemical analysis to contain antimony. No anion could be found by analysis. However, from its physical properties the deposit appears to be one or more of the oxides of antimony which could well be the decomposition product of stibine under these conditions.

(2-b) Efficiency of Stibine Scrubber

94. The efficiency of the MSA stibine scrubber cartridge is shown in Plate 7. The gas stream passed through this scrubber was almost constant in rate with an average of 0.92 liters per minute which is approximately double the minimum amount needed to operate one side of the detector. The actual flow to be expected in service use is unknown so this value for the flow was selected arbitrarily. In one attempt to estimate the probable maximum flow rate to be expected in service a flow of between three and four times this value was measured for the maximum flow condition. The concentration of stibine in the input gas varied from 5 to 10 ppm. with an average value of 7.9 ppm. It is apparent from the shape of this curve that the first visible effect on the indication of the instrument mentioned in paragraph 89 above but for which no analysis of the gas could be carried out probably was caused by a concentration of stibine of the order of 0.03 ppm.

95. For the work shown in Plate 8 an MSA scrubber cartridge was carefully opened and emptied. The sample of Material "A" used to fill this empty cartridge was then selected to give the same grain size as the average value for the MSA material removed. The cartridge was filled with this material and carefully closed. The gas stream passed through this cartridge varied from 0.56 to 0.90 liters per minute with 0.71 as the average value. The stibine concentration varied from 5.5 to 50.2 ppm. with 21.3 as the average. The ppm. output was about the

same between the two cartridges tested when the MSA cartridge had had 4.3×10^{-2} liters of stibine passed in and the material "A" cartridge had had 46×10^{-2} liters of stibine passed in. The percent of the input stibine passing through was 3.3 and 1.0 respectively at that time. The fact that the average gas flow rate and stibine concentration were respectively 3/4 and 3 times those used in the MSA stibine scrubber cartridge test must be taken into consideration in comparison of the results of these two tests.

96. Plate 9 contains a comparative test designed to decrease the time required to obtain a comparison of the efficiency of material "B" to the other two scrubber materials. The shape of these curves are somewhat indefinite due to the small number of points it was possible to obtain under the conditions. However, the general location of the curves, in respect to each other, shows that material "B" is more effective over a period of time than material "A" and both of these are much more effective than the material in the MSA scrubber cartridge.

97. An analysis of the MSA material was carried out which showed it to be mainly carbon which apparently served simply as a carrier for the catalytic material. The other material present was mainly copper with small amounts of aluminum, iron, and calcium and a trace of sodium.

(3) Temperature Effect

98. The effect of temperature on the indication, as shown in Plate 10, is of sufficient size to result in appreciable error in the use of this instrument. Whether the difference between the results on the two sides is inherent in this instrument or results from the particular filaments used in these sides during this test has not been investigated. The zero point appears to be little effected by the change in temperature, the maximum changes observed were 0.1%. The fact that these were not consistent with the temperature changes involved, and the order of the magnitude of these changes lead to the conclusion that these zero changes might result in large part from secondary effects and hence the curves in Plate 10 are corrected to give

the same zero point for all temperatures.

(4) Pressure Effect

99. No effect on the indication of the instrument could be found resulting from 20% reduction in ambient pressure throughout the range of normal hydrogen concentrations in the input gas.

(5) Gas Composition Effect

100. The effect on the indication of the variation of the concentrations of carbon dioxide, oxygen and water vapor in the input gas is shown in Table 4. Note that the effect of addition of CO_2 to a normal atmosphere is slightly greater than in the presence of an oxygen deficient atmosphere. Also that the magnitude of this effect is sufficient to indicate that a correction for it might be advisable. At 25°C there was a negligible effect on the indications of the instrment throughout the range of normal hydrogen concentration in changing from an input gas stream dried over solid potassium hydroxide to gas saturated with water at that temperature.

101. These gas composition effects cannot be compensated for by the use of the check cylinder.

(6) Voltage Effect

102. The voltage effect shown in Plate 11 indicates the need for this instrument to be operated from a source of essentially constant voltage. Since the instrument indication is practically independent of the voltage input between 90 and 110 volts it might be possible to arrange the instrument to make that region its normal operating range. However, this may lead to complications in the ease of poisoning of the filaments and other unforseeable results. Although the data contained in this plate was determined on only one pair of filaments in one side of the instrument, the effect was evident in other cases of input voltage change. Both sides of the instrument and other filament pairs have shown about the same magnitude of effect.

(7) Miscellaneous Tests

(7-a) Leakage

103. The data shown in Table 5 indicates the leakage

only as it applied to the instrument at the particular time shown. The instrument at that time was being operated on a stream of air forced through it. The flow indicator harness had been removed up to the valves and a flow indicator system substituted which was known to be free from leakage. The check gas inlet ports to the valves had been sealed. The filaments and scrubbers had been changed several times and only the normal precautions to obtain a tight system had been observed. The number 1 condition in Table 5, therefore, probably can be considered to be an approximation to the condition which the instrument, independent of the flow indicator harness, might be in after a period of use.

104. It is not considered desirable to have to apply the gasket cement employed in steps 6 and 7 to attain tightness in actual usage. The joinings and seals should be tight in their own right.

105. Leakage of the system should be avoided for three reasons. First, when the leakage lies ahead of the filament chamber, if the gas leaking into the system has a different composition than that in the ventilation duct, an incorrect reading will be obtained due to dilution. Second, if the leakage is between the filament and the pump the flow may drop below the minimum needed for correct reading. Third, any gas which passes into the filament chamber without first passing through the purification process will be likely to cause poisoning of the filament with consequent inaccurate readings.

(7-b) Pump

106. A set of flow-head-voltage characteristic curves for this pump are contained in Plate 12. Note that these curves show no appreciable increase in head in passing from the probable maximum flow rate of 6 liters per minute to a condition of no flow. Therefore, if any condition arises which increases the resistance to flow a decrease of the flow stream occurs which is not offset by an increase in the head supplied by the pump. If the static resistance in the system increases to an amount beyond the vacuum pulled by the pump the flow will stop completely. In the case of a vane, gear, piston or other type of positive displacement pump the

characteristic curves show a sharp increase in head as the flow decreases toward zero so that any tendency toward stoppage would result in a decreased flow instead of a stopped flow and the resistance would be largely offset by an increased head supplied by the pump.

107. The chance of this flow stoppage actually occurring in service depends on several factors. First, the input gas line to the detector is supposed to be taken from the ventilation duct on the output side of the blower, therefore, the pressure developed by this blower should also be effective toward moving the gas stream through the hydrogen detector. This pressure varies with the rate of ventilation and becomes very small at low flow rates. Second, neglecting the pressure derived from the ventilation blower, the available head due to the instrument pump must be sufficient to overcome the resistance of the flow indicators, scrubbers, and flame arrestors of the detector while a minimum flow is passing. This pressure head was measured on the instrument while in a normal operating condition and it was found to be 1.6 inches of water. At a flow rate 50% greater than the minimum the head was 2.3 inches of water. These values, however, only apply to a strictly normal condition. When a few drops of water were introduced into the bottom of the flow indicator, as would occur if condensation took place in the sampling line, the pressure head of this part of the instrument changed from its normal value of 0.2 to a range of from 0.5 to 2 inches of water for the gas stream to start passing. Third, the streams from the two sides of the instrument join at a tee just preceding the pump, therefore, if the two ventilation systems being sampled are operating with considerably different heads there is the possibility that sufficient sample may pass through one side of the instrument to decrease the available head of the pump below the value needed to move a minimum sample to the second side, especially if the second side happened to be flooded with condensed water at that time.

108. In fact, the complexities of the interrelation of these variables is such as always to raise the question whether there actually is a flow to the detector in service until it is known to be present.

109. The pump mechanically required little attention during about 5000 hours of operation. Twice the motor stopped due to failure of the brushes to slide in the brush holders to keep contact with the commutator of the armature. In order to get at the brush holders the motor must be removed in its shock-mounted cradle and the cable splice broken. A suitable separable connector instead of the splice at this point would be definitely advantageous. Reference (h) reported difficulty reassembling the motor which was overcome by employing instead of the slotted head through-bolts rods threaded on each end permitting assembly of the motor outside the cradle and fastening to the cradle by means of two nuts on these bolts.

(7-c) Check Cylinders

110. Table 6 shows the pertinent data relative to two cylinders obtained with the instrument and two cylinders later purchased from the company. From this table it is evident that the gas contained in these cylinders was accurately represented by the markings on the cylinder. As indicated, one cylinder when received contained only 1/4 of a full charge. Whether it was not full when shipped or leaked in transit is not known.

111. The use of the main cylinder valve for control of the sample flow rate is unsatisfactory in that it is very difficult to obtain and keep the proper flow. The use of either an adjustable pressure reducer valve with an orifice or capillary following it or a fixed pressure reducer valve with an adjustable needle valve would permit obtaining the proper flow rate readily.

112. The loss of the gas from cylinder 19857 resulted when it was thought that the cylinder was tightly closed. This cylinder had been used once connected to the instrument's normal sampling system. It was turned off and left connected to that system when the instrument check had been finished. When a second check was tried one week later the cylinder was empty. The chance of this type of occurrence would be greatly reduced by the use of a control valve as mentioned above which would form a second seal on the cylinder outlet during idle periods.

(7-d) Circuit Independence

113. The electrical circuit of this instrument is so

arranged that the two analysis circuits are arranged in series on the power supply and the leads to the alarm and pilot light systems are carried through the separable connector in conjunction with certain parts of the analyzer circuit. Due to this interrelation between the two sides the effect of any probable change in the operation of one side on the indication of the other side was made the subject of some study.

114. The passage of either side of the detector into a state of alarm due to zero offset was found to give a negligible change in the zero balance of the other side. The burn out or removal of the pilot lights from the alarm system gave only negligible changes in the balance of either side of the detector. The removal or burn out of either filament of one side of the detector was found to change the balance of the other side by 0.1 to 0.2% hydrogen indication. The left panel meter showed a shift of balance in the positive direction due to this change in the other half of the system. The right panel meter gave a negative deflection under comparable circumstances.

C. Davis Installed Hydrogen Detector Tests

(1). Normal Operation

(1-a) Filament Deterioration

115. It would appear from the data contained in Table 7 on filament pairs 1, 2, and 3 that the useful life of the filaments for this instrument due to deterioration alone would be appreciably less than that of the MSA instrument. Although pair 2 gave slightly over 1500 hours of use pairs 1 and 3 had to be discarded before 1000 hours. Since both pairs 1 and 3 were used in the remote analysis head whereas pair 2 was used in the integral head, it appeared that the difference in life might result from some difference between the two heads or their associated circuits. Only negligible differences between the remote and integral heads could be found both as to filament current and zero balance range. Since these are the only two apparent possible causes which can be readily measured the probable filament life must be taken, at present, as within the range of the values for these three filaments, that is, 800 to 1500 hours.

116. It was thought that information of interest in regard to both filament deterioration and stibine poisoning might be obtained by measurement of the operating temperature of the active filament of both the installed detectors. This measurement was attempted first by use of two optical pyrometers which were available. It was found that due to the small area of the filaments and the low temperatures involved the values obtained were very questionable. No readings were possible on the MSA filament and on the Davis they were only possible within a limited medium range of hydrogen concentrations.

117. An attempt was also made to determine indirectly the approximate temperature by measurement of the filament resistance under various conditions and applying this to the temperature coefficient of resistance of platinum. This gave temperature values about 2/3 to 3/4 as large as those obtained by the optical pyrometer.

118. It was found from this work that the Davis detector filaments operate at a considerably higher temperature than do the MSA filaments. This should make the Davis filament less susceptible to poisoning. Since the filament for the Davis is 0.005 inch diameter platinum wire compared to the 0.002 wire used in the MSA filament, the relative filament temperatures alone do not directly determine the relative filament deterioration rates.

(1-b) Zero Change

119. The zero changes which occurred during normal operation with three filament pairs are shown in Plates 13 and 14. Plate 13 shows the changes while filament pair 2 was being used in the integral head. Note that the scale used is half that used on the similar MSA plate. The slopes of the solid lines up to about 1000 hours of operation are fairly equal and all positive. The cause of the large negative value just beyond that time is not known. It is of interest that the remote head filament, Plate 14, showed a similar but smaller zero change and that the MSA instrument showed no peculiarities in the zero change at that same time. During the period of operation when this zero change took place the indication of the integral head was erratic for a time and then dropped, while operating on between 2 and 3% hydrogen, to a stable value about 0.6 percent hydrogen below the correct value which was the amount

of the zero change later found. The remote head did not show the erratic character but did give a single, appreciable, permanent drop at about the same time. After this one anomalous period the integral head appeared to operate normally for several hundred hours. It is evident from the early operation of the replacement filaments that the integral head later passed into an unstable state. The changes shown in Plate 14, however, indicate that this part of the instrument was quite unstable from the time of the one large drop to the end of the record.

120. The zero changes shown in these plates are, as in the case of the MSA instrument, the result of several factors. There should be a continuous drift of the zero in the positive direction due to the evaporation and transportation of platinum in the filament. It is thought that changes for the first 1000 hours of operation, as shown in Plate 13, are mainly the result of this drift. Superimposed on this drift are effects due to erratic and unpredictable changes of resistance in the circuit. The zero balance rheostat contains one of these variable resistances which probably results from corrosion and may be partially eliminated by wearing-in the rheostat. However, this cure is not of a permanent nature and the same spontaneous change soon again occurs. Any other spontaneous change which gives a variation of any of the various resistances which exist in the circuit may give rise to an effect either in the zero balance or the calibration. One of these was found in the shunting resistors in the remote filament jack. Other causes of variation may exist which have not been isolated up to the present time due to the presence of the factors mentioned above.

(1-c) Calibration Shift

121. Two calibration checks on each of two pairs of filaments are contained in Plate 15. The two checks on pair 3 in the remote head were separated in time by over 90% of the useful life of that set of filaments. The checks on pair 2 in the integral head for 350 and 950 hours were separated by about 35% of the useful life of that filament pair. The third curve on pair 2,

that for 1375 hours, was obtained indirectly and hence is probably not of the same accuracy as the other curves. It does show, however, an approximate check about 200 hours before the end of the useful life of the filament pair and extends the range covered to about 65% of that life.

