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SALINE WATER RESEARCH AND DEVELOPMENT PROGRESS REPORT NO. 115

DEVELOPMENT OF AN ANALYTICAL METHOD FOR MEASURING
THE HYDROCARBON CONTENT IN WATER

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Created in 1849, the Department of the Interior--America's Department of Natural Resources--is concerned with the management, conservation, and development of the Nation's water, wildlife, mineral, forest, and park and recreational resources. It also has major responsibilities for Indian and Territorial affairs.

As the Nation's principal conservation agency, the Department of the Interior works to assure that nonrenewable resources are developed and used wisely, that park and recreational resources are conserved for the future, and that renewable resources make their full contribution to the progress, prosperity, and security of the United States--now and in the future.

FOREWORD

This is the one hundred and fifteenth of a series of reports designed to present accounts of progress on saline water conversion with the expectation that the exchange of such data will contribute to the long-range development of economical processes applicable to large-scale, low-cost demineralization of sea and other saline waters.

Except for minor editing, the data herein are as contained in a report submitted by the Koppers Company, Inc. under Contracts Nos. 14-01-001-204 and 14-01-0001-344 which have been accepted as fulfilling the provisions of these contracts. The data and conclusions given in this report are essentially those of the Contractor and are not necessarily endorsed by the Department of the Interior.

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I. INTRODUCTION AND SUMMARY

An analytical method has been developed for monitoring the propane content of the potable water and effluent streams from the Koppers' Hydrate Process for the desalination of sea water. This method is capable of determining propane in water over the range of 0.05 to 2.0 ppm. by weight. It is applicable also to the determination of Freon-12, under consideration for use in Koppers' Hydrate Process, and to the determination of n-butane, isobutane, and butene-1, compounds now under consideration as working fluids for freezing processes for desalination. Utilization of a gas stripping unit in conjunction with a hydrogen flame ionization detector frees this method from interference from salts, from other organic matter normally present in the sea water, and from the water itself. Specifications were written for the design of a prototype analyzer. A summary report was made on this part (A) of the work to the Office of Saline Water dated April 15, 1963, "Development of an Analytical Method for the Determination of Propane, n-Butane, Isobutane, Butene-1 and Freon-12 in Water and Brine by Gas Stripping and Flame Ionization Detection", by Marjorie A. Phillips, William R. Holden, Edgar W. Albaugh and Harold A. Sweeney. This investigation was carried out under the joint sponsorship of the Office of Saline Water (Contract No. 14-01-001-204) and the Koppers Company, Inc., Research Department.

From the specifications an analytical unit has been designed to measure the hydrocarbon content in potable water and reject brine streams emanating from saline water conversion pilot plants at the Research and Development Test Station, Wrightsville Beach, North Carolina. A sub-contract was placed with Research Appliance Company, Allison Park, Pennsylvania for construction of the analytical unit. The completed unit was installed in the Monroeville Research Center of Koppers Company, Inc. and tested to ascertain that it met the method specifications developed above. The unit was calibrated for n-butane over the range 0.05 to 2.0 ppm. by weight in water. Aqueous blends of butane were prepared and analyzed and the results compared with those obtained in the method development. The analyzer was shipped to Wrightsville Beach, North Carolina where it was installed in the analytical laboratory. The personnel designated by Mr. Walter L. Barnes, Manager of the Research and Development Test Station, were trained to operate the analyzer. A summary report on this second part (B) of the work was made to the Office of Saline Water dated March 10, 1964, "Assembly, Testing and Installation of a Unit for Measuring the Hydrocarbon Content in Water", by William E. McKinstry, William R. Holden and Harold A. Sweeney. This part of the work was carried out under the sponsorship of the Office of Saline Water (Contract No. 14-01-0001-344).

II. JUSTIFICATION

For the ultimate acceptance of Koppers' Hydrate Process for the conversion of saline water to fresh water, the volatile hydrocarbon content of the potable water and the effluent stream must be within specified limits. In a letter from Mr. F. M. Middleton, Advanced Water Treatment Research Branch, to Mr. J. J. Strobel, Office of Saline Water (OSW), of February 16, 1962, it is suggested that 0.2 ppm. by weight of propane be tentatively considered as an upper limit of safety in order to avoid the danger of an explosion, which could result from mixing the dissolved propane with air. A similar limit was calculated by Dr. L. A. Cutter, Koppers Company, Inc. and reported in a memorandum dated March 2, 1962. Since the effluent from freezing processes, in which n-butane, isobutane, or butene-1 may be used as working fluids, must meet the same standards of purity as that from the Hydrate process, Mr. W. W. Rinne, OSW, in discussion with Dr. E. E. Donath, Koppers Company, Inc., on February 21, 1962, suggested that the method required for the propane determination be worked out also for the determination of these C₄ hydrocarbons.

In order to verify that the specification limits are being met, an analytical instrument was needed to monitor the volatile hydrocarbon content of these streams emanating from the conversion pilot plants at the Research and Development Test Station, Wrightsville Beach, North Carolina.

III. BACKGROUND

A preliminary literature search was conducted and several methods were noted which appeared suitable for the determination of small amounts of hydrocarbons. Andreatch and Feinland have described a method for the continuous analysis of trace quantities of hydrocarbons (4). Morris and Chapman have described a Beckman flame ionization hydrocarbon analyzer (19). Wehe and McKetta utilized a vapor pressure procedure for estimating the total hydrocarbon dissolved in water (26). The detection and measurement of trace hydrocarbons in compressed gases by infrared and hydrogen flame ionization techniques have been described in ASTIA AD-265, 962 (6). An ultraviolet photolysis method was employed by Beattie, Bricker, and Garvin for determining trace amounts of organic material in water (8). Nelson, Eggertsen, and Holst have investigated the determination of volatile hydrocarbon in aqueous emulsions and latexes (20). Aromatic hydrocarbons in the atmosphere were determined by Altshuller and Clemons (1), by use of flame ionization detection. Swinnerton, Linnenbom, and Cheek have investigated the determination of dissolved gases in aqueous solutions by gas chromatography (24). The analysis of traces of hydrocarbon in water using a flame ionization detector was discussed by Dunton at the spring meeting of the American Chemical Society, March 21-24, 1962, at Washington, D. C. (13). Williams and Miller (27) removed dissolved gases from water with a gas stripping unit and determined the stripped gases by vapor phase chromatography.

On the basis of this information three methods of detection appeared suitable for this development: 1) hydrogen flame ionization detection, 2) non-dispersive infrared analysis, and 3) calorimetric or thermal measurement on combustion of the hydrocarbon. Since the presence of solids and, in some cases, presence of water were expected to interfere with the proper functioning of an analytical detector in use for continuous monitoring of the process, the method required was expected to include a unit for the separation of the hydrocarbon from the water. Since ionization-type detectors, due to their remarkable sensitivity and linear response in the desired concentration range, had already gained widespread acceptance in gas chromatography for monitoring traces of hydrocarbons present in gases, this approach seemed most feasible. A further advantage was the insensitivity of the detector to small amounts of water and air. In the light of this decision, a comprehensive literature search was conducted which included the determination of hydrocarbons in water and in brine, the determination of Freons in water and in brine, physical data for these compounds, and the preparation of standard solutions of these compounds. References containing data and information pertinent to this project are listed in the attached bibliography.

IV. EXPERIMENTAL

The experimental work on this project was divided into two parts. Part A included the investigational work necessary for the development of the analytical method and the design of the prototype analytical instrument. Part B included the assembly, testing and installation of the analytical instrument.

A. Development of the Analytical Method

Development of the proposed method was divided into five phases, and each phase of the investigation was carried out as reported below.

Phase 1

Procurement, assembly, and installation of instruments and accessory apparatus.

A schematic diagram of the system is shown in Appendix I, Drawing No. C66782. By use of a Sigmamotor pump the aqueous solution is fed at a known (constant) rate to a gas stripping unit. Nitrogen is used as the stripping gas and is supplied to the unit at a known flow rate and flowing in the direction opposite to the water flow. The water leaving the stripping unit is discarded; the effluent gas vents through the sample loop of a gas sampling valve connected to a hydrogen flame ionization detector. At intervals the valve is actuated, and a sample of the stripper gas is injected into the carrier gas stream of the detector unit. The signal from the detector is amplified and recorded on a standard strip-chart recorder. From the recorded peak and the suitable calibration curve the concentration of the hydrocarbon in the aqueous solution can be calculated.

The glass sample bottles for the calibration mixtures (225-ml. capacity) and the aqueous solution reservoir (2000-ml. capacity) were of the same special design (Drawing C-66801). The pump was a Sigmamotor pump Model T-8 with a Model 14 Zero-Max speed changer with a vernier adjustment. Some difficulty was encountered in the preliminary operation of this pump in attempts to depend solely upon it for maintaining a constant water level in the stripping unit, i.e., the same flow rate in and out. This problem was resolved by the installation of heavier springs, which allowed a constant flow rate to be maintained in one direction, and by the installation of a stand-pipe arrangement in the stripper exit line so that a constant water level was maintained.

The gas stripping unit was constructed to specifications which were based on those of a unit described by Mr. D. D. Williams of the United States Naval Laboratory, Washington, D. C. (27). After minor changes in positioning the discs and the internal magnet, this unit gave completely satisfactory and maintenance-free operation. Final specifications for the unit are attached (see Appendix I).

The detector unit was an F & M Scientific Corporation Hydrogen Flame Ionization Detector Model 1609. The gases employed (breathing air for the oxidizing atmosphere, dry nitrogen for the carrier gas, and prepurified hydrogen for the fuel gas) were further purified by passage through molecular sieve columns. The inherent noise level and background signal of the detector unit were determined according to the manufacturers' instructions and found to be more than adequate for our purpose. Over a period of five days of continuous operation essentially no electrometer drift was noted on the sensitivity ranges employed in this investigation.

The recorder used was a Leeds & Northrup Speedomax G Model S AZAR. Its speed of response was found to be quite adequate for this analysis.

Phase 2

Determination of detector response linearity with calibration mixtures of propane in nitrogen and Freon-12 in nitrogen.