122. It is evident from this plate that an appreciable shift of the calibration does take place during normal use due to deterioration of the filaments. It appears that the manufacturer may have intentionally set the indication above the actual hydrogen concentration to allow for this change. In this way the indication obtained would never, normally, be less than the actual hydrogen concentration but with new filaments might be appreciably more than the actual concentration. This is probably preferable to low indications but still may give two undesirable results. First, if operating personnel by checking the instrument with new filaments find that the indications are above the actual concentrations they may erroneously consider that the calibration will always be high and make an allowance on the reading which does not actually apply when the filaments become aged. Second, with new filaments the instrument will indicate a dangerous condition before that condition is actually reached.

(2) Stibine Effect

123. No part of this equipment was apparently specifically intended to remove stibine from the input gas stream. It must be concluded, therefore, that either the instrument was intended to be free from stibine effect due to the conditions of operation employed, that is filament temperatures and so forth, or that outside protection from stibine would have to be employed, which was not mentioned in the instructions, or that the stibine effect was given no consideration.

124. As had been found previously there is a tendency for the stibine to decompose before reaching the filament chamber. This effect apparently continues for an appreciable time before stibine begins to come through. In order to hasten the passage as much as possible the connecting tubing between the stibine generator and the integral analysis head was replaced by glass tubing.

125. It was found, in general, that this instrument was less effected by stibine than is the MSA installed detector without its scrubber cartridges. At low hydrogen concentrations immediate, complete poisoning of the filament with reversal of the indication took place. In the presence of a high hydrogen concentration a gradually decreasing positive indication was obtained which finally reversed. The rate of recovery of a filament, as in the MSA, was slow. Recovery, however, seldom appeared to bring these filaments completely back to the original indication. The same white deposit was found on the supports of these filaments when they had been exposed to stibine as was found in the MSA instrument.

126. It is apparent that if continued satisfactory operation of the instrument is expected all stibine must be removed from the gas stream input. Otherwise a gradually decreasing indication will apparently be obtained with a final reversal of the indication if the stibine concentration is relatively high and the hydrogen concentration is low.

(3) Temperature Effect

127. The effect of ambient temperature variation is shown in Plate 16. It is evident from this plate that the effect of this variable is of such size as to require that some means of compensation or correction for the effect should be employed if accurate readings are desired over the range of temperatures which may be encountered in service use.

(4) Pressure Effect

128. The effect of a 20% reduction of the ambient pressure on the indication at several hydrogen concentrations covering the normally useful range was found to be negligible.

(5) Gas Composition Effect

129. The effect on the indication resulting from changes in the concentration of the secondary constituents of the gas mixture sampled is shown in Table 8. It is thought that all these values are negligible especially in comparison to the effect of other variables.

(6) Voltage Effect

130. Each of the two analysis circuits of this instrument contains a transformer for reducing the input voltage from the 115 volts input to the low voltage which, when rectified, is used to supply the filament current. The transformer in the remote head circuit bears no name plate. The transformer in the integral head circuit carries a name plate which states that it is a constant output voltage transformer. This is reported by the manufacturer to give a constant output voltage with changes of 1% or less from the rated output voltage on any voltage input between 90 and 125 volts. This transformer is, however, sensitive to frequency change in that a change of 1% in the frequency input changes the ouput voltage by 1.7 to 1.8%. The normally useful temperature range for this transformer is from 10 to 40°C. Temperatures below and above these limits require special design. The output rating is 0.7 amperes whereas the current through the filaments alone is 0.85 amperes and the resistors forming the other half of the bridge must use some current in addition to this. Apparently the transformer for the remote head is essentially the same as the one for the integral head.

131. The above points indicate, especially when considered in conjunction with reference (1), that the use of the particular transformer employed in the integral head circuit, and apparently that in the remote head circuit also, should be given further study before being put to service use.

(7) Miscellaneous Tests

(7-a) Leakage

132. The remote analysis head, which had never been disassembled, was found to leak less than 5 cc. per minute at 5 inches of water pressure. The integral analysis head was disassembled for the stibine test and after reassembly into what was thought to be essentially its original condition was found to leak about 1300 cc. per minute under the same pressure.

133. The valve assembly was removed and tested separately. This was found to leak about 100 cc. per

minute under 5 inches of vacuum. By immersing in water and applying some pressure a small amount of the gas was seen to be leaking out around the packing on the valve stem. The remainder was leaking past the valve seat and out at the air inlet. By operating the valve a few times and forcing the valve facing against its seat the leakage was reduced to about 30 cc. per minute.

134. No particular attempt was made to study the measures necessary to obtain a seal of the system. This system is made up mainly of standard fittings and hence it should be possible to make it tight with some work. The arrangement of this assemblage within the case, however, makes it difficult to work on the joints. Either the case should be slightly altered so that the joints can be reached or the entire system should be made removable as a unit to permit work on it outside of the case. It is thought that all these joints probably should be soldered since they exist between the filament chamber and the external flame arrestors.

135. No leakage around the seal of the filaments to the filament chamber could be found.

(7-b) Pump

136. The characteristic curve of the pump is practically a linear relation between pressure and air flow with a free flow of about 0.65 cubic feet per minute and a maximum vacuum of about 27 inches of mercury (30 feet of water). Since the flow rate drawn by this pump is greatly in excess of the maximum amount which can be passed through the instrument with a negligible effect on the indication due to flow, a vacuum relief valve was teed into the gas stream piping between the pump and the instrument. The relief point on this valve was so set that the vacuum obtained was sufficient to move the gas stream through the instrument at the maximum permissible rate. The additional flow required by the pump to operate at that characteristic point was then admitted through the relief valve. This system has, therefore, the same fundamental disadvantage as the pump employed on the MSA detector. In the case of the MSA instrument the pump itself has a flat characteristic and in this

instrument the relief valve has a flat characteristic.

137. This pump was operated for 1680 hours without trouble of any kind. From then on it tended to either not draw enough oil or to draw too much oil into the pump. When it did not draw oil it, of course, gummed up and either the vanes stuck causing loss of characteristic or the rotor stuck causing the motor to stop. When it drew too much oil the excess was either pumped through the entire output system or was thrown out at the shaft seal. After 4200 hours of use the motor was in good condition but the entire pump was replaced.

(7-c) Electrical Leakage.

138. After about 435 hours of use the instrument was indicating and recording correctly the medium concentration of hydrogen being passed. However, it was suddenly found that none of the signal lights were on and that the input voltage was passing to the case. The integral head showed a state of alarm on the primary relay despite the fact that neither the hydrogen concentration nor the indication were near the alarm point. Further, this state of alarm would immediately return after release. On trading the signal bulbs among the various sockets the signal light system suddenly began to operate satisfactorily. The ground on the case still existed, however. The system was then left in operation overnight and in the morning the ground was gone too. No cause of the various effects and for their essentially spontaneous removal could be found.

D. Portable Combustible Gas Indicator Tests

(1) Calibration

(1-a) MSA Explosimeter, Model 2

139. Two of these instruments, serial C-333 and C-467, were available and the indications obtained with each on gas samples of the hydrogen concentrations shown are contained in Plate 17. The left half of the plate shows the instrument indication directly whereas the right half shows these same indications converted to percent of hydrogen by use of the calibration chart furnished by the manufacturer for use with these instruments.

140. It is evident that only one of these instruments had an actual calibration which approached the theoretical values given for it by the manufacturer. The difference between the other calibration and the theoretical calibration is considerably larger than should be present in this instrument.

141. Note that the indications were plus and minus up to 3 or 4 units from the best average values throughout the range of concentrations employed.

(1-b) Davis Combustible Gas Indicator, Model M-1

142. The calibration check of this instrument is contained in Plate 18. The figure in the left half of this plate again is the instrument indication and that in the right half is the indication converted to percent of hydrogen by use of the manufacturer's chart.

143. The actual calibration of this instrument again differs somewhat from the theoretical values. It is notable here that the dispersion of points is considerably less than in the similar MSA instrument.

(2) Battery Life

144. The MSA instrument C-467 was put onto a battery life test in which the filament current was turned on and off by the previously described machine. The current was gradually raised to its operating value over a period of 4.2 seconds. It was then retained on full for 14.4 seconds and then turned off for a period of 41.4 seconds. Using six new number 2 cells the instrument was on this test for 13.2 hours and current was passing for a total of 4.1 hours before the batteries were discharged to the point where balance could no longer be attained.

145. It was thought that this rapid cycle might not closely enough approach the actual operating conditions. Therefore the build-up and on parts of the cycle were retained the same and the off part increased by four minutes. With this longer idle cycle the instrument was on test for about 570 hours and the current was actually passed for about 38.5 hours.

146. It must be appreciated, in consideration of this, that neither of these cycles can be considered to approximate service use since the use cycle of the instrument will undoubtedly be widely variable in service. Further, the batteries deteriorate even on standing idle.

147. The filament current and minimum voltage required to operate both the MSA and Davis portables were determined. It was found that among the units of the MSA instrument available neither the voltage nor the current are the same from unit to unit nor do these values appear to remain constant over a period of time for a single unit. Neither the cause nor the effect of this variation has been studied.

(3) Stibine Effect

(3-a) MSA Portable

148. This instrument was put onto a continuous stream of hydrogen-air mixture containing stibine. This gas stream was passed for 4.5 hours and no unusual effect which could be ascribed to the stibine was noted in the operation of the instrument. It was found by analysis that part of the stibine was actually passing out of the instrument in the exhaust. On opening the instrument to examine the filament it was found that water had condensed inside the filament chamber and a thick white coating was present on the filament supports. The presence of any after-effect on the calibration due to passage of the stibine was not studied.

(3-b) Davis Portable

149. Operating on part of the same gas stream used in the MSA test above the Davis portable was found to give gradually decreasing indications until after a few minutes a reversal of the indication took place. On inserting a stibine scrubber cartridge in the gas stream ahead of the instrument the indication of the instrument again became positive.

150. At a later date an attempt was made to use this instrument for hydrogen analysis in some other work being performed at this Laboratory. The filaments

were the same ones which had been used in the stibine test. It was found that very low indications were obtained which varied from one day to the next. Fairly consistent results could be obtained in the range up to 1 or 1.5% hydrogen by previously operating the instrument for a time on a stream of 4 to 5% hydrogen. On interchanging the filaments in the instrument so that the poisoned filament was used as the inactive filament and the previously unpoisoned inactive filament was used as the analysis element, consistent results still could not be obtained. A pair of filaments were made in this Laboratory which closely approximated the manufacturer's filaments and with these filaments a normal and consistent calibration curve was obtained. It therefore appears that this instrument is susceptible to stibine and for satisfactory operation it should probably be carefully protected from stibine.

151. It was found as part of this work that the flame arrester can be taken apart and if it is not put together again in exactly its original condition completely erroneous low readings will be obtained due to a low flow rate.

SUMMARY OF RESULTS

A. Mark I Hydrogen Detector

152. The cause of the unsatisfactory operation of unit 46 must ultimately be ascribed to an unsatisfactory system for the care and repair of these instruments.

153. The direct cause of the unsatisfactory operation was found to have been the replacement of the platinum screen on the catalyst cell by an iron screen.

154. A number of other malarrangements of this unit were found.

155. Indications lower than theoretical after the overhaul and an increased gas flow rate to attain flow independence were found which should be further investigated on other used Mark I detectors.

156. The methods of testing, calibrating and recalibrating should be critically examined for necessary changes.

B. MSA Installed Hydrogen Detector

157. The filament life which can be expected with proper protection of the filaments from gas stream impurities is apparently considerably in excess of 1000 hours.

158. The zero drift due to deterioration of the filament appears to be negligible, probably in the order of 0.1% per 100 hours over most of the life of the filament. Changes of zero point due to other causes are of such a greater order of magnitude as to preclude exact knowledge of the zero drift proper.

159. There appears to be some drift of calibration due to aging of the filament.

160. Poisoning of the filament by stibine occurs at such very low concentrations as to require that the operation of the gas purification system be drastically improved.

161. Two materials developed for other use are much more effective for stibine decomposition than is the present material. A silver nitrate bubbler scrubber should also be effective.

162. The effect of temperature change on the indication of this instrument is of sufficient size to require compensation or correction in some manner for this effect.

163. The effect of ambient atmosphere pressure changes of the order which might be encountered in service is negligible.

164. The effect of change of concentration among the secondary constituents of the gas mixture is, in general, appreciable but small.

165. The effect of change of input voltage on the indication of the instrument is great enough to necessitate that the voltage input be kept constant or other means of compensation be employed.

166. The leakage of the gas flow system of the instrument is excessive under normal usage.

167. The pump is mechanically good. A minor modification of the fastening bolts and the replacement of the lead

splice by a separable connector would ease its maintenance. Whether the pump is sufficient to insure a proper gas sample flow under service conditions is not ascertainable in the laboratory.

168. The check cylinders were found to contain gas mixtures accurately represented by the manufacturer's markings. The mechanical arrangement for use should be improved.

169. The balance rheostats were found to be too unstable for satisfactory use with this instrument. The separable connector appears also to introduce a variable resistance. Other similar points may be present but cannot be isolated until present known sources of variation have been removed.

170. The presence of an arrangement to indicate the attainment of a satisfactory flow rate is undoubtedly of value. The present equipment appears to be unsatisfactory because the gasket at one end of the tube tends to brush against the float which restricts its movement, the presence of water in the indicator causes false readings, and the soft solder joints in the tubing are susceptible to breakage under strain.

171. Nearly all the analysis filaments used in this work showed corrosion inside the filament assembly. It has not been possible as yet to arrive at any conclusion as to the cause and effect of this corrosion.

172. The alarm system was found to operate satisfactorily at all times during this work.

173. The burn-out or removal of either filament from one side of the detector changes the zero indication of the other side by 0.1 to 0.2% hydrogen. One side is deflected positive and the other side negative. Other than this effect the two sides appear to be independent of each other in normal operation.

174. It is thought that definite advantages would be found over a period of time by isolating the pump in a separate compartment of the case and in closing the analysis compartment in such a fashion as to exclude dust and other extraneous matter.

175. The terminals for the cable to the remote indication panel on this unit were not as reported in the instruction manual and the hook-up had to be determined experimentally.