Since a 1 to 1 ratio of water flow rate to nitrogen flow rate was planned for preliminary testing of the stripping unit, calculations of the hydrocarbon content of the stripping gas from aqueous solutions over the concentration range of 0.05 to 2.0 ppm. by weight of propane and of Freon-12 were made on this basis. Under the ambient conditions of our laboratory, the concentration of propane in the stripping gas (nitrogen), assuming 100 per cent stripping efficiency, would range from 28.5 to 1140 ppm. by volume and that of Freon-12 from 10.5 to 420 ppm. by volume (see Appendix II for calculations). A preliminary blend of propane in nitrogen was prepared and operating parameters established to give adequate sensitivity without having to work near the sensitivity limit of the detector unit. Under the chosen conditions of flow, flame temperature, etc., 0.5 ppm. by volume of propane in nitrogen (less than 1 ppb. by weight in water) could be quite adequately determined.

Before final conditions of operation were established, and even though this type of detector is claimed to be insensitive to small amounts of water, the effect of water vapor on the detector response was investigated. Propane blends of the same concentration in dry nitrogen and in water-saturated nitrogen were prepared and analyzed. Identical response was obtained from the two mixtures. Operating parameters were established then as follows: detector block temperature, 110°C.; injection port temperature, 85°C.; column oven temperature, 40°C.; nitrogen flow rate, 30 ml. per minute; hydrogen flow rate, 50 ml. per minute; air flow rate, 275 ml. per minute; flame temperature, 200°C.; sample size, 1/2 ml.; and chart speed, 30 inches per hour. An empty 8-inch length of 1/4-inch O.D. copper tubing was used as a jumper tube to replace the conventional gas chromatographic column.

The unit was calibrated with gas blends of propane in nitrogen and Freon-12 in nitrogen over the range of 0 to 1800 ppm. by volume. For preparation of the higher concentrations, gas-tight hypodermic syringes were used to transfer measured volumes of pure propane or Freon-12 to calibrated bulbs containing water-saturated nitrogen. For preparation

of the low concentrations, preliminary synthetic mixtures of propane in nitrogen and Freon-12 in nitrogen were prepared using an all-glass gas blending system. Known volumes of these mixtures were then transferred by means of a gas-tight hypodermic syringe to calibrated bulbs containing water-saturated nitrogen. One-half ml. samples of these final blends were then injected directly into the carrier gas stream of the ionization detector unit by means of the transfer system and the gas sampling valve (see Drawing No. F-22611-V).

The calibration curves are shown on the attached graphs. Figures 1 and 2 show the response for propane over two concentration ranges on the same electrometer range setting (input) but on different attenuations (divided output). Figure 3 shows the low-concentration propane response on a more sensitive scale. Figures 4 and 5 show the response for Freon-12 over two concentration ranges on the same electrometer range setting but on different attenuations. Figure 6 shows the low-concentration Freon-12 response on a more sensitive scale. The detector response to both compounds was found to be linear over the entire range of interest; i.e., over the range of 1×10^{-8} to 1×10^{-6} grams of propane and over the range of 4×10^{-8} to 4×10^{-6} grams of Freon-12.

Phase 3

Preparation of calibration mixtures of propane and of Freon-12 in water, study of the direct injection of these water samples, and testing of the gas stripping unit.

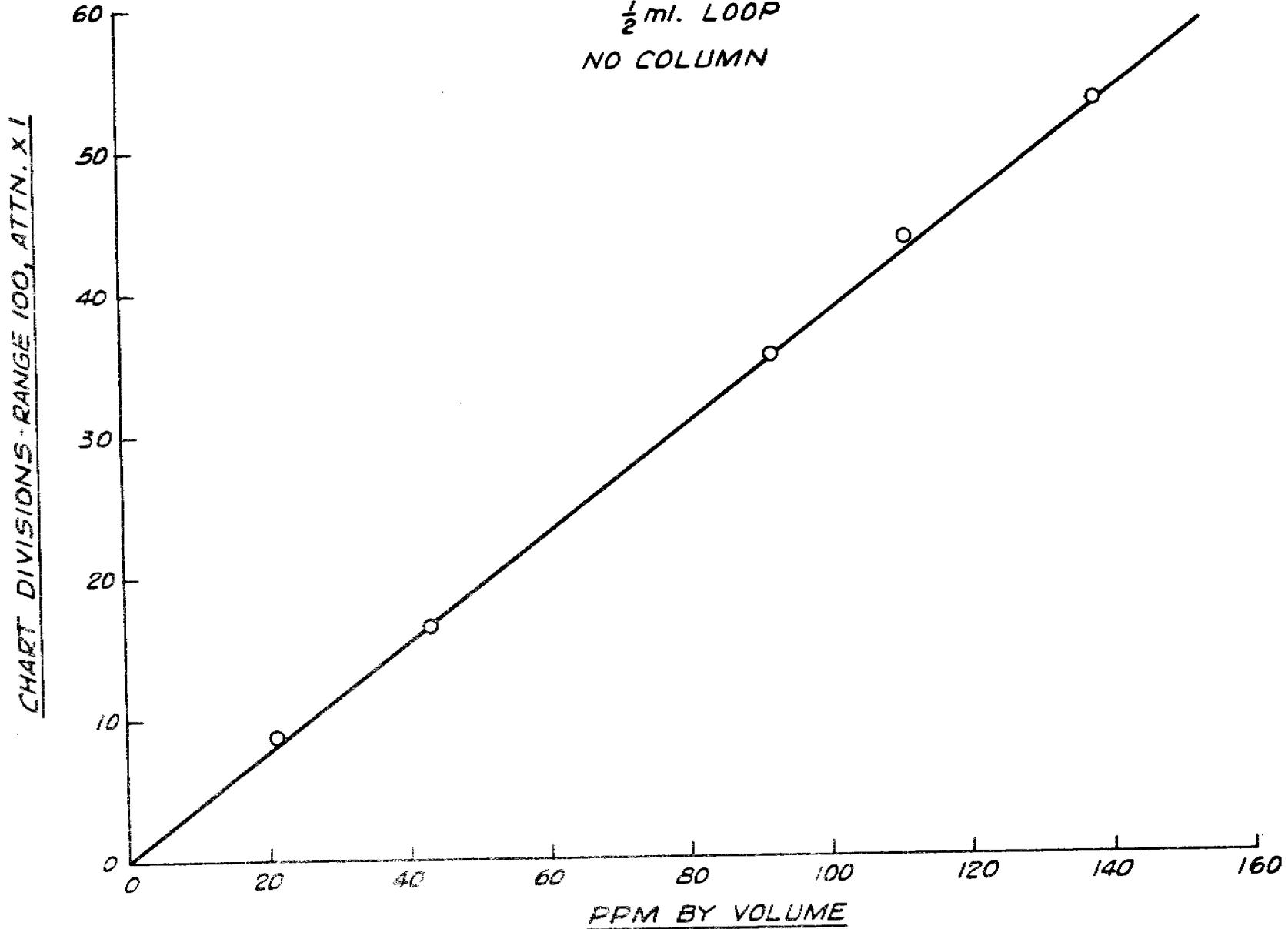
Various methods of preparing aqueous solutions of propane were investigated. The most convenient and reliable method for preparing solutions of adequate stability for testing the stripping unit appeared to be the syringe injection of the hydrocarbon into a known volume of air contained in a bulb containing also a known volume of water. Equilibrium was achieved in a 10-minute period of agitation and was found to be maintained for a period of at least 1 hour. This was sufficient time for determining the stripping efficiency of the system. Preparation of these solutions was found (by subsequent analyses) to be reproducible to ± 0.02 ppm. by weight.

A brief study of the feasibility of direct injection of these water samples was made under the operating conditions listed above. The flame was extinguished consistently with water samples exceeding 0.05 ml. and at times with samples of even less than 0.005 ml. volume. Aside from the difficulties encountered with the flame, variations were obtained also in the hydrocarbon response. These were attributed to poor reproducibility of the water sample size by hypodermic injection and to variable speed of injection and hence vaporization rate of the water. This preliminary study indicated that a column must be included in the system for the analysis of water samples by direct injection. Interest in a direct injection procedure lay not in the desire to perform the final on-stream analysis in this manner, but in the need to have an independent method for checking the hydrocarbon concentration of the aqueous calibration mixtures.

FIGURE 1

PROPANE IN NITROGEN

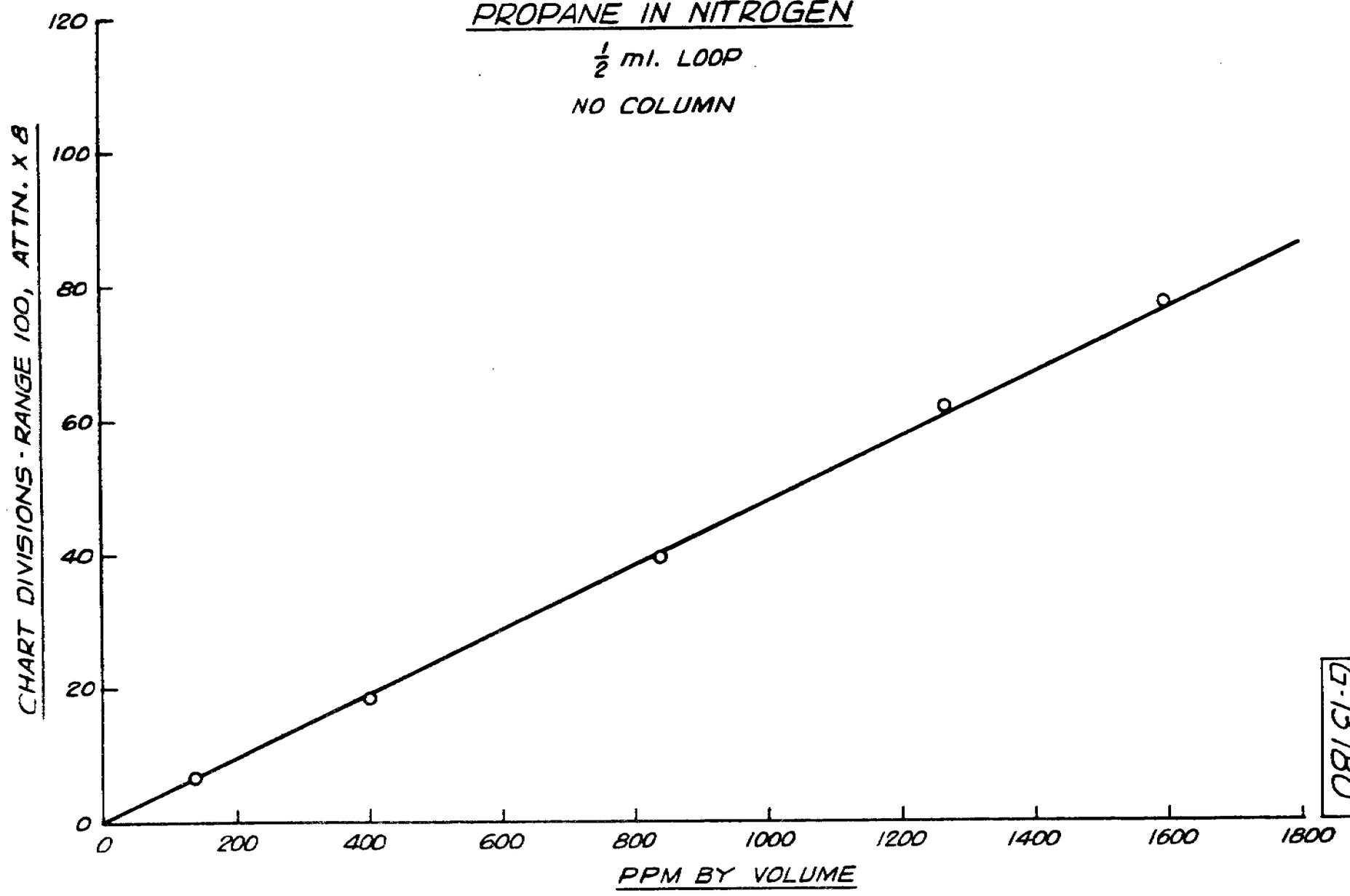
$\frac{1}{2}$ ml. LOOP
NO COLUMN



G-13779

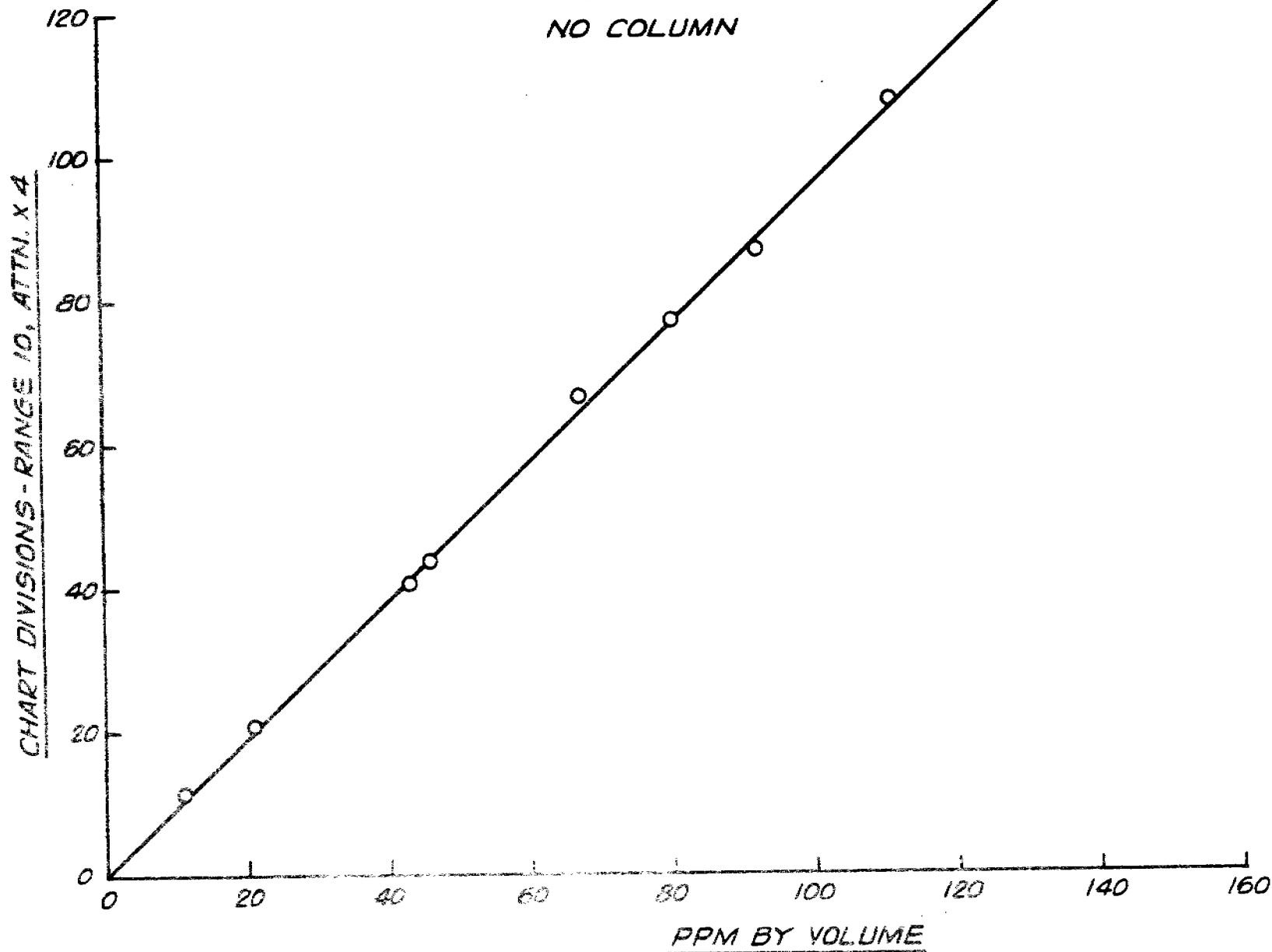
FIGURE 2
PROPANE IN NITROGEN

$\frac{1}{2}$ ml. LOOP
NO COLUMN



G-13780

FIGURE 3
PROPANE IN NITROGEN
 $\frac{1}{2}$ mi. LOOP
NO COLUMN



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FIGURE 4
FREON-12 IN NITROGEN