176. In two cases the front terminal of the filament assembly, which also extends inside as one of the filament supports, broke loose from the remainder of the assembly in the process of removal of the filament jack. This ruined these filaments for any further use.

177. Other tests such as shock and vibration should be carried out on this instrument after its fundamental operational characteristics have been improved.

C. Davis Installed Hydrogen Detector

178. The filament life which can be expected with proper protection of the filaments from gas stream impurities is apparently between 800 and 1500 hours.

179. The zero drift due to deterioration of the filaments appears to be negligible during the early life of the filament, about 0.1% per 100 hours. The rate of drift increases with the age of the filament. Changes of zero point due to other causes were of such a greater order of magnitude, after the early operation of the instrument, as to prevent exact knowledge of the zero drift proper.

180. The calibration of the instrument was found to change as the filaments deteriorate.

181. This instrument is apparently less sensitive to stibine than is the MSA instrument. However, it must be protected from stibine before continued, satisfactory operation can be expected.

182. The effect of ambient temperature change on the indication of the instrument is sufficient to require some kind of compensation or correction for this variable.

183. The effect of ambient pressure changes of the order expected in service is negligible.

184. The effect of change of concentrations among the secondary constituents of the gas mixture is negligible.

185. The indication of the instrument is reported by reference (1) to be dependent on input voltage. Apparently it would also be dependent on the frequency input. The load and temperature limits of the transformer appear to be too narrow for this use.

186. The instrument showed negligible leakage as received. Certain changes in the gas flow assembly are recommended both for safety and to avoid leakage.

187. The pump gave considerable trouble and was replaced after about 4200 hours of use mainly as a result of lubrication troubles. Whether the pump system with its flat characteristic due to the vacuum relief valve is suitable to ensure a proper gas sample flow under service conditions is not ascertainable in the laboratory.

188. One case of grounding of the input voltage to the case accompanied by completely faulty operation of the alarm pilot light system was experienced. No cause for this could be found.

D. MSA Explosimeter

189. The calibration of two units of this instrument differed considerably. The indications of one unit were essentially correct. The indications of the other unit were about 20% below the theoretical values.

190. The individual values varied up to plus and minus 4% of full scale from the best value curve.

191. The battery life under one set of arbitrary conditions was found to be 4.1 hours of use. Under a second set of conditions a life of 38.5 hours of use was obtained.

192. The instrument showed no effect of stibine on its indication during passage of the stibine.

E. Davis Combustible Gas Indicator

193. The calibration of the one unit of this instrument available differed from the theoretical values by 10% (low).

194. The individual values of this calibration varied up to 2% of full scale value from the best value curve.

195. Stibine caused a gradual decrease and reversal of the indication of the instrument. A filament which has been poisoned by stibine gives non-reproducible indications whether used as the analysis or compensation filament.

CONCLUSIONS AND RECOMMENDATIONS

A. Mark I Hydrogen Detector

(1) Repair of Instrument

196. Some system for repair of these instruments should be set up which will ensure continued satisfactory operation. Such a system is outlined in paragraphs 78 and 79.

(2) Upkeep of Instrument

197. In conjunction with (A-1) above, these instruments should be withdrawn from service at reasonable intervals for cleaning, general overhaul and recalibration.

(3) Low Indication and High Flow Requirement

198. Other used Mark I hydrogen detectors should be tested to ascertain if these changes are the normal result of service use of the instrument.

(4) Calibration Method

199. The system employed in calibrating the instrument should be examined to ascertain needed changes.

(5) Improvement of Instrument

200. Considerable improvement should be possible if it is intended to again manufacture this instrument.

B. MSA Installed Hydrogen Detector

(1) Gas Flow System

(1-a) Flow Indicator Harness

201. This system should be completely removed until such time as redesign and test has developed a suitable successor if the system is found necessary at all in the light of other changes recommended.

(1-b) Calibrating Cylinder Connection System

202. The valve controlling the flow of this gas to the instrument during check should be of a needle type to give a reasonable degree of ease of setting this control. Preferably this would be combined with a gauge to show the pressure in the cylinder and a pressure reducing valve. The method of supplying this gas from the control valve to the instrument should be designed in the light of other changes in the system.

(1-c) Gas Purification

203. The gas purification system should be altered along one of the two following lines:

(1) The material used in the dry scrubber cartridge should be much more efficient than that now employed. Provision should be made to trap condensed water before it reaches the scrubber cartridge. It would also be necessary to ensure that all entering gas passes through the cartridge and is drawn from the sampling line.

(2) The entire present purification system should be discarded and a gas bubbler containing silver nitrate solution substituted. This apparently could be arranged to replace the present flow indicators, sample valve and dry scrubber. It should be followed by an iron screen arrangement similar to that in the Mark I hydrogen detector.

(1-d) Filament Chamber Seal

204. The method of securing the filament assembly into the filament chamber should be changed to permit a gas-tight seal to be readily obtained. A change to a rubber or rubber-like gasket might be sufficient or a change from the threaded ring to a plate held down by three or four machine screws might be necessary.

(1-e) Pump

205. If this pump in service use has been found to suffice for use with this instrument it should be supplied with through-bolts threaded at both ends to

permit reassembly after overhaul. If the pump is not sufficient a different pump must be found.

(2) Electrical System

(2-a) Balance Rheostats

206. The present balance rheostats should be replaced by a balance resistance arrangement free from variable contact effects. Until a sufficiently constant rheostat can be found this might require the use of a straight resistance wire with the divider connection assured by soldering the side wire to the resistance wire.

(2-b) Separable Connector

207. This part should be removed and the connection between the two parts of the cable soldered either directly or through a suitable terminal strip.

(2-c) Pump Motor Lead Splice

208. This splice should be superseded by a suitable separable connector or by other connection means which can be more readily detached than the present splice.

(2-d) Power Supply

209. This instrument should be operated from a source of constant voltage of the rated value. If no circuit of that type is available the instrument should have a suitable voltmeter and adjustable resistor for manual control in the supply circuit ahead of the instrument. In this case it may be necessary to replace the voltage dropping resistor of the instrument with a lower resistance unit to permit operation at the lowest voltage input if this is below the present rated value. A reduction of filament operating current should permit operation of the instrument in a region where the instrument indication is relatively little effected by operating voltage. Secondary effects of this reduction would require further study.

(2-e) Isolation of Systems

210. Possibly in present and certainly in any future models of this instrument the detector system should be completely isolated from the remainder of the electrical system of the instrument. If it is desired to bring the

separate parts through a single input switch that switch should be of better characteristic than the present type employed.

(3) General

(3-a) Temperature Compensation

211. Some form of temperature compensation should be applied to this instrument. This could be done by applying a correction obtained by a chart and a thermometer if it is shown that the effect is constant in amount from one set of filaments to another in a single unit. It also appears that the effect could be compensated for within the instrument by use of temperature sensitive resistors in place of certain resistors now in the circuit.

(3-b) Filament Protection

212. The spare filaments should probably be protected by some suitable means such as a hermetical seal from possible poisoning by stibine up to the time of installation in the detector. Present knowledge extends only to the extent that the filaments are poisoned by such small concentrations of this gas that unprotected spare filaments aboard submarines might be poisoned before any actual use.

(3-c) Filament Breakage

213. The design of the filament lead jack or of the filament assembly should be altered sufficiently to avoid breakage of filaments during change. A low resistance, reproducible contact must still be attained.

(3-d) Filament Assembly Corrosion

214. Materials suitable for use in these assemblies should be available which would not be susceptible to the corrosion found in the present units. Up to the present time the effect, if any, of this corrosion on the operation of the instrument is unknown.

C. Davis Installed Hydrogen Detector

(1) Gas Flow System

(1-a) Assembly

215. The instrument as to both of its analysis heads should be redesigned sufficiently to permit installation and removal of these parts with their connecting tubes and flame arrestors as units. All joints within these parts preferably should be soldered to assure tightness and prevent tampering.

(1-b) Gas Purification

216. A protective device against gas impurities should be added to each analysis system. This probably could be a gas bubbler containing silver nitrate solution followed by an iron screen spray trap installed between the valve and the instrument. It is thought that by proper arrangement of this the valve now in the system could be omitted.

(1-c) Pump System

217. The pump system rate-head characteristic should be improved so that small changes in resistance to flow will not cause large changes in flow rate. Adding flow resistance to the system would have some of this effect since the small spontaneous changes would then become a negligible part of the entire resistance.

(1-d) Pump

218. The lubrication system of this pump should be improved to avoid the under and over lubrication of the pump found in this work.

(2) Electrical System

(2-a) Balance Rheostats

219. The present balance rheostats should be replaced by a balance resistance arrangement free from variable contact effects.

(2-b) Filament Transformers

220. The filament transformers should be replaced by transformers which have a higher load capacity, wider useful temperature limits and an interrelation between input and output voltage which has been shown to be negligible. Even then, with this type of transformer, the instrument would have to be operated

on a power supply with a very constant frequency of the rated value.

(2-c) Alarm System

221. The present pilot lights should be replaced by lights of sufficient intensity to constitute an actual visual signal.

(2-d) Filament Current

222. If the instrument were protected from gas impurities as suggested in (1-b) above it should be possible to reduce the filament operating temperatures which would increase the life of the filaments and decrease the rate of zero drift.

(3) General

(3-a) Temperature Compensation

223. The instrument should be compensated for the effect of temperature variation on the indication. A chart and thermometer could be used. The replacement of certain resistances now in the circuit by temperature sensitive resistances to give compensation might be possible. These will only be effective if it is shown that the temperature effect is constant from one filament pair to another in the same instrument and must be individually applied to the detectors unless the effect can be shown to be constant from one unit to another.

(3-b) Filament Protection

224. The spare filaments probably should be protected by some suitable means from possible poisoning by stibine before installation in the instrument.

(3-c) Calibration Check Method

225. The method for checking the calibration outlined in the instruction manual should be considered to be of doubtful validity until the actual materials and operations which are expected to be employed in such calibrations have been shown by laboratory experiments to be satisfactory

D. Portable Combustible Gas Indicators

(1) MSA Explosimeter, Model 2

(1-a) Calibration

226. These instruments should be so made that they have the correct calibration. Proper control and testing during manufacture should suffice to obtain essentially correct calibrations. This could also be done by correction of the indication with a table or graph determined for each instrument providing the filaments are reproducible.

(1-b) Gas Purification

227. Although the instrument was found to be free from effect due to the passage of stibine under the conditions employed, it is probable that the instrument and its spare filaments will have to be protected from gas impurities at all times before satisfactory operation will be obtained.

(2) Davis Combustible Gas Indicator, Model M-1

(2-a) Calibration

228. The one unit of this instrument available had a calibration which was not correct. If other units are also found to have incorrect calibrations the measures recommended in (1-a) above should be applied to this instrument.

(2-b) Gas Purification

229. This instrument apparently should be protected from gas impurities. Possibly a dry scrubber of one of the materials previously discussed would serve for this purpose. The spare filaments also probably should be protected up to the time of use.

E. General

230. Most of the above alterations have not been tried in this Laboratory since, in general, only one instrument of each type was available for test. Hence, each of these instruments had to be retained in essentially its original condition until sufficient data had been obtained to ascertain its normal mode of operation. Preferably, such

work should be done with two instruments carried along together, one of which could then be changed from time to time as appeared advisable and the other retained in its original condition or altered at a later date after the effect of the alteration had been established. Further investigation on the MSA Installed Detector should be carried out to determine the adequacy, in so far as is readily possible in the laboratory, of the above suggested alterations. This would probably take the form of making the suggested alterations except those concerned with gas flow and purification. A period of operation on pure hydrogen and air would then prove the adequacy of these alterations or show the need of further change. After this the gas flow and purification system should be altered and a period of operation either on a stibine containing gas sample or preferably on actual battery ventilation gas should be used to test the adequacy of these changes. For further study of temperature effect and compensation and possible automatic compensation for input voltage change effect a second detector unit and a reasonable number of representative samples of spare filaments should be available for study. Further points requiring change probably would appear as these alterations were carried out and tested.

231. Further work along the same line could be carried out simultaneously on the Davis Installed Detector. However, it is felt that since this is an experimental model the manufacturer might preferably be offered the chance to make changes in the instrument in line with the recommendations above and submit a revised model. Otherwise, the changes could be made and tested in this Laboratory and the manufacturer supplied at a later date with specific instructions and perhaps even the working model if it were desired to obtain service units from this source.

232. Further work on the portable detectors should comprise such points as actual operation on a battery ventilation gas stream, determination of stability of calibration during the life of the filaments, life of the filaments under simulated operating conditions and tests of variables such as temperature, pressure, gas composition, and so forth. A number of spare filaments

and ballast lamps for the MSA instrument and a second unit of the Davis instrument and a number of spare filaments for this instrument should be available if these tests are to be undertaken.

233. It is realized that some points of reference (b) have not been studied. It is expected that in any further study of these instruments these various points will be taken up along with the work outlined above.

TABLE I

SUBMARINE STORAGE BATTERY VENTILATION GAS

Approximate Composition

NAME	SYMBOL	CONCENTRATION
Oxygen	O_2	17 to 21%
Hydrogen	H_2	0 to 3%
Water Vapor	H_2O	1 to 8.5%
Carbon Dioxide	CO_2	0 to 3%
Impurities	-	Less than 1%
Nitrogen	N_2	Residue

NOTE: Percentages by volume.

TABLE 2

MARK I HYDROGEN DETECTOR

Malarrangements Found in No. 46

No.	Description	Result of	Significance Toward Service Use
1.	Output of bubbler blocked with solution residue.	Normal use.	Resistance to normal flow.
2.	Lunkenheimer fitting at input to manifold broken.	Probably shipment.	If not, leakage.
3.	Copper in electrolysis cell.	Unknown cause.	None apparent.
4.	Filter plug gasket worn out.	Normal use.	Permits leakage and cat. poisoning.
5.	Insufficient flow meter fluid and adulterated with immiscible liquid.	Improper service.	Attainment of proper flow questionable.
6.	Furnace housing cover lacking three hold down screws.	Improper service.	With No. 1 - leakage.
7.	Insufficient catalyst charge present on receipt.	Improper service.	Low indications.
8.	Iron screen on catalyst cell, faultily applied.	Improper service.	Low indications.
9.	Catalyst cell holder blocks and springs removed.	Improper service.	Possible leakage around catalyst - low indications.
10.	Thermocouple binding posts loose.	Normal use.	With No. 1 - leaks - low indications.
11.	Black coating on thermocouples and mounting.	Unknown.	Questionable.
12.	Heater series resistor burned out.	Unknown.	Probably not service condition.
13.	Thermocouple leads loose at meter terminals.	Normal use.	Possible low, erratic indications.
14.	Meter needle sticks at 4% indication.	Unknown.	Meter needs overhaul.
15.	Thermocouples touching.	Probably shock.	Possible low and erratic indications.

TABLE 3

MSA INSTALLED HYDROGEN DETECTOR

Filament Chart

Pair No.	Supersedes	Type of Operation	Hours Use	Hyd. Hours Use	Reason for Removal if significant	Remarks	Corrosion
1	-	)46 hrs.-eylinder	246	580	Erratic and low	Reported in letter.	Bad
2	-	)200 hrs.-battery					
3	1	)560 hrs.-battery	1054	2400	No zero		(Medium
4	2	)494 hrs.-cylinder					(Bad
5	4	)	1371	3155		(Still good	Slight
		)Cylinder only			New test.	(when removed.	
6	3	)				(Std. broken.	Very slight
7	5	)	(87	137	Opened for visual		Medium
		)	(		inspection for		
		)Cylinder + stibine,	(		cause of erratic		
		) no scrubbers	(		indication		
8	6	)	(231	609	New test		Very slight
9	7	)Cylinder - stibine	(1170	3052	New test		Medium
10	8	)MSA scrubbers	(2132	4876	New test	Still good when removed.	Slight
11	9	Cylinder + stibine, used scrubber	564	1337	New test		Bad
12	11	Cylinder-also + stibine	398	387	New test	External filament support loose.	Very bad
13	10	)Cylinder-variables	-	-		Still good.	Not opened
		) test					
14	12	)					

TABLE 4

MSA INSTALLED HYDROGEN DETECTOR

Gas Composition Effect

CONSTITUENT CHANGE	EFFECT AT ZERO	EFFECT AT 3.5% H_2
Saturation of dry gas at 25°C.	Neg.*	Neg.
Add 5% CO_2 to gas.	Neg.	-0.3
Decrease O_2 to 15%.	Neg.	Neg.
Add 5% CO_2 and drop O_2 to 15%	Neg.	-0.2

* Neg. = Negligible.

TABLE 7

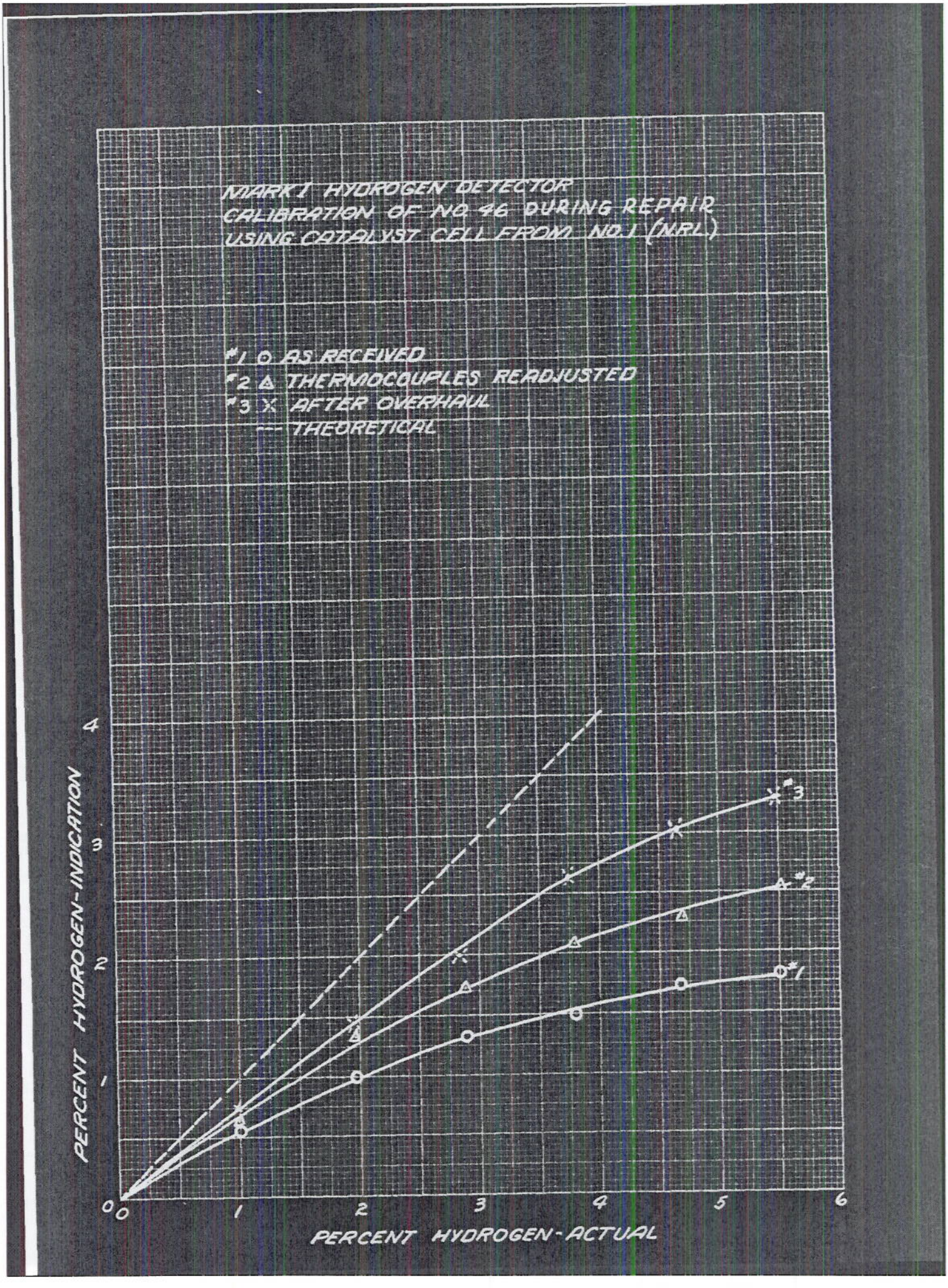
DAVIS INSTALLED HYDROGEN DETECTOR

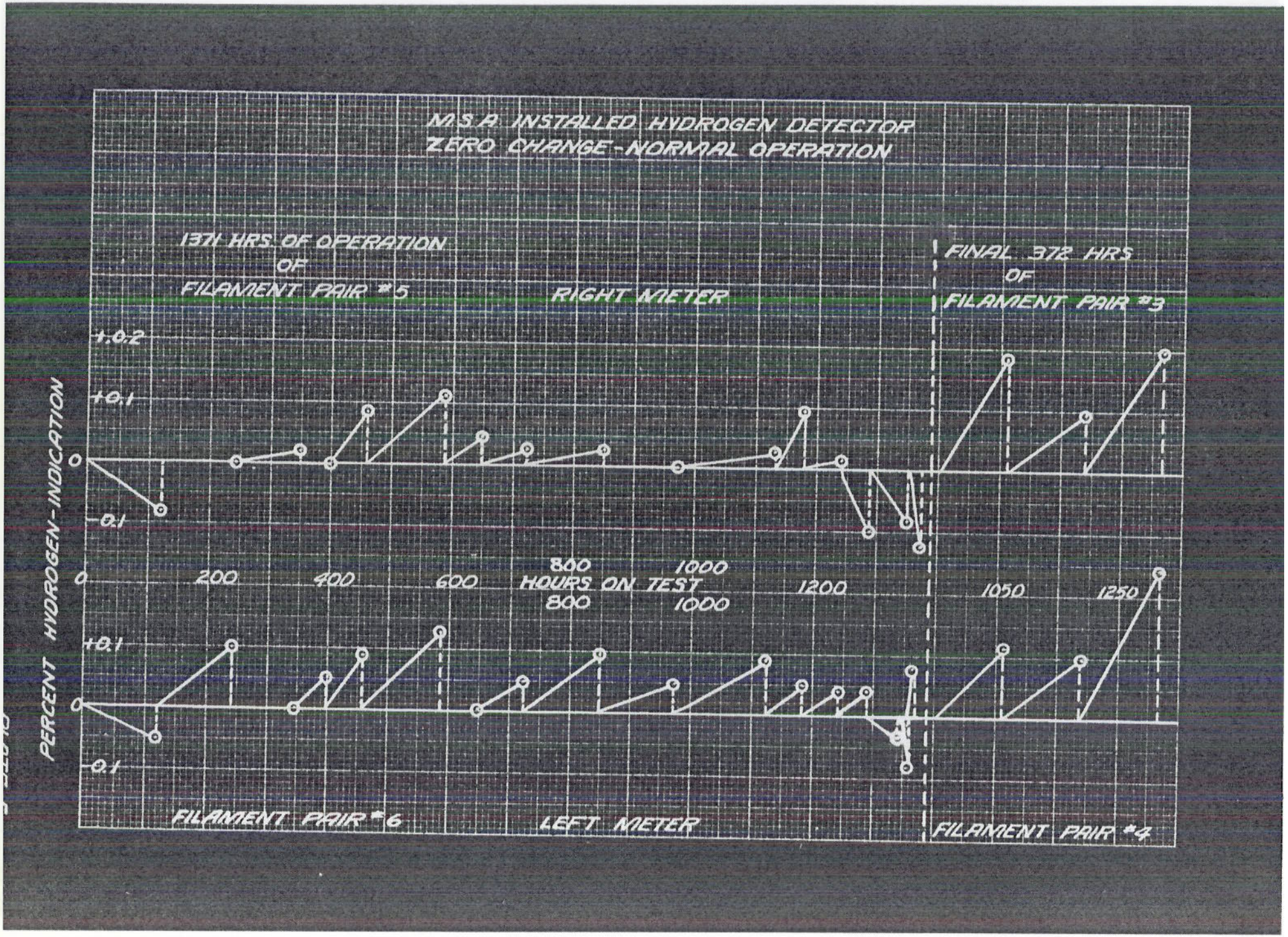
Filament Chart

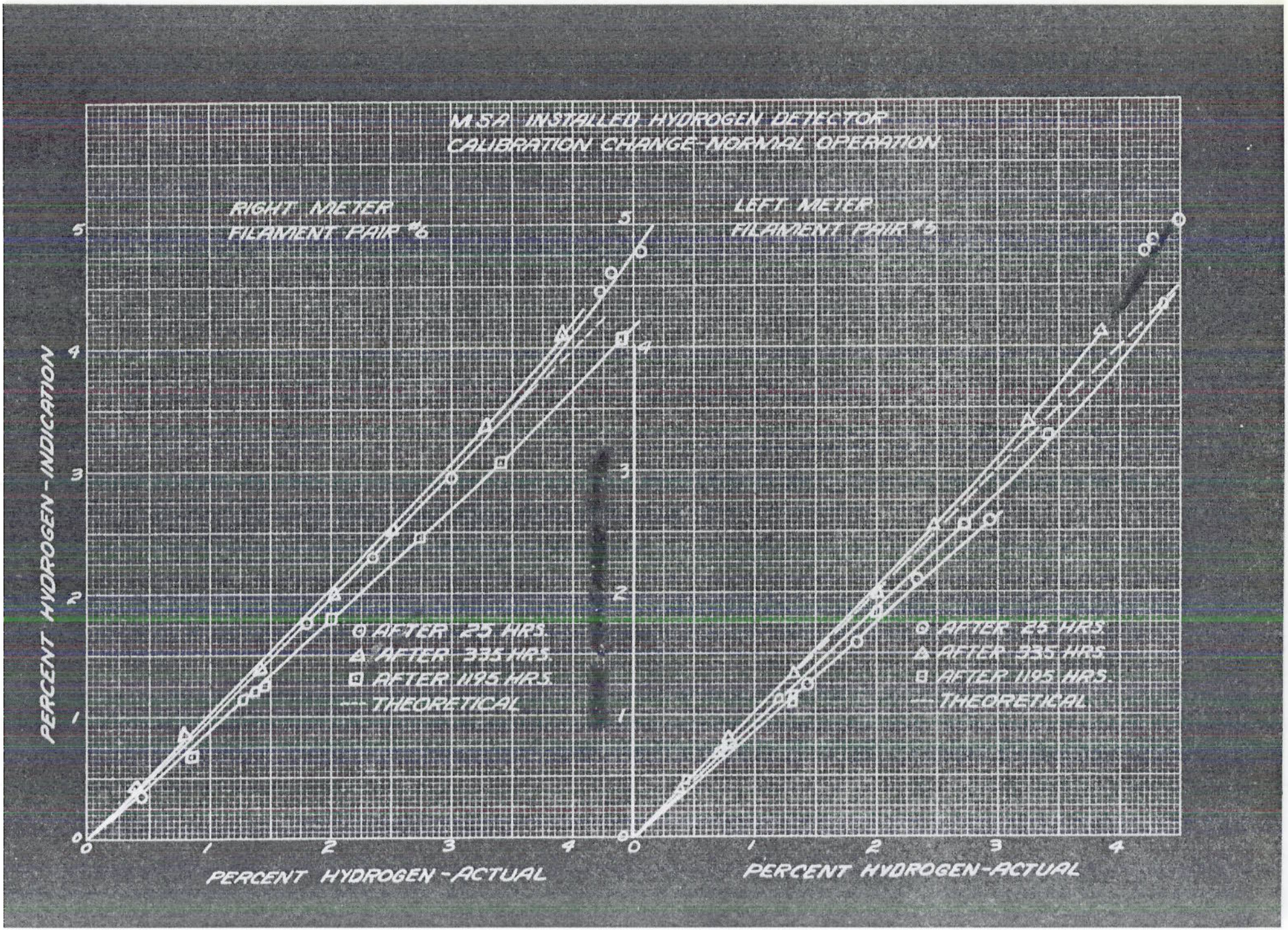
Pair No.	Super-sedes	Head *	Type of Operation	Hours Use	Hyd. Hours Use	Reason for Removal if significant	Remarks
1	-	R.	Cylinder hydrogen	916	1850	No zero	
2	-	Int.	Cylinder hydrogen	1549	3444	Active burnt out	
3	1	R.	Cylinder hydrogen	943	2314	No zero	
4	2	Int.	310 hrs. on cylinder 121 hrs. plus stibine	431	1008	Calibration had dropped	Large white deposit on filament and supports
5	4	Int.	Cylinder + stibine	34	96	New test	Poisoned-deposit
6	5	Int.	Cylinder + stibine	148	354	New test	Poisoned-deposit
1-6	6	Int.	Cylinder + stibine	450	858	New test	External active filament-was inactive of No. 1.
7	1-6	Int.	)Cylinder hydrogen,	-	-	Still good	----
X	3	R.	)variables tests				(Two used inactive (filament