$\frac{1}{2}$ ml. LOOP
NO COLUMN

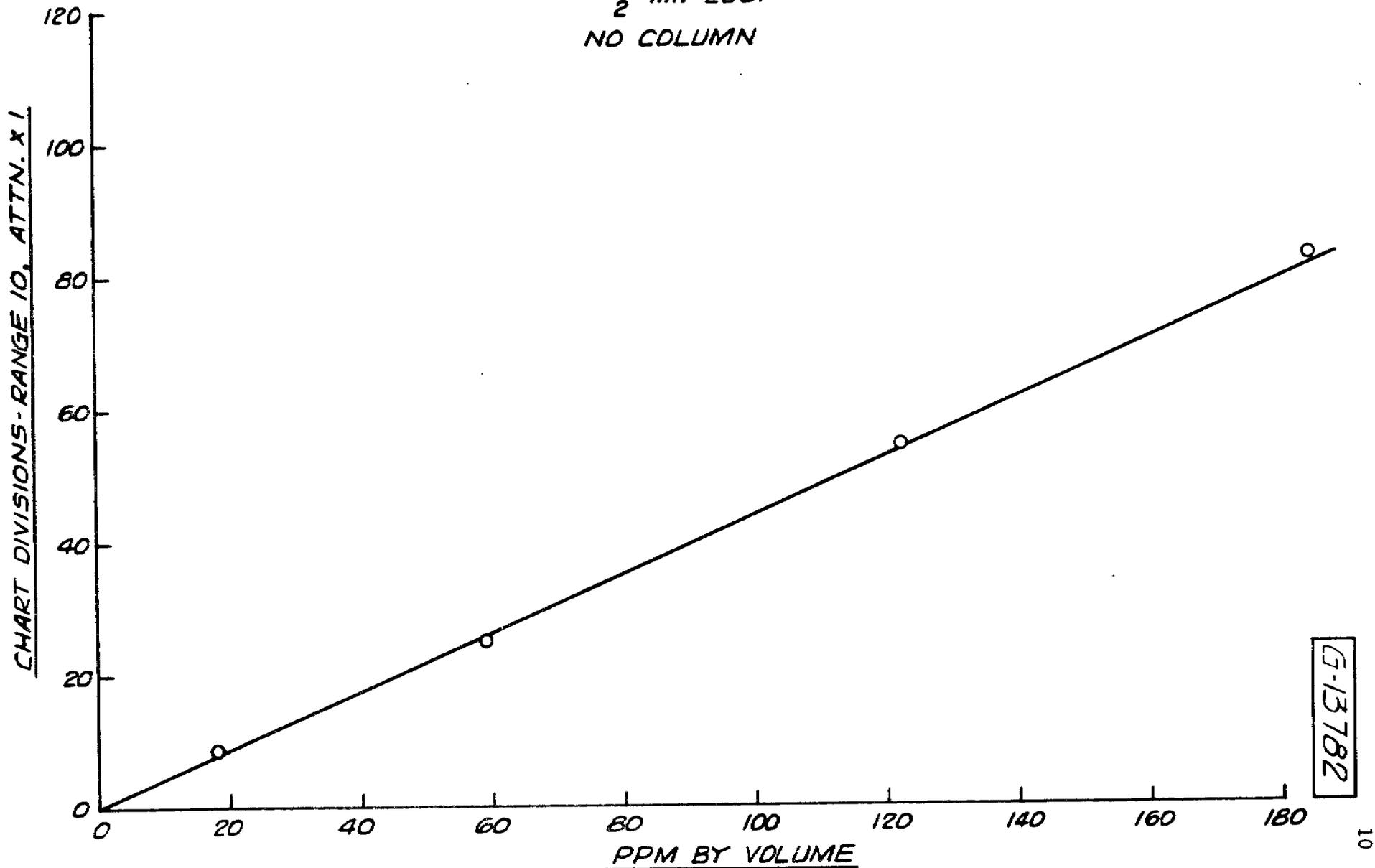
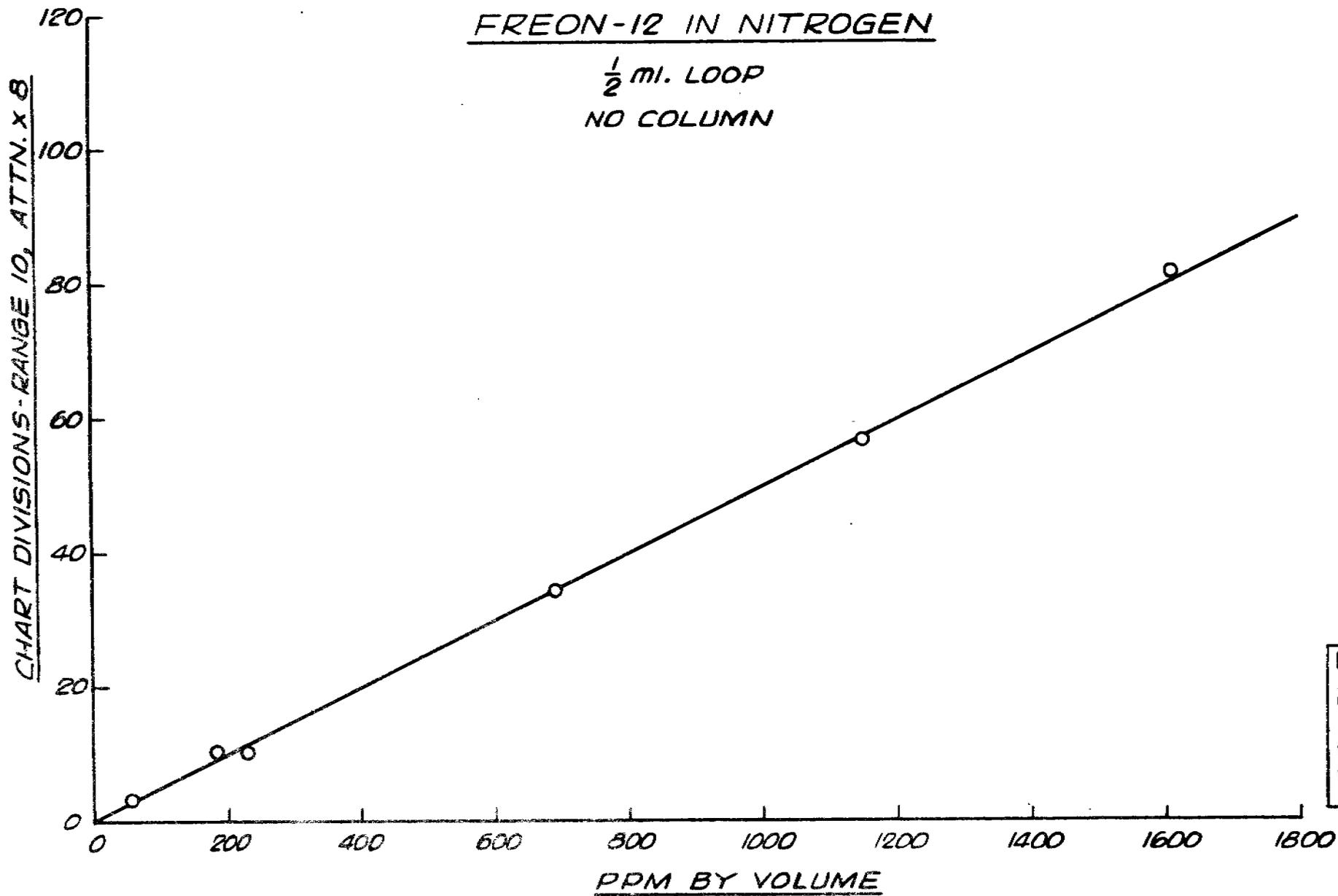


FIGURE 5

FREON-12 IN NITROGEN

$\frac{1}{2}$ MI. LOOP
NO COLUMN

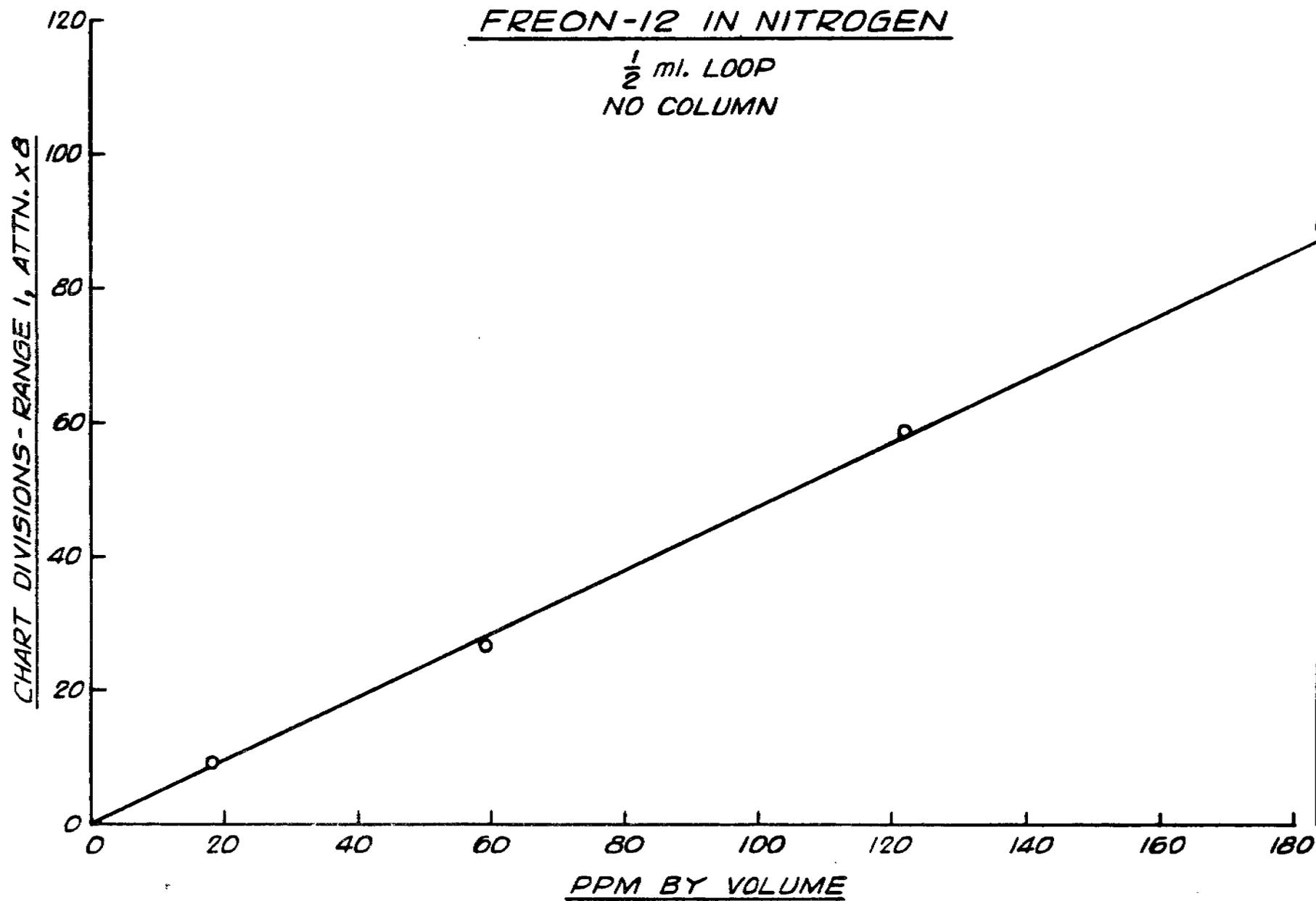


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FIGURE 6

FREON-12 IN NITROGEN

$\frac{1}{2}$ ml. LOOP
NO COLUMN



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A 2-foot chromatographic column, 1/4-inch in diameter and packed with the standard silicone rubber material supplied by the F & M Scientific Corporation was installed in the instrument. The injection port temperature was raised to 160°C. for a faster vaporization rate, but all other operating parameters were the same as those used for the calibration with gas mixtures with only the empty jumper tube. Synthetic gas mixtures were then analyzed by use of both syringe injection and gas sampling valve injection. Since addition of the column resulted in slightly lower response factors for propane and Freon-12, new calibration curves for both these compounds were prepared for both types of injection with the silicone rubber column. It was found that 0.05-ml. volumes of the water solutions could be injected under these conditions without extinguishing the flame and the appropriate curves used to calculate the concentration of the propane or the Freon-12.

Preliminary stripping tests were made using aqueous solutions prepared to contain 0.1 to 0.6 ppm. by weight of propane in distilled water. Results of these tests indicated stripping efficiencies of 92 to 99 per cent (Table I). When preliminary testing was begun with Freon-12 solutions, it was found that, due to the low response of Freon-12 relative to that of propane, the background signal and trace impurities from the water (when the direct injection procedure was used) were quite significant. Since solutions of concentrations above 1 ppm. by weight could be analyzed at an electrometer range setting high enough to make the water background negligible, preliminary runs were made using the high concentrations of Freon-12. Stripping efficiencies of 84 to 92 per cent were calculated on the basis of the direct injection procedure (Table II).

TABLE I

RESULTS OF PRELIMINARY STRIPPING TESTS WITH AQUEOUS SOLUTIONS OF PROPANE

<u>Propane Concentration in Original Solution, ppm by Weight (a)</u>	<u>Propane Concentration in Stripping Gas, ppm by Volume (b)</u>	<u>Propane Concentration in Original Solution, ppm by Weight Calc. from Stripping Gas Analysis</u>	<u>Per Cent Stripping</u>
0.10	59	0.10	100
0.26	143	0.25	96
0.64	340	0.59	92

(a) Analyzed by direct injection of water solution using the silicone rubber column.