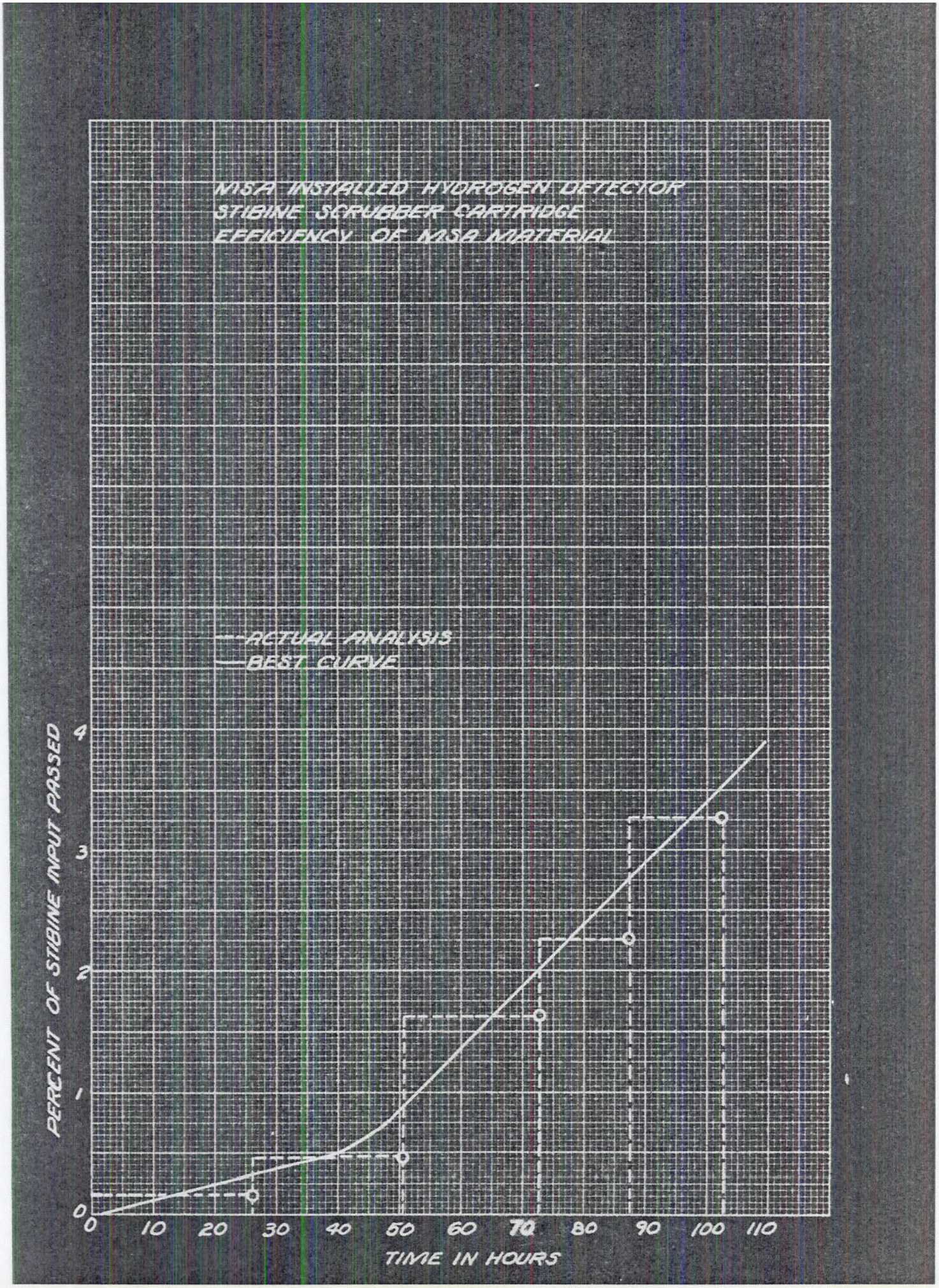
* R. = Remote

Int. = Integral


MARK I HYDROGEN DETECTOR
CALIBRATION OF NO. 46 DURING REPAIR
USING CATALYST CELL FROM NO. 1 (NRL)
#1 ○ AS RECEIVED
#2 △ THERMOCOUPLES READJUSTED
#3 X AFTER OVERHAUL
--- THEORETICAL
PERCENT HYDROGEN-INDICATION
PERCENT HYDROGEN-ACTUAL
0
1
2
3
4
5
6
#1
#2
#3


M.S.A. INSTALLED HYDROGEN DETECTOR
ZERO CHANGE - NORMAL OPERATION
1371 HRS. OF OPERATION OF FILAMENT PAIR #5
RIGHT METER
FINAL 372 HRS OF FILAMENT PAIR #3
+0.2
+0.1
0
-0.1
PERCENT HYDROGEN-INDICATION
0
200
400
600
800
1000
1200
1050
1250
HOURS ON TEST
800
1000
+0.1
0
-0.1
FILAMENT PAIR #6
LEFT METER
FILAMENT PAIR #4


M.S.A. INSTALLED HYDROGEN DETECTOR
CALIBRATION CHANGE-NORMAL OPERATION
RIGHT METER
FILAMENT PAIR #6
LEFT METER
FILAMENT PAIR #5
PERCENT HYDROGEN - INDICATION
PERCENT HYDROGEN - ACTUAL
PERCENT HYDROGEN - ACTUAL
○ AFTER 25 HRS.
△ AFTER 335 HRS.
□ AFTER 1195 HRS.
--- THEORETICAL
○ AFTER 25 HRS.
△ AFTER 335 HRS.
□ AFTER 1195 HRS.
--- THEORETICAL


NASA INSTALLED HYDROGEN DETECTOR
STIBINE SCRUBBER CARTRIDGE
EFFICIENCY OF NASA MATERIAL
---ACTUAL ANALYSIS
—BEST CURVE
PERCENT OF STIBINE INPUT PASSED
0
1
2
3
4
0
10
20
30
40
50
60
70
80
90
100
110
TIME IN HOURS

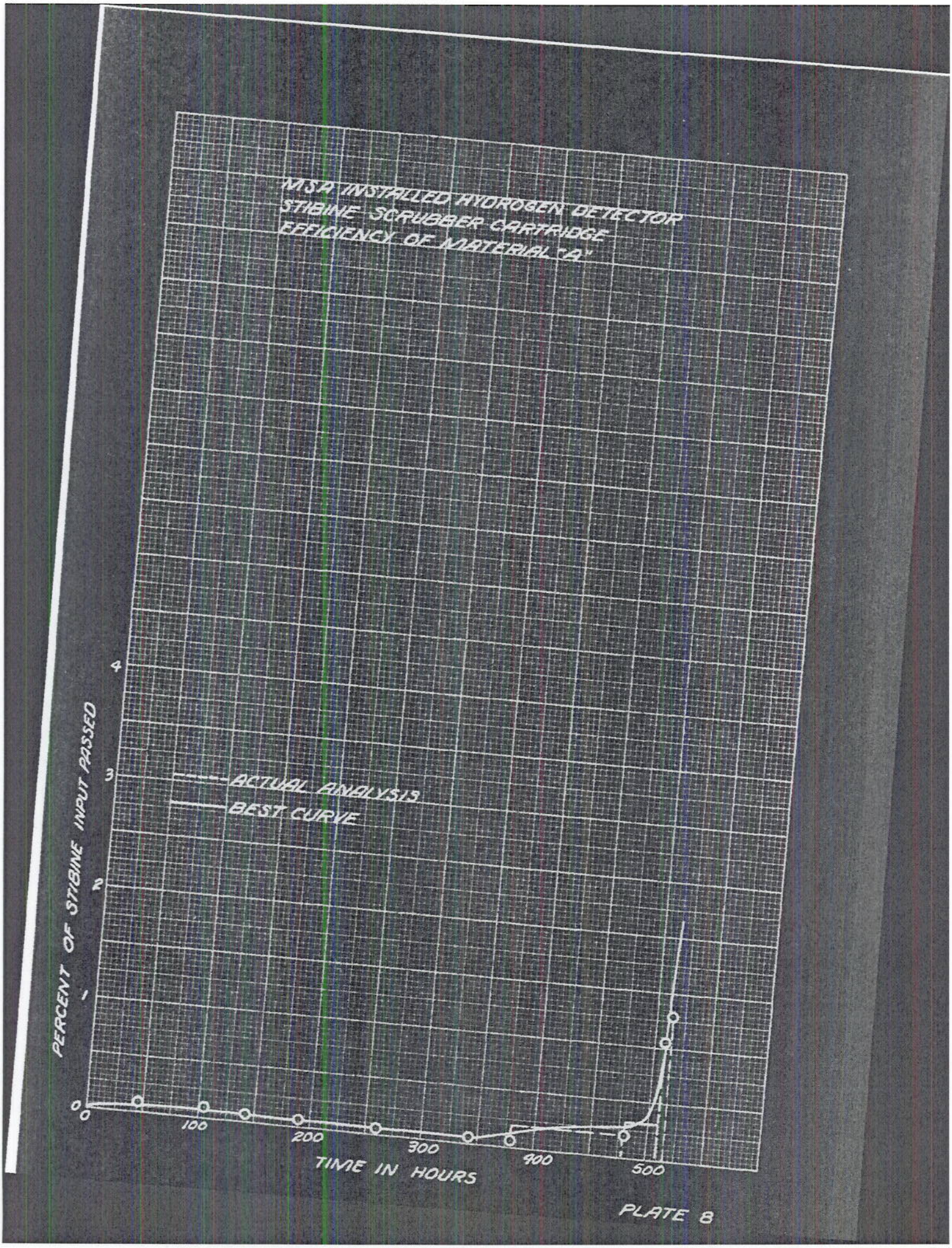

MSA INSTALLED HYDROGEN DETECTOR
STIBINE SCRUBBER CARTRIDGE
EFFICIENCY OF MATERIAL "A"
PERCENT OF STIBINE INPUT PASSED
4
3
2
1
0
ACTUAL ANALYSIS
BEST CURVE
0
100
200
300
400
500
TIME IN HOURS