(b) Using the silicone rubber column with the 1/2-ml. volume sample loop.

TABLE II

RESULTS OF PRELIMINARY STRIPPING TESTS WITH AQUEOUS SOLUTIONS OF FREON-12

<u>Freon-12 Concentration in Original Solution, ppm by Weight (a)</u>	<u>Freon-12 Concentration in Stripping Gas, ppm by Volume (b)</u>	<u>Freon-12 Concentration in Original Solution, ppm by Weight Calc. from Stripping Gas Analysis</u>	<u>Per Cent Stripping</u>
8.3	1454	7.3	88
4.5	755	3.8	84
4.5	790	4.1	92
2.2	386	1.9	86

(a) Analyzed by direct injection of water solution using the silicone rubber column.

(b) Using the silicone rubber column with the 1/2-ml. volume sample loop.

Because there are errors inherent in the calculation of the solution concentration by direct injection, due to human factors involved in measuring the very small samples used, and in the actual injection procedure itself (speed of injection), a more accurate picture of the stripping efficiency was considered to be that obtained from results of restripping the original stripped solution. Only an additional 1 to 2 per cent of the Freon-12 present in the original solution was found on restripping. At least for the low concentrations of Freon-12 (0.05 to 0.5 ppm. by weight) in water, this method of determining the stripping efficiency was believed to be more accurate than the direct injection procedure.

During this preliminary testing, difficulty was encountered in maintaining a constant pumping rate of the water in and out of the stripping unit. After replacement of springs and tests with various types of tubing supplied by the manufacturer, it was found that by using polyurethane tubing through the pump head a constant rate could be maintained in one direction for the period of time necessary to make several stripping tests. A stand-pipe arrangement was installed on the exit line from the stripper to maintain a constant water level in the unit. The lines from the reservoir to the pump and from the pump to the stripping unit were of 1/4-inch O.D. copper tubing to avoid adsorption of the hydrocarbon by Tygon tubing, rubber tubing, etc. that might have been chosen for use.

Since some time had elapsed during the solutions of the mechanical difficulties with the pump, several gas blends were prepared and analyzed in order to check the validity of the calibration curves. The response was found to have changed to a considerable degree. A water solution was prepared and analyzed. Reproducible results could not be obtained, and the absolute results failed to approach the concentration expected on the basis of past experience. The difficulty was traced to the accumulation of water in the chromatographic column. Since more time would have been needed than was available to prepare a new column and work out new conditions

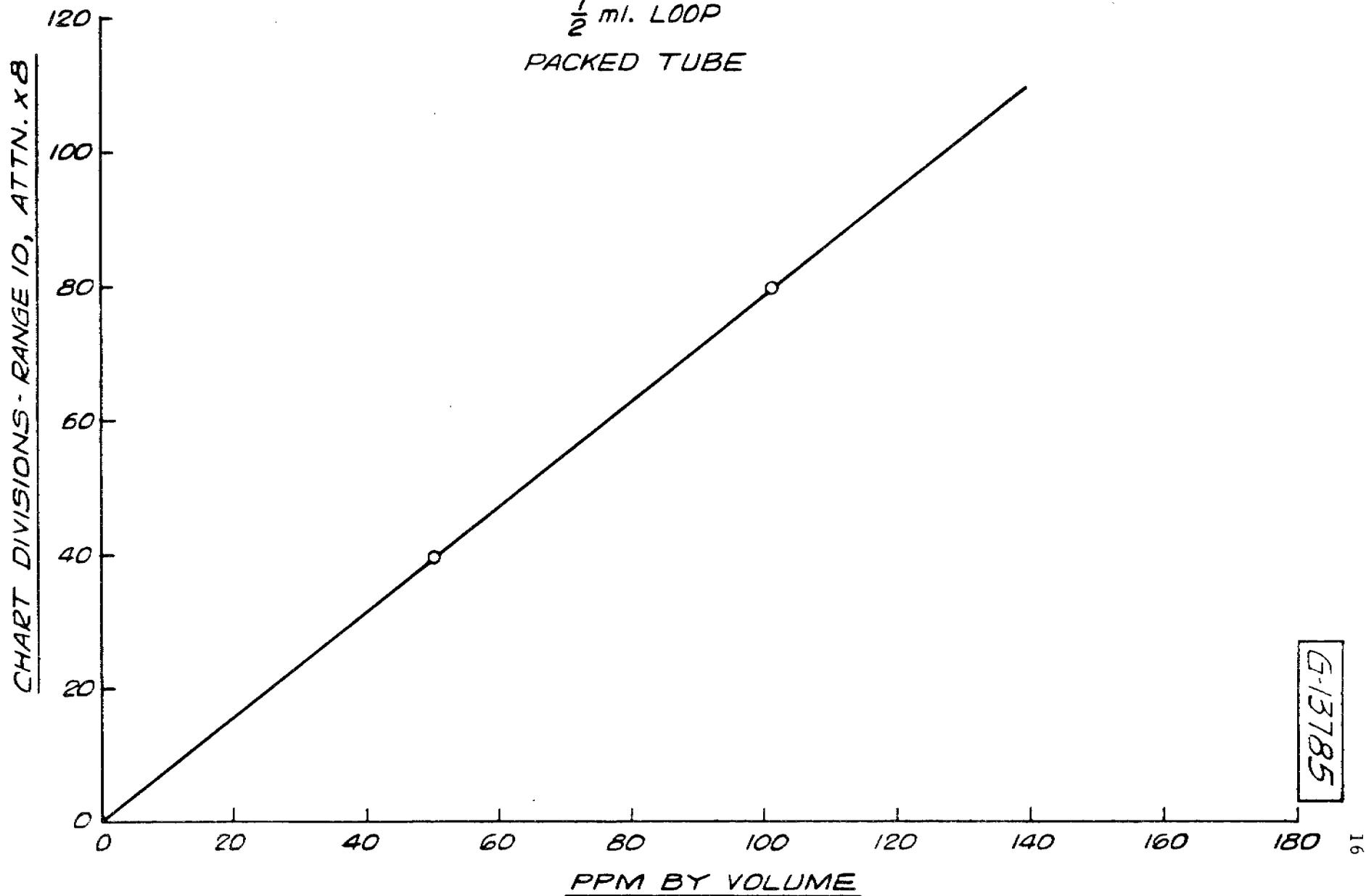
of analysis that would avoid water buildup in the column (for example, addition of column temperature controls to the system and/or a pre-column to absorb the water irreversibly and/or a back-flush arrangement to remove the water after the elution of the hydrocarbon, etc.), a second procedure was developed for determining the hydrocarbon content of the aqueous solution. The injection procedure would have had to have been discarded eventually when saline water mixtures were tested since injection of these solutions would have resulted in salt buildup in the injection port of the instrument.

This alternative method of ascertaining the concentration of the aqueous solution before stripping was as follows. The solution was prepared as before--a known volume of propane or Freon-12 was injected into a calibrated bulb containing known volumes of air and water, the mixture was subjected to a 10-minute period of agitation, and then it was allowed to stand at least 10 minutes to attain equilibrium. The air mixture above the water solution was analyzed and the amount of propane or Freon-12 in the water was found by subtracting the amount found in the air from the amount injected initially. For the analysis of the air mixture, 0.05-ml. volumes were injected by means of a gas-tight hypodermic syringe. Since the air mixtures were much more concentrated than the water solution, errors involved in the syringe measurement and the rate of injection were significant. To cut down the effect of the rate of injection, the jumper tube used in the initial calibration, was packed with an ordinary chromatographic packing material, 10 per cent by weight QF-1-0065 on Chromosorb P. Appropriate calibration curves were prepared over the range of 20 ppm. to 2 per cent by volume of propane and of Freon-12 by use of this packed tube with both gas sampling valve and syringe injection (see Figures 7-12).

Stripping unit conditions of operation were established as follows: water flow rate, 50 ml. per minute; nitrogen stripping gas rate, 50 ml. per minute; and disc rotating speed, 260 rpm. The detector unit was operated under the same conditions as previously described. Aqueous solutions of propane were prepared over the range of 0.05 to 2.0 ppm. by weight and the propane concentration determined by the air injection procedure. These solutions were stripped in the gas stripping unit and the stripping gas analyzed. The stripped solutions were then restripped and the stripping gas analyzed. The results of these analyses are shown in Table III.