PLATE 8

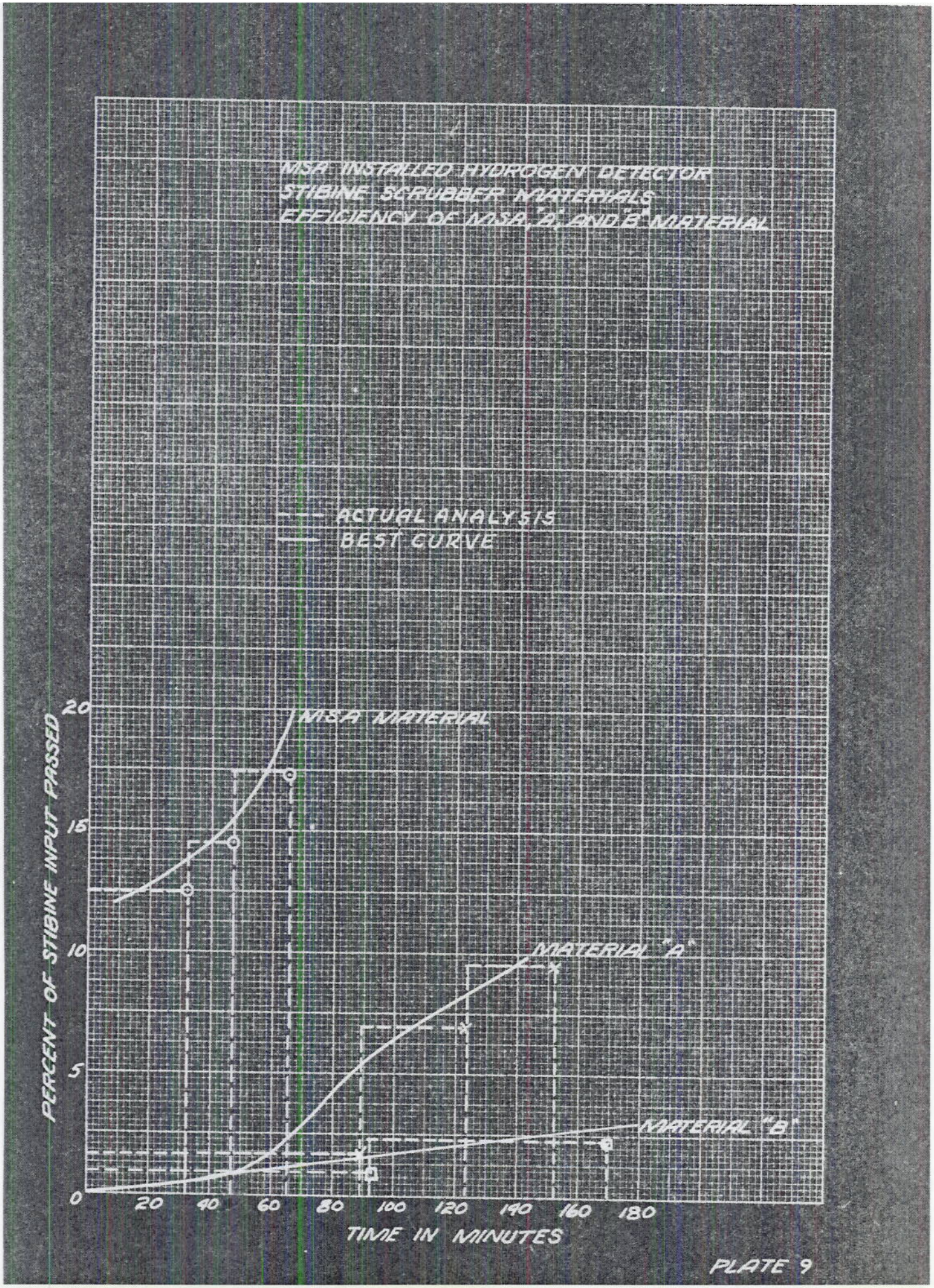
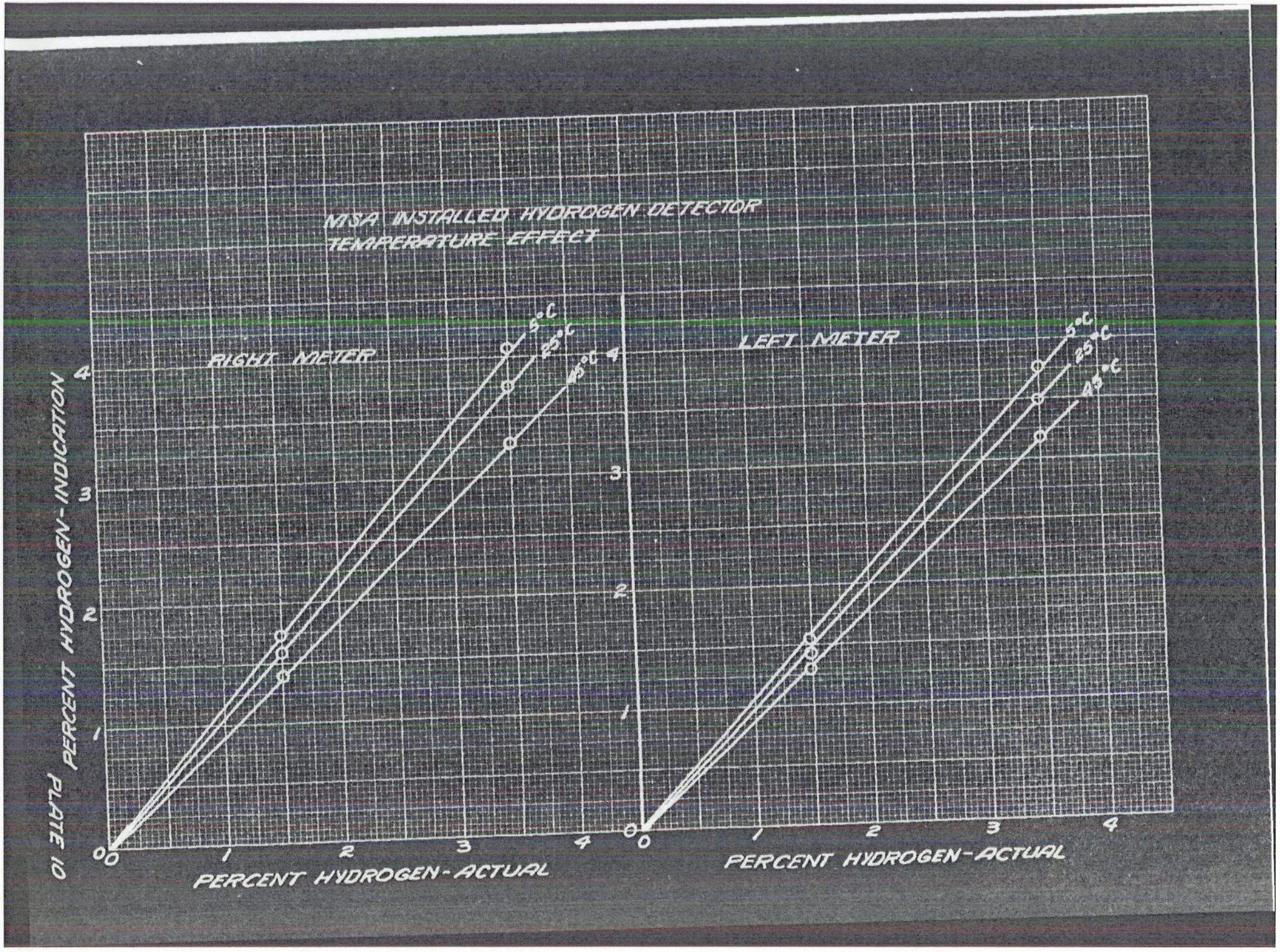
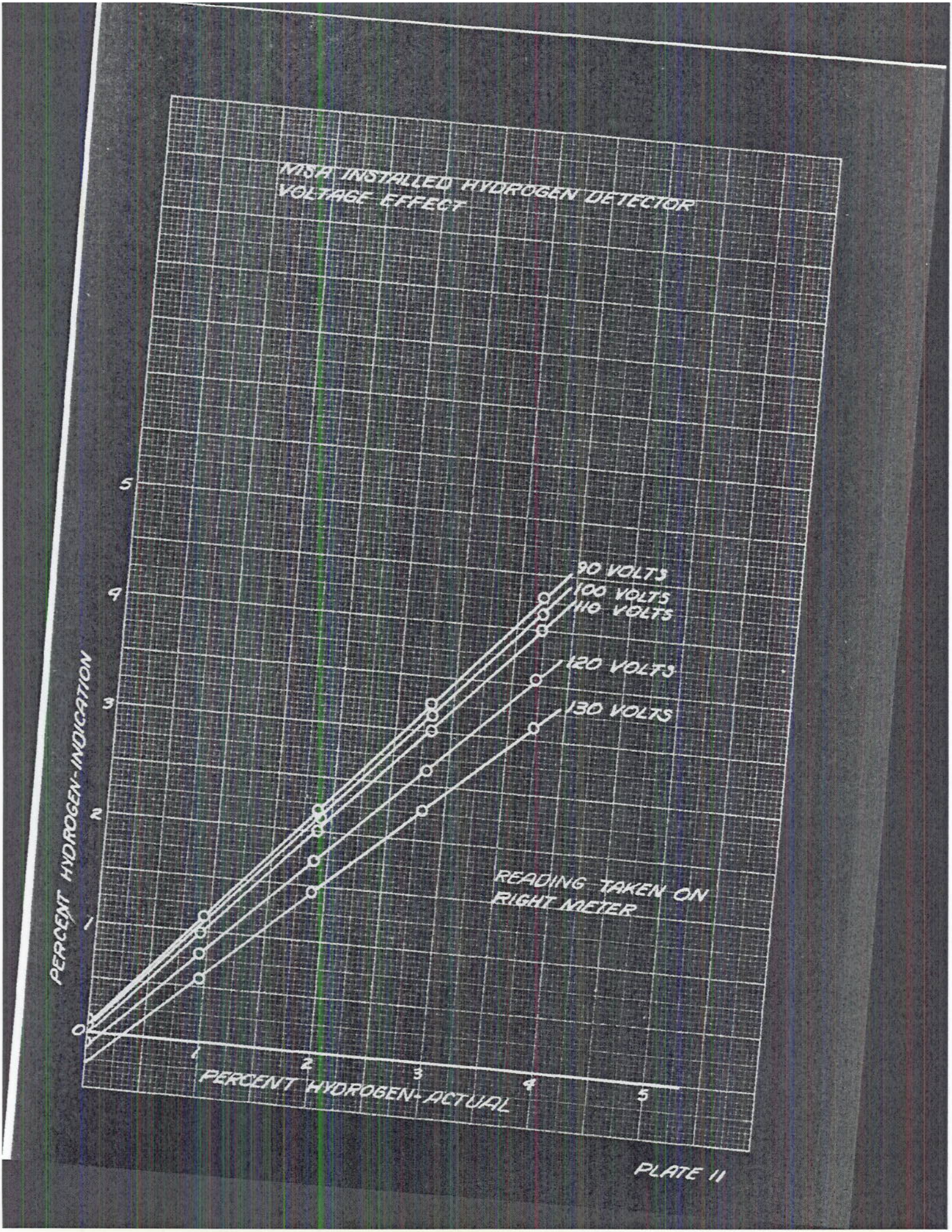

MSA INSTALLED HYDROGEN DETECTOR
STIBINE SCRUBBER MATERIALS
EFFICIENCY OF MSA, 'A' AND 'B' MATERIAL
ACTUAL ANALYSIS
BEST CURVE
MSA MATERIAL
MATERIAL "A"
MATERIAL "B"
PERCENT OF STIBINE INPUT PASSED
0
5
10
15
20
20
40
60
80
100
120
140
160
180
TIME IN MINUTES

PLATE 9


MSA INSTALLED HYDROGEN DETECTOR
TEMPERATURE EFFECT
RIGHT METER
LEFT METER
5°C
25°C
45°C
PLATE 10 PERCENT HYDROGEN-INDICATION
PERCENT HYDROGEN-ACTUAL
PERCENT HYDROGEN-ACTUAL
0
1
2
3
4


MSA INSTALLED HYDROGEN DETECTOR
VOLTAGE EFFECT
90 VOLTS
100 VOLTS
110 VOLTS
120 VOLTS
130 VOLTS
READING TAKEN ON
RIGHT METER
PERCENT HYDROGEN-INDICATION
PERCENT HYDROGEN-ACTUAL
0
1
2
3
4
5
PLATE 11