FIGURE 7
PROPANE IN NITROGEN

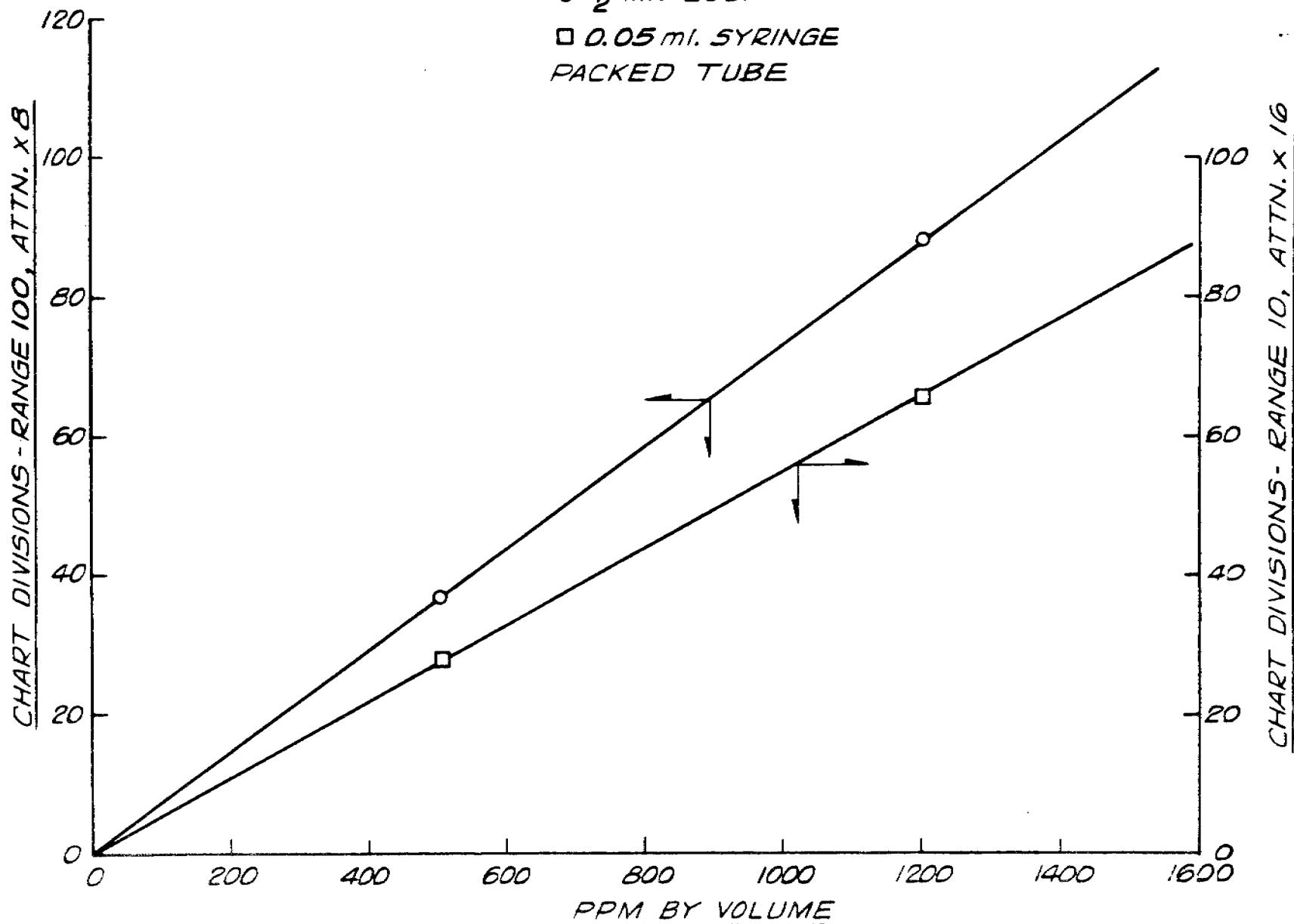
$\frac{1}{2}$ ml. LOOP
PACKED TUBE



G-13785

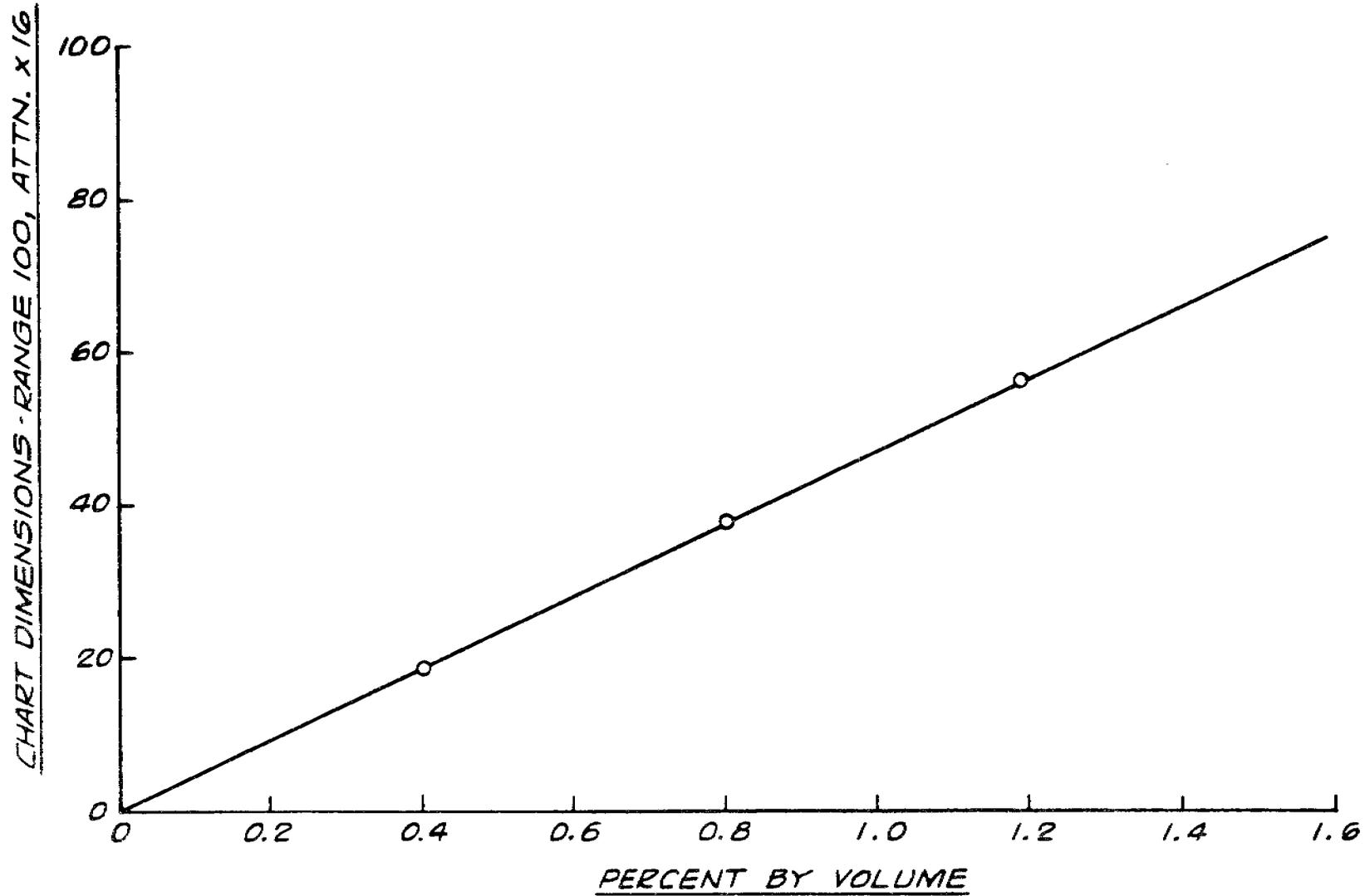
FIGURE 8
PROPANE IN NITROGEN

○ $\frac{1}{2}$ ml. LOOP
□ 0.05 ml. SYRINGE
PACKED TUBE



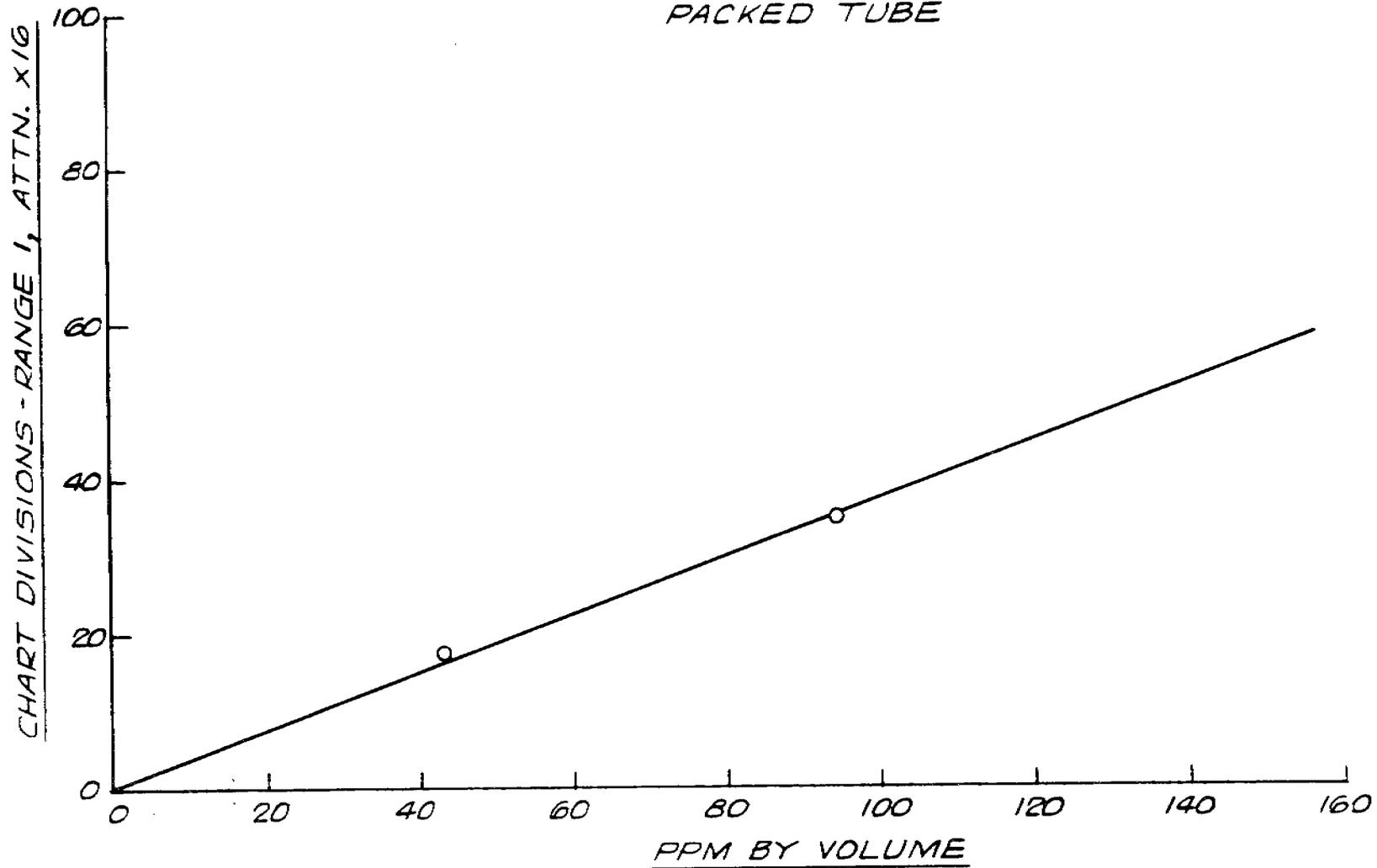
G-13786

FIGURE 9
PROPANE IN AIR
0.05 ml. SYRINGE
PACKED TUBE



G-13787

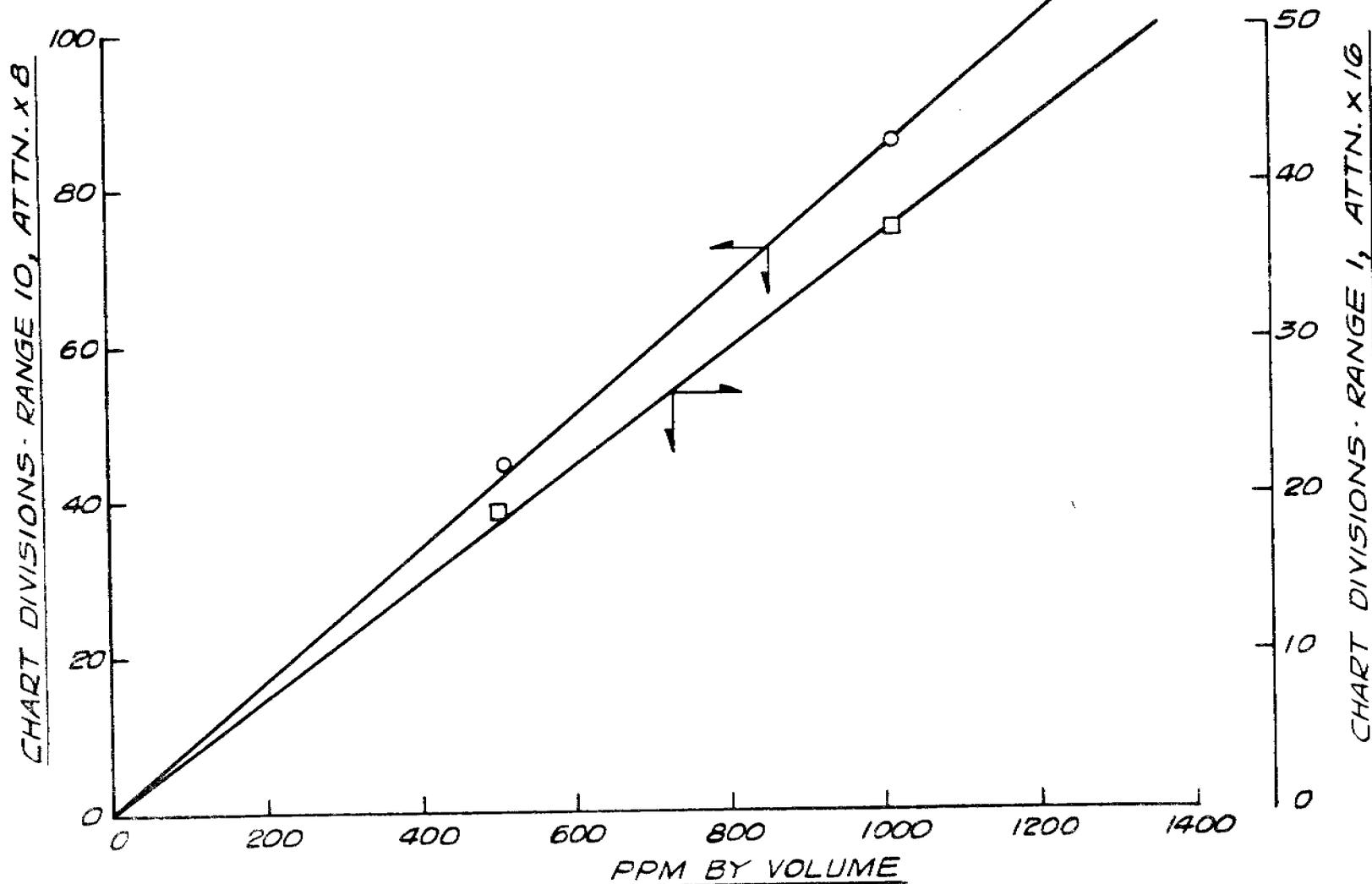
FIGURE 10
FREON-12 IN AIR
 $\frac{1}{2}$ ml. LOOP
PACKED TUBE



G-13788

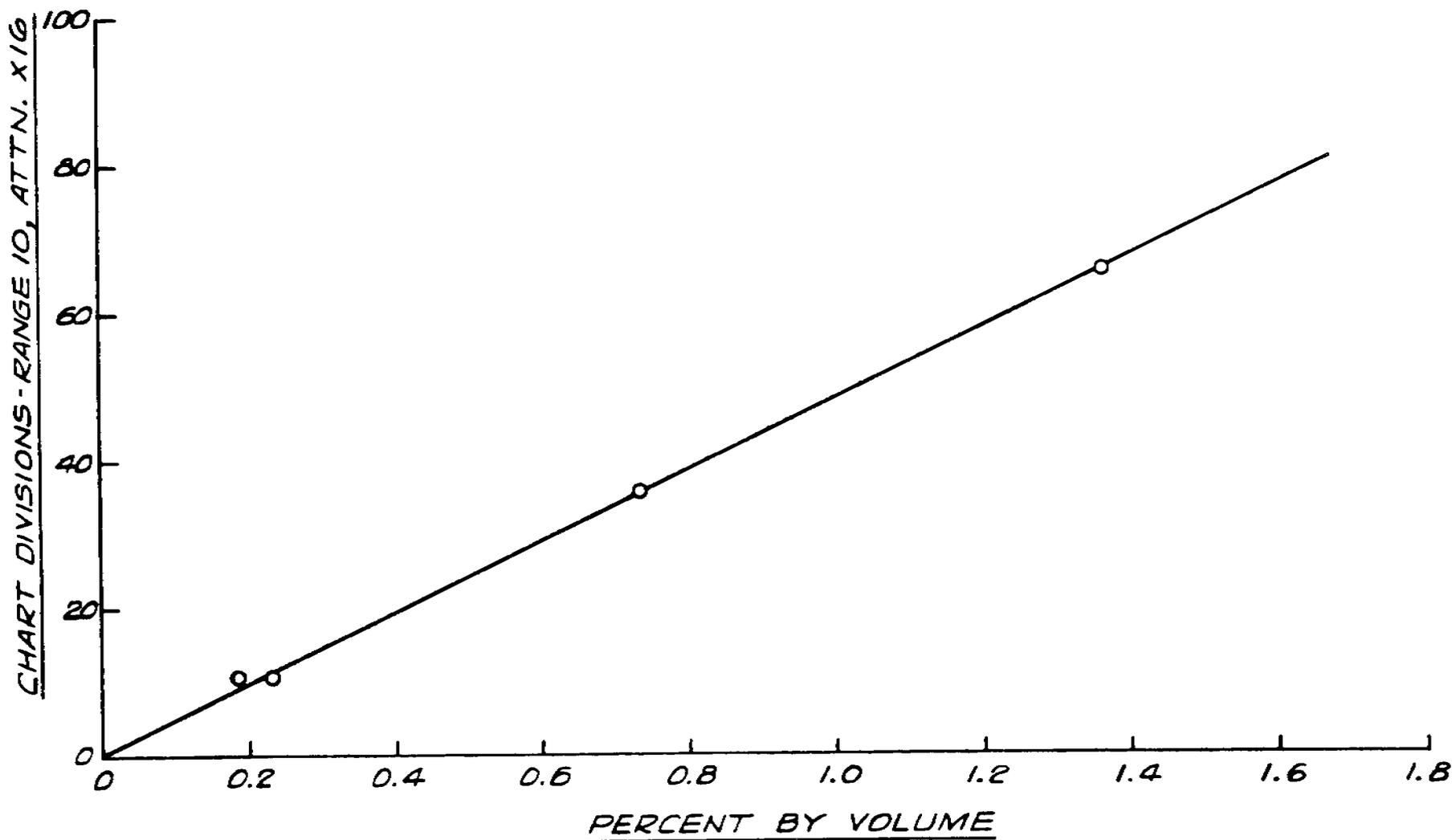
FIGURE 11
FREON-12 IN AIR

○ $\frac{1}{2}$ ml. LOOP
□ 0.05 ml. SYRINGE
PACKED TUBE



5-13789

FIGURE 12
FREON-12 IN AIR
0.05 ml. SYRINGE
PACKED TUBE



G-13790

TABLE III

DETERMINATION OF PROPANE IN WATER

<u>Propane,</u> <u>ppm by Weight</u>	<u>Per Cent Recovery</u> <u>Calculated from</u> <u>Complete Analysis</u>	<u>Per Cent Stripping</u> <u>Calculated from</u> <u>Air Injection Procedure</u>	<u>Per Cent Stripping</u> <u>Calculated</u> <u>from Analysis</u> <u>on Restripping</u>
0.049	99	94	99
0.117	99	92	98
0.129	101	104	100
0.167	100	100	100
0.222	102	102	98
0.510	101	90	98
0.988	102	101	98
1.98	101	97	99

In this table the per cent recovery was calculated from the total amount of propane found from the three analyses and the amount of propane initially injected to prepare the solution. These values give an indication of the overall accuracy of this procedure for preparing standard