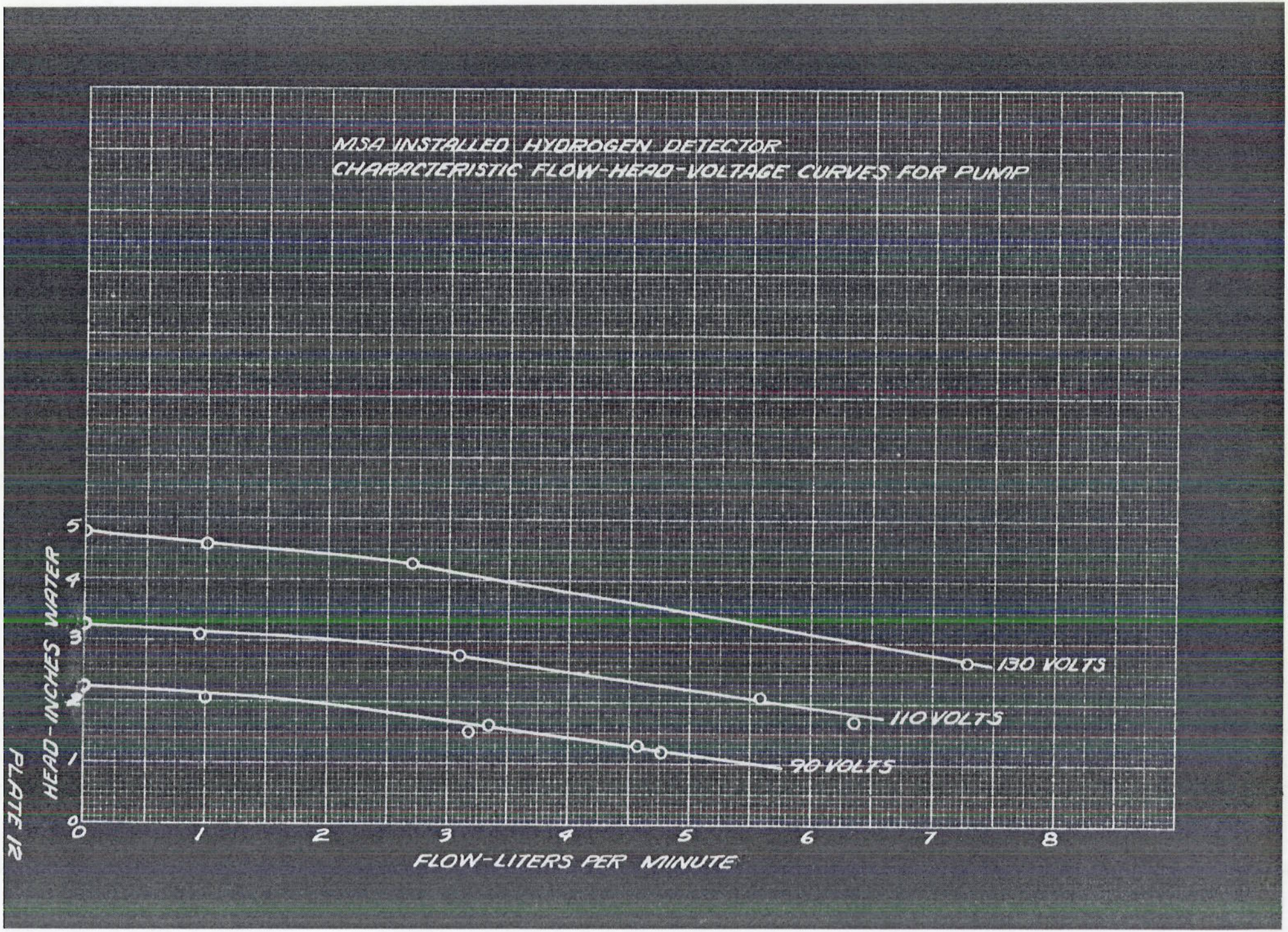
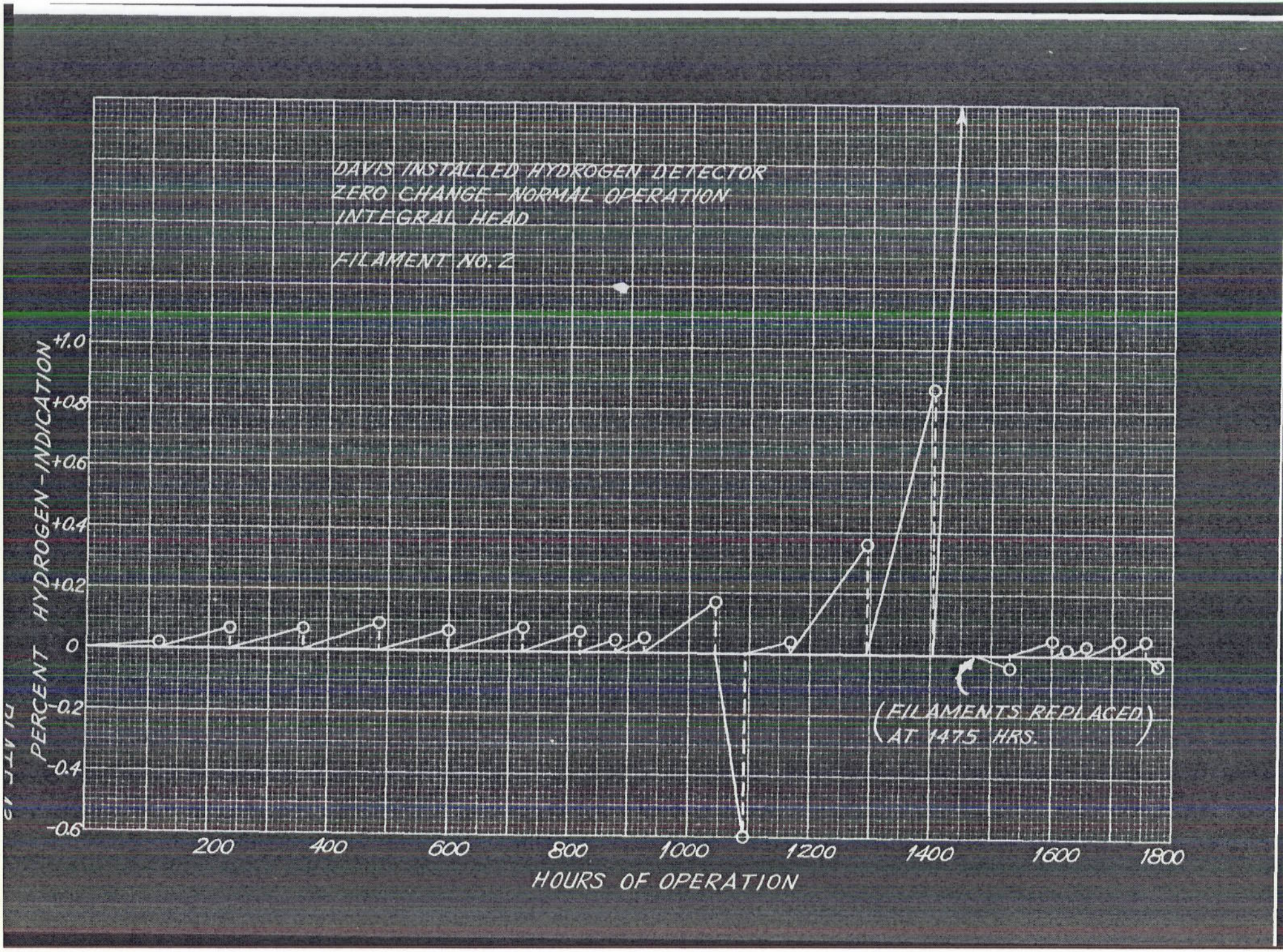
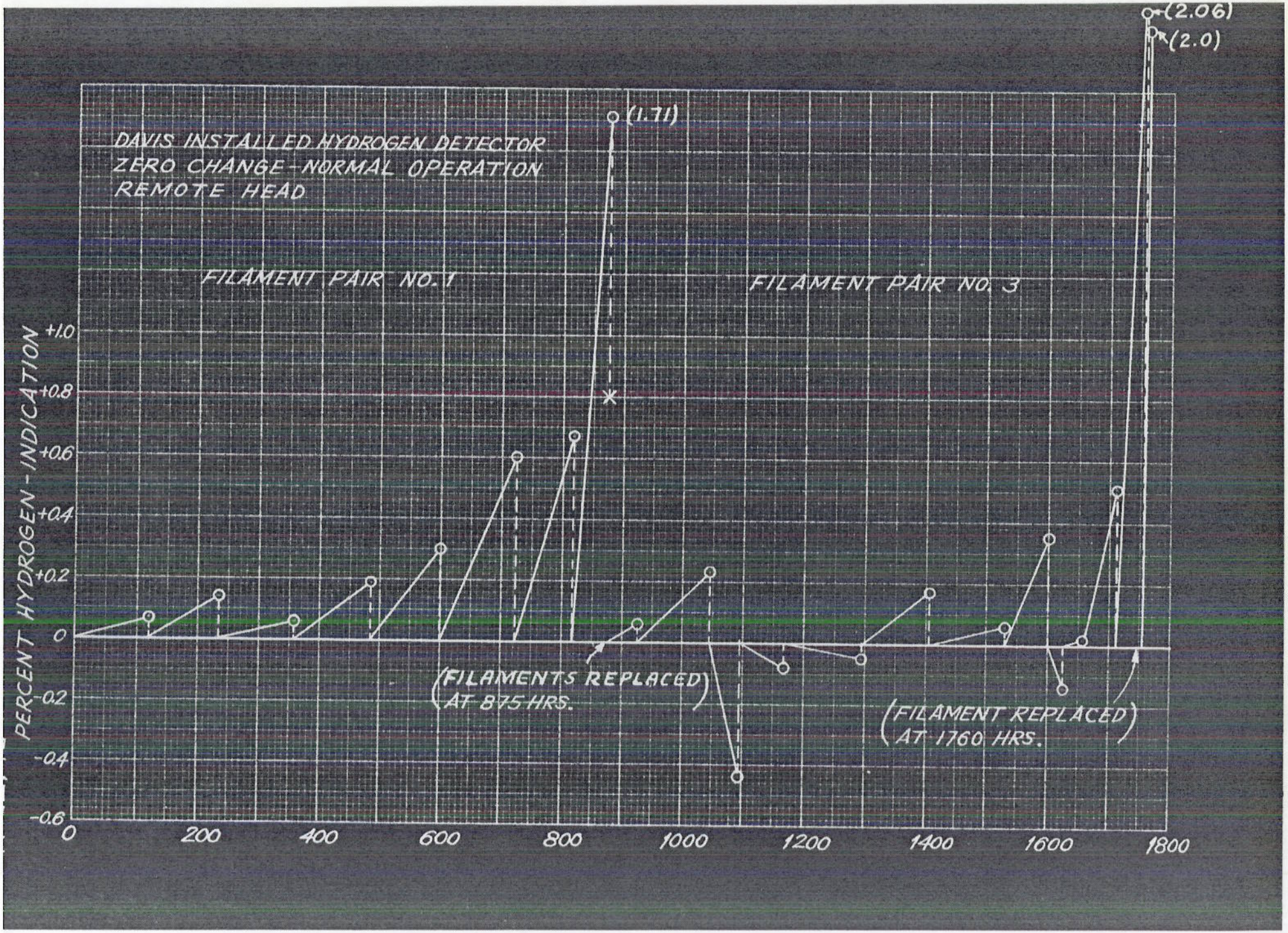
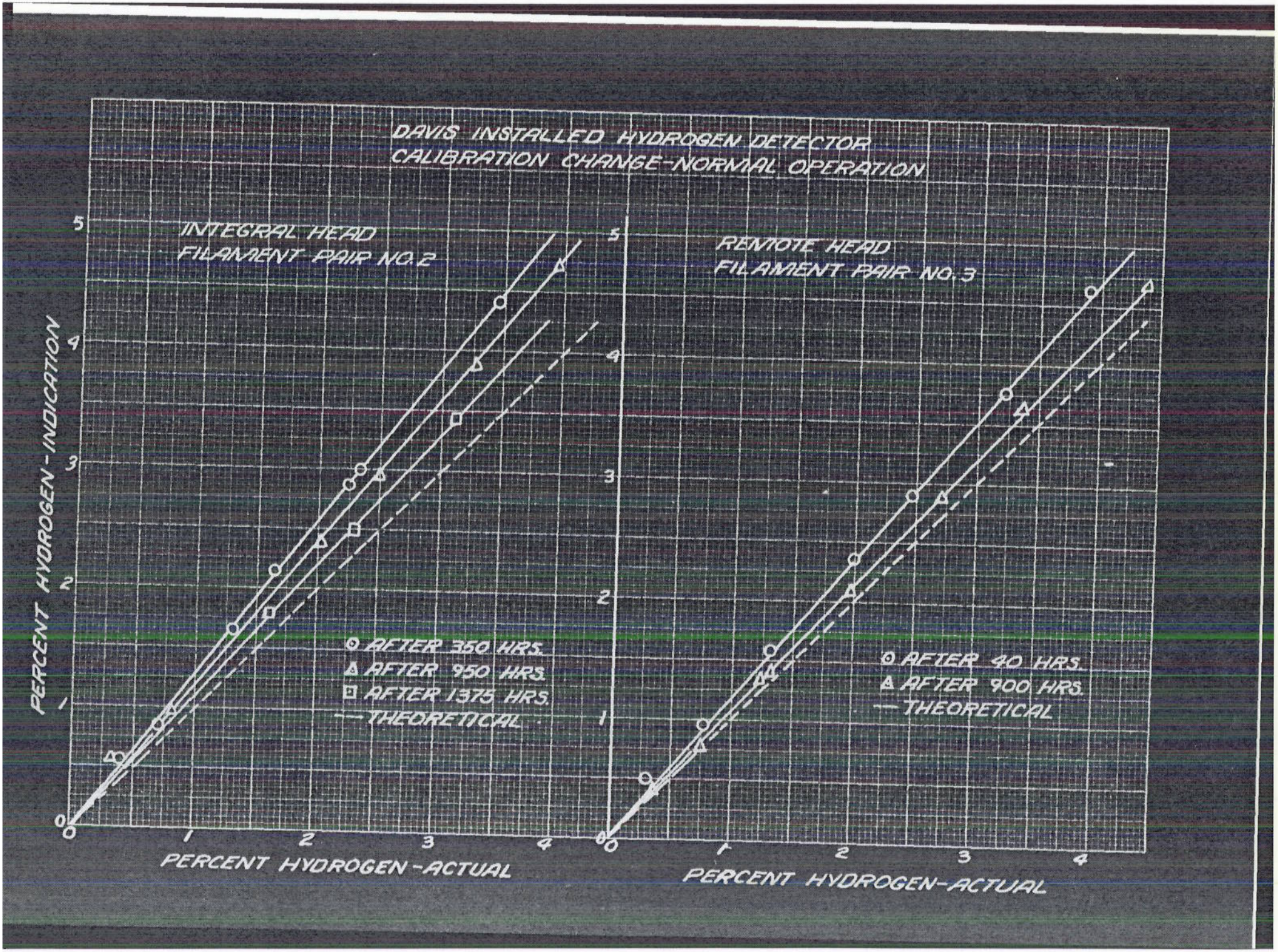
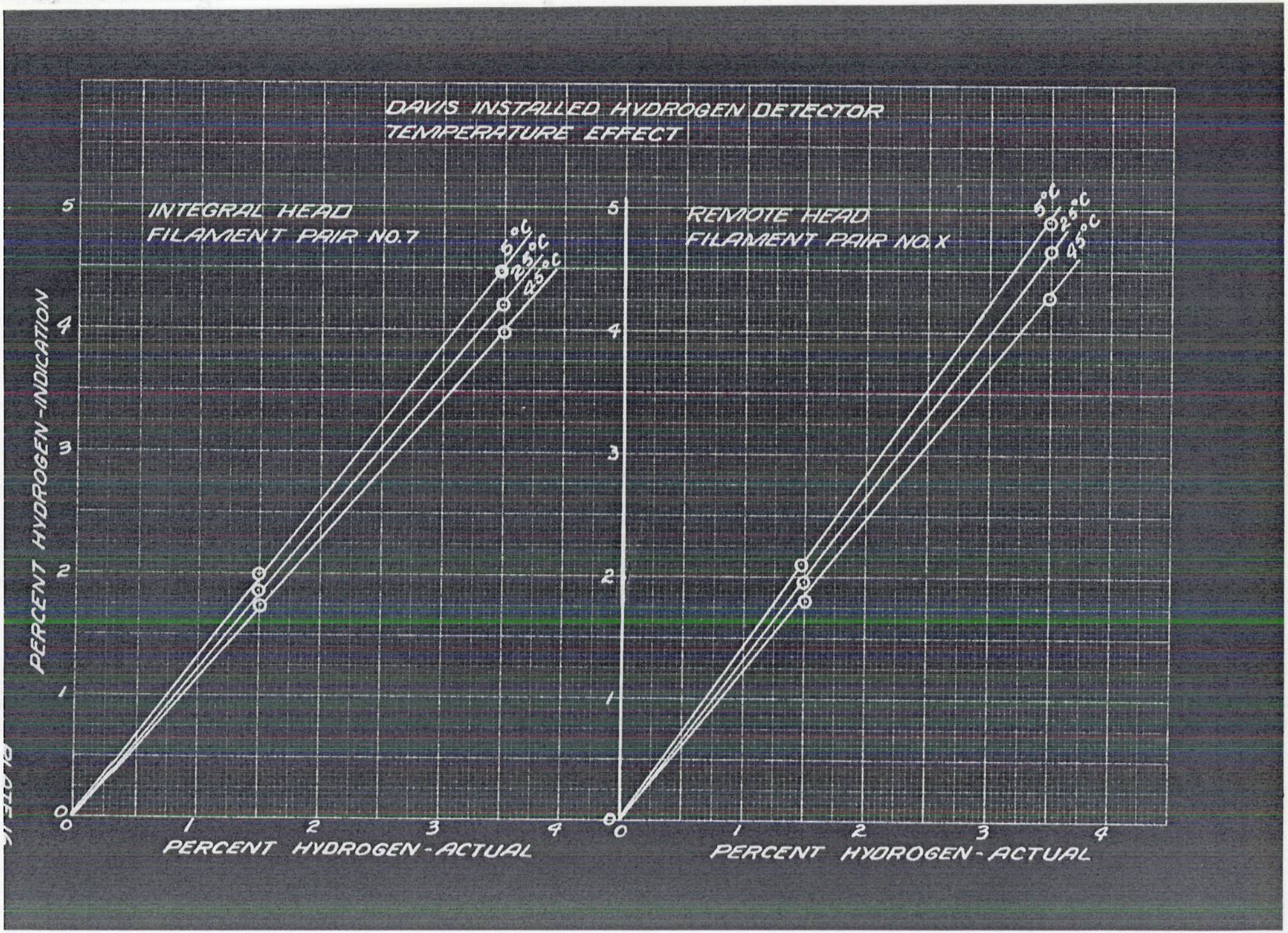

MSA INSTALLED HYDROGEN DETECTOR
CHARACTERISTIC FLOW-HEAD-VOLTAGE CURVES FOR PUMP
HEAD-INCHES WATER
0
1
2
3
4
5
FLOW-LITERS PER MINUTE
1
2
3
4
5
6
7
8
130 VOLTS
110 VOLTS
90 VOLTS

PLATE 12


DAVIS INSTALLED HYDROGEN DETECTOR
ZERO CHANGE – NORMAL OPERATION
INTEGRAL HEAD
FILAMENT NO. 2
PERCENT HYDROGEN – INDICATION
+1.0
+0.8
+0.6
+0.4
+0.2
0
-0.2
-0.4
-0.6
200
400
600
800
1000
1200
1400
1600
1800
HOURS OF OPERATION
(FILAMENTS REPLACED AT 1475 HRS.)


DAVIS INSTALLED HYDROGEN DETECTOR
ZERO CHANGE - NORMAL OPERATION
REMOTE HEAD
FILAMENT PAIR NO. 1
FILAMENT PAIR NO. 3
(1.71)
(2.06)
(2.0)
PERCENT HYDROGEN - INDICATION
+1.0
+0.8
+0.6
+0.4
+0.2
0
-0.2
-0.4
-0.6
0
200
400
600
800
1000
1200
1400
1600
1800
(FILAMENTS REPLACED AT 875 HRS.
(FILAMENT REPLACED AT 1760 HRS.


DAVIS INSTALLED HYDROGEN DETECTOR
CALIBRATION CHANGE-NORMAL OPERATION
INTEGRAL HEAD
FILAMENT PAIR NO. 2
REMOTE HEAD
FILAMENT PAIR NO. 3
PERCENT HYDROGEN - INDICATION
PERCENT HYDROGEN - ACTUAL
PERCENT HYDROGEN - ACTUAL
0
1
2
3
4
5
○ AFTER 350 HRS.
△ AFTER 950 HRS.
□ AFTER 1375 HRS.
— THEORETICAL
○ AFTER 40 HRS.
△ AFTER 900 HRS.
— THEORETICAL


DAVIS INSTALLED HYDROGEN DETECTOR
TEMPERATURE EFFECT
INTEGRAL HEAD
FILAMENT PAIR NO. 7
REMOTE HEAD
FILAMENT PAIR NO. X
5°C
25°C
45°C
PERCENT HYDROGEN - INDICATION
PERCENT HYDROGEN - ACTUAL
PERCENT HYDROGEN - ACTUAL
0
1
2
3
4
5

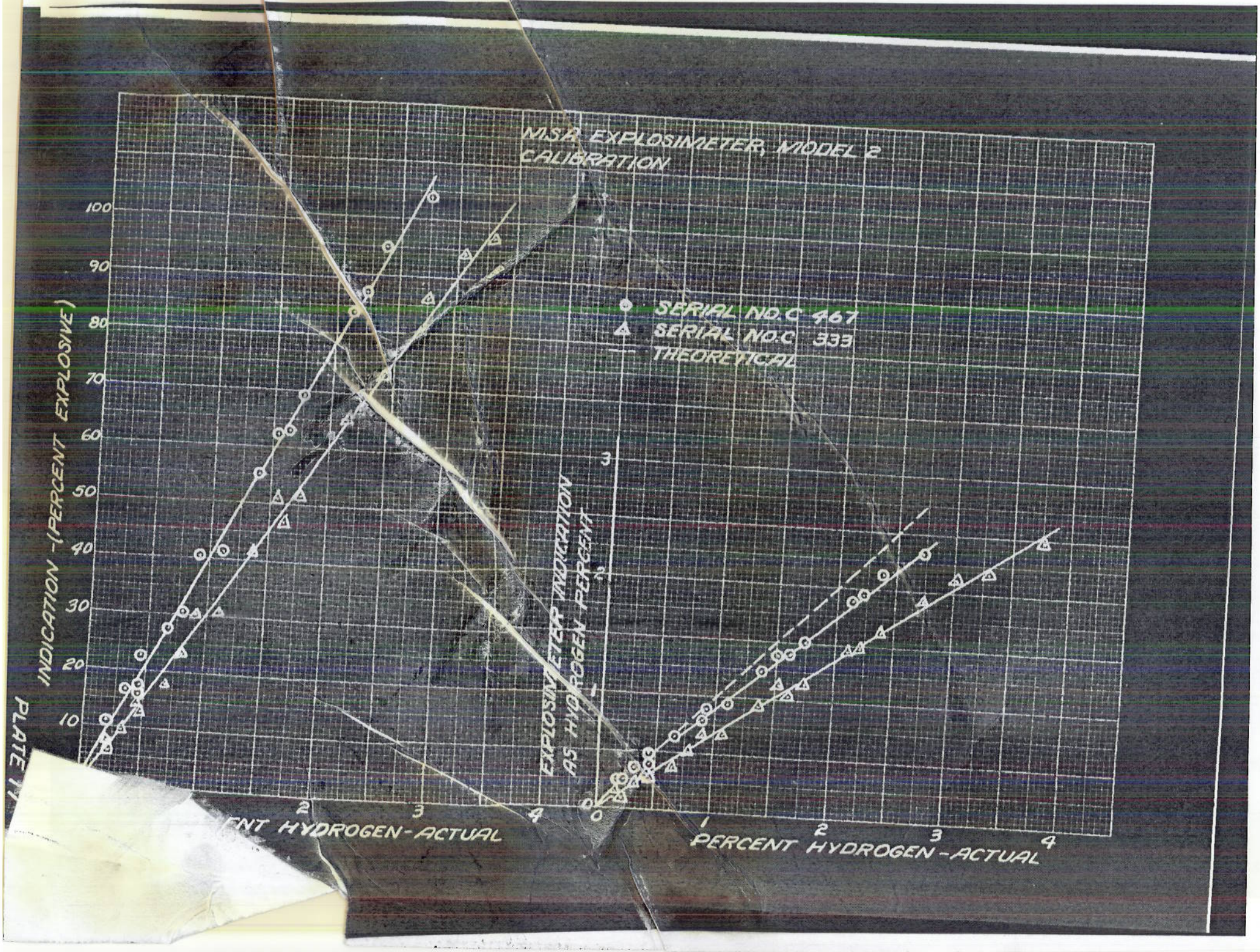
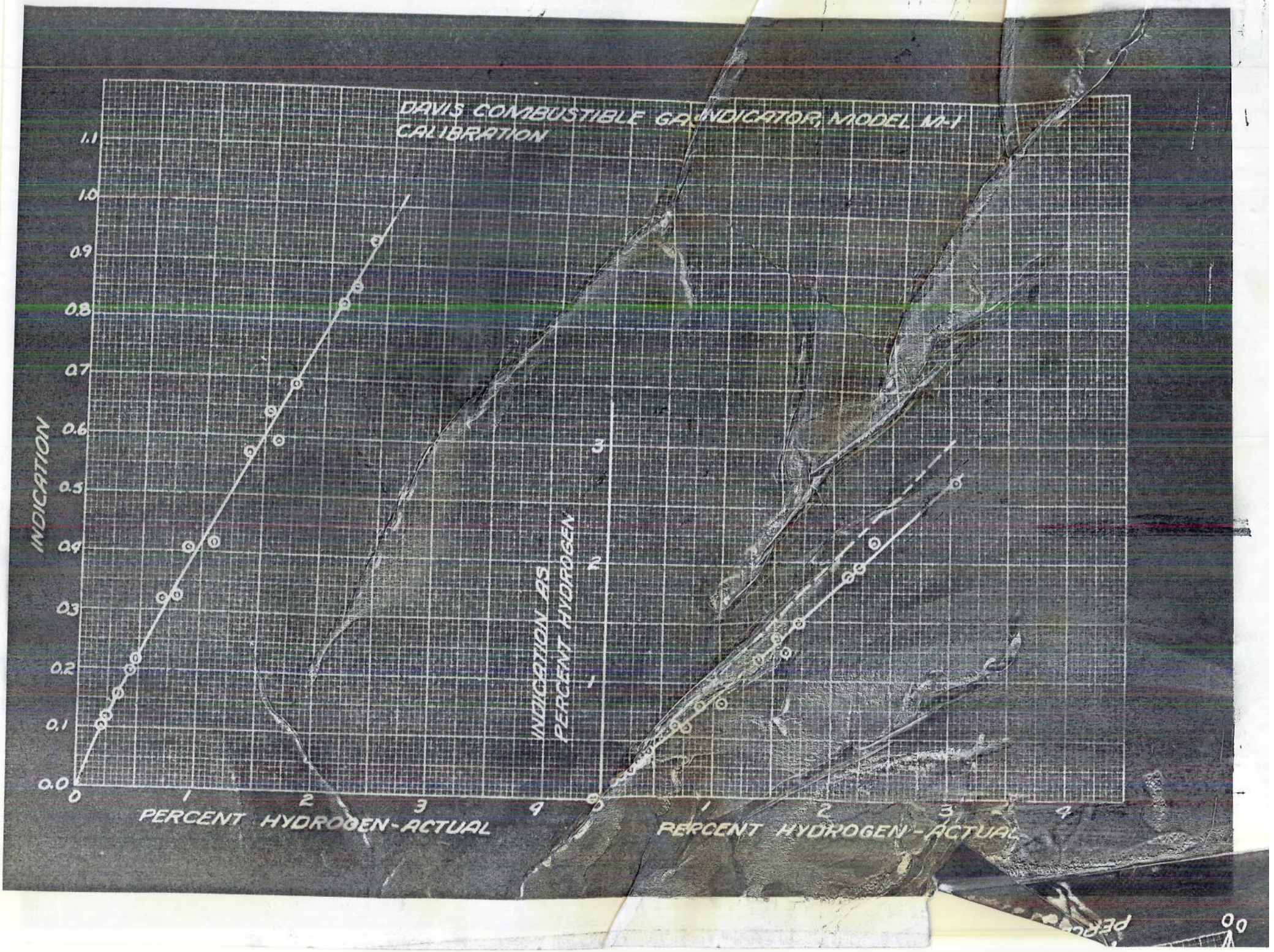

M.S.A. EXPLOSIMETER, MODEL 2
CALIBRATION
SERIAL NO. C 467
SERIAL NO. C 333
THEORETICAL
INDICATION - (PERCENT EXPLOSIVE)
EXPLOSIMETER INDICATION AS HYDROGEN PERCENT
PERCENT HYDROGEN - ACTUAL
PERCENT HYDROGEN - ACTUAL

PLATE 1


DAVIS COMBUSTIBLE GAS INDICATOR, MODEL M-1
CALIBRATION
INDICATION
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
PERCENT HYDROGEN - ACTUAL
INDICATION AS PERCENT HYDROGEN
PERCENT HYDROGEN - ACTUAL

APPENDIX A

Calculation of Temperature Rise of Gas Stream Across Catalyst Bed of Mark I Hydrogen Detector

It is commonly known that the temperature rise of any body of material is related to the quantity and heat capacity of that material and the quantity of heat supplied by the following expression:

$$\text{Temp. Rise} = \frac{\text{Quantity of Heat}}{\text{Quantity of Material Heat Capacity}}$$

provided the various parts of the expression are kept in consistent units. Therefore, abbreviating and supplying units:

$$dT_{(^\circ C)} = \frac{H_{(g\text{-cal})}}{Q_{(\text{mols})} \cdot C_{(g\text{-cal/mol/}^\circ C)}}$$

In the present case the heat supplied to a given sample of gas is the heat of reaction of the hydrogen reacted from that gas. Therefore:

$$H_{(g\text{-cal})} = dH_{(g\text{-cal/mol } H_2)} \cdot \text{mols } H_2 \text{ reacted.}$$

Further, since the gas to be heated is made up of several constituents having different heat capacities the product of the quantity and heat capacity of each constituent of the exhaust gas must be summed. Therefore:

$$dT_{(^\circ C)} = \frac{dH_{(g\text{-cal/mol } H_2)} \cdot \text{mols } H_2 \text{ reacted}}{\sum_{o}^{x} \left(Q \text{ of } X_{(\text{mol})} \cdot C \text{of } X_{(g\text{-cal/mol/}^\circ C)}\right)}$$

Now:

$$\text{Mols } H_2 \text{ reacted} = \frac{\text{Vol. of sample}_{(\text{l. at STP})} \cdot \%\ H_2 \cdot \%\ \text{Eff.}}{22.4 \cdot 100 \cdot 100}$$

and:

$$Q \text{ of } X_{(\text{mols})} = \frac{\text{Vol. of exhaust}_{(\text{l. at STP})} \cdot \% X}{22.4 \cdot 100}$$

Combining and reducing the above equations:

$$dT_{(^{\circ}C)} = \frac{dH_{(\text{g-cal/mol } H_2)} \cdot \text{Vol.}_{(\text{sample})} \cdot \% H_2 \cdot \% \text{ Eff.}}{\text{Vol.}_{(\text{exhaust})} \sum_{o}^{x} (\text{C of X}_{(\text{g-cal/mol/}^{\circ}C)} \cdot \%X) \cdot 100}$$

In order to evaluate this expression the following values may be assumed:

$$dH_{(\text{g-cal/mol } H_2)} = 58300$$

$$\% \text{ Eff.} = 100$$

$$\frac{\text{Vol.}_{(\text{sample})}}{\text{Vol.}_{(\text{exhaust})}} = \frac{100}{100 - 1/2(\% H_2)} \text{ which approaches 1}$$

as the $\% H_2$ approaches zero.

$$C \text{ of } X_{(\text{g-cal/mol/}^{\circ}C)} = 7.0 \text{ for the entire exhaust}$$

gas since it can be shown from calculation that the average for the entire exhaust gas can vary by less than 3% in value within the range of concentrations stated in Table 1. Hence, since:

$$\sum_{o}^{x} \% X = 100,$$

it follows that:

$$\sum_{o}^{x} (\text{C of X}_{(\text{g-cal/mol/}^{\circ}C)} \cdot \% X) = 700$$

Therefore, substituting:

$$dT_{(^{\circ}C)} = \frac{58{,}000 \cdot \% H_2 \cdot 1 \cdot 1}{700 \cdot 100} = 83^{\circ}C \cdot \% H_2$$