solutions. The "per cent stripping calculated from air injection procedure" values were calculated from the amount of propane in the aqueous solution as determined by the air injection procedure and the amount of propane determined by analysis of the stripping gas from the first stripping. The last column, "per cent stripping calculated from analysis on restripping" was calculated by subtracting from 100 per cent the per cent of the original sample found on restripping the stripped solution. Aqueous solutions of Freon-12 were also prepared and analyzed in the same manner as the propane solutions. The results are shown in Table IV.

TABLE IV

DETERMINATION OF FREON-12 IN WATER

<u>Freon-12,</u> <u>ppm by Weight</u>	<u>Per Cent Recovery</u> <u>Calculated from</u> <u>Complete Analysis</u>	<u>Per Cent Stripping</u> <u>Calculated from</u> <u>Air Injection Procedure</u>	<u>Per Cent Stripping</u> <u>Calculated</u> <u>from Analysis</u> <u>on Restripping</u>
0.071	104	117	100
0.079	98	94	100
0.295	94	82	98
0.795	93	79	97
0.950	107	124	100

A study of the effect of changing flow rate on the stripping efficiency of the unit was made using propane solutions of approximately 0.1 ppm. by weight. Ratios of water flow to nitrogen flow of 1 to 1, 1 to 1.5, 1 to 2,

and 2 to 1 were studied, and efficiencies of 99 and 100 per cent were calculated. Actual results of changing these variables are shown in Table V.

TABLE V
STUDY OF STRIPPING CONDITIONS

<u>Propane,</u> <u>ppm by Weight</u>	<u>Water Flow,</u> <u>ml./min.</u>	<u>Nitrogen Flow,</u> <u>ml./min.</u>	<u>Per Cent</u> <u>Recovery</u>	<u>Per Cent</u> <u>Stripping</u> <u>(Injection)</u>	<u>Per Cent</u> <u>Stripping</u> <u>(Restripping)</u>
0.133	50	25	99	91	99
0.132	50	25	98	91	100
0.141	50	75	100	97	99
0.161	25	50	102	111	100
0.163	35	35	102	112	100

Since there is a possible need for this method in pilot plant desalination studies where the hydrocarbon or Freon-12 content in the effluent streams may be greater than 10 ppm. by weight, one solution of Freon-12 of about 130 ppm. by weight was run through the stripping unit. The effluent gas was analyzed and the effluent water from the unit was restripped. Less than 2 per cent of the original concentration was found in the second stripping gas analysis. On the basis of this test it is believed that this method can be applied to solutions of much higher hydrocarbon or Freon-12 concentration than 2 ppm. by weight.

Phase 4

Application of the method to synthetic sea water and actual sea water samples and to aqueous solutions of C₄ hydrocarbons.

Solutions of both propane and Freon-12 were prepared in artificial sea water (6% synthetic brine), and stripping efficiencies were determined. These results are shown in Tables VI and VII. Again the stripping efficiencies based on the analysis of the restripped solution are 98 to 100 per cent. The poor results for the per cent stripping calculated from the air injection analysis are believed to be due entirely to the difficulty of this injection. Since the solubility of both propane and Freon-12 is much less in brine than in distilled water, the concentrations of these compounds in the air mixture were much higher. Errors in this analysis therefore became quite significant in terms of overall recovery. Syringe injection of the air-Freon-12 mixtures was particularly difficult to reproduce consistently.

TABLE VI

DETERMINATION OF PROPANE IN SYNTHETIC BRINE

<u>Propane,</u> <u>ppm by Weight</u>	<u>Per Cent Recovery</u> <u>Calculated from</u> <u>Complete Analysis</u>	<u>Per Cent Stripping</u> <u>Calculated from</u> <u>Air Injection Procedure</u>	<u>Per Cent Stripping</u> <u>Calculated from</u> <u>Analysis on Restripping</u>
0.035	100	103	100
0.082	97	82	100
0.202	97	84	100
0.501	95	74	100
0.947	96	78	100
0.982	105	145	100
2.76	97	86	98

TABLE VII

DETERMINATION OF FREON-12 IN SYNTHETIC BRINE

<u>Freon-12,</u> <u>ppm by Weight</u>	<u>Per Cent Recovery</u> <u>Calculated from</u> <u>Complete Analysis</u>	<u>Per Cent Stripping</u> <u>Calculated from</u> <u>Air Injection Procedure</u>	<u>Per Cent Stripping</u> <u>Calculated from</u> <u>Analysis on Restripping</u>
0.043	89	70	100
0.086	92	70	100
0.267	92	71	100
0.481	85	55	100
0.486	87	59	100
1.06	92	72	98

In an attempt to resolve this difficulty, a limited amount of work was done using a Perkin-Elmer chromatograph with thermal conductivity detection. A 50-ft. column of n-propylsulfone and dimethylsulfolane on Columpak was employed at an operating temperature of 35°C. This long column allowed sufficient time for equilibrium after sample injection so that the speed of the injection, the human factor, was virtually eliminated. Several Freon-12 solutions (0.95 ppm by weight) were prepared and the air mixtures analyzed by both methods. With the use of the results obtained with the Perkin-Elmer instrument for the air concentration, the stripping efficiency calculated from the air injection procedure was 100 ± 5 per cent. This figure was in good agreement with that obtained for the stripping efficiency as calculated on the basis of the restripping. This brief study reconfirmed the earlier belief that the results obtained on restripping the stripped solution were the more meaningful values in determining the efficiency of the stripper unit.

Since the Perkin-Elmer instrument was not available for prolonged use, an attempt was made to improve the analysis of the air mixture using the ionization detector. A system was devised for injecting this mixture by means of the sample loop of the stripping system rather than by means of a syringe. This procedure was followed for the solutions prepared for studying the applicability of the method to C₄ hydrocarbons used in freezing processes for the desalination of sea water. Although manipulation of the large bulbs was difficult, improved results were obtained. Tables VIII, IX and X show the stripping efficiencies obtained with isobutane, n-butane, and butene-1. The calibration curves for these compounds prepared from the analysis of synthetic mixtures (Figures 13-15) show the detector response to these C₄ hydrocarbons to be linear over the range investigated. This response was also found to be very nearly that predicted on the basis of a theoretical calculation of their effective carbon numbers from data reported by Morris and Chapman (19).

TABLE VIII

DETERMINATION OF ISOBUTANE IN WATER

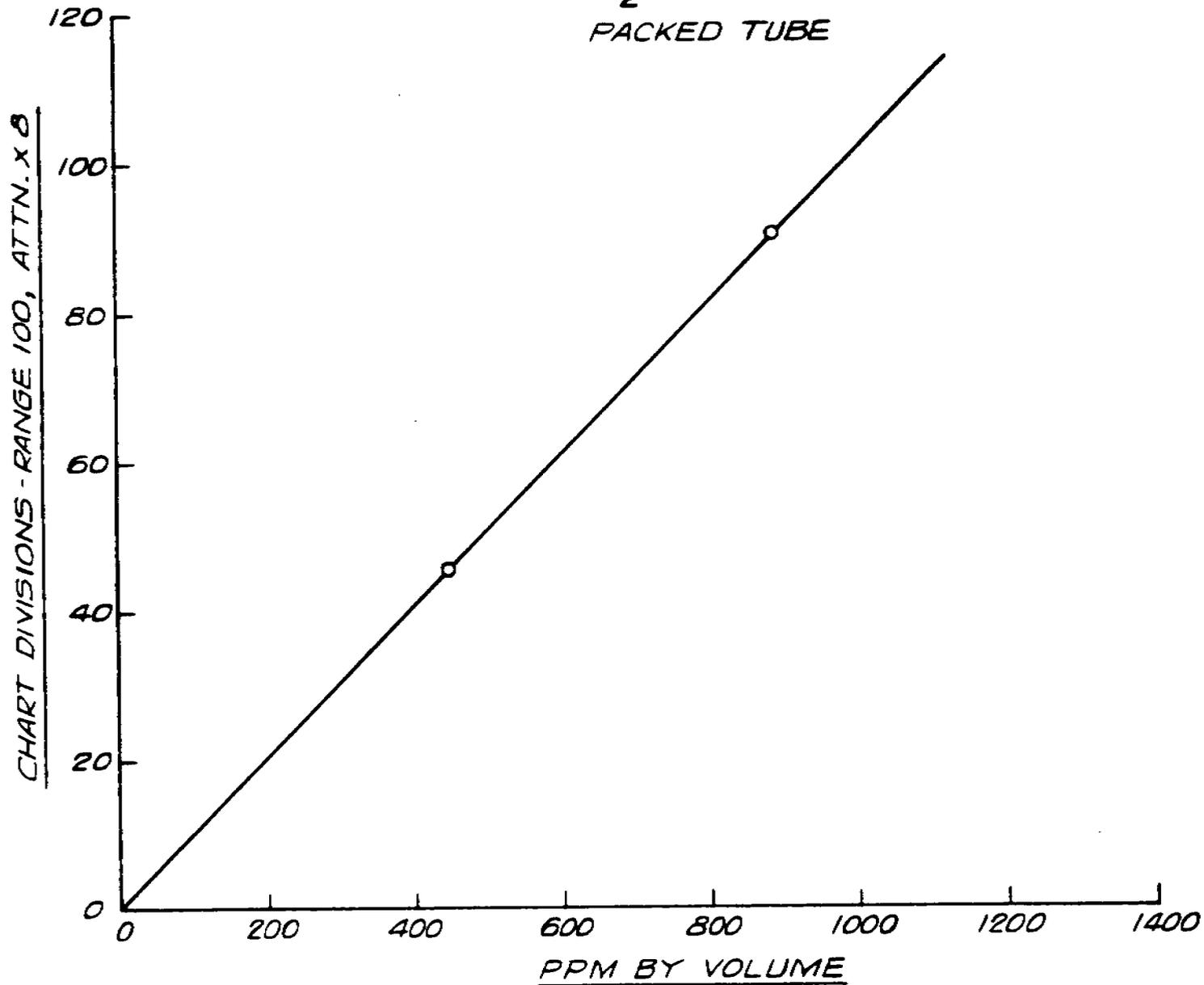
<u>Isobutane,</u> <u>ppm by Weight</u>	<u>Per Cent Recovery</u> <u>Calculated from</u> <u>Complete Analysis</u>	<u>Per Cent Stripping</u> <u>Calculated from</u> <u>Air Injection Procedure</u>	<u>Per Cent Stripping</u> <u>Calculated from</u> <u>Analysis on Restripping</u>
0.224	100	99	98
0.269	98	84	100

TABLE IX

DETERMINATION OF n-BUTANE IN WATER

<u>n-Butane,</u> <u>ppm by Weight</u>	<u>Per Cent Recovery</u> <u>Calculated from</u> <u>Complete Analysis</u>	<u>Per Cent Stripping</u> <u>Calculated from</u> <u>Air Injection Procedure</u>	<u>Per Cent Stripping</u> <u>Calculated from</u> <u>Analysis on Restripping</u>
0.127	103	115	98
0.231	100	99	100
0.266	101	105	100
0.602	103	112	98
1.03	99	91	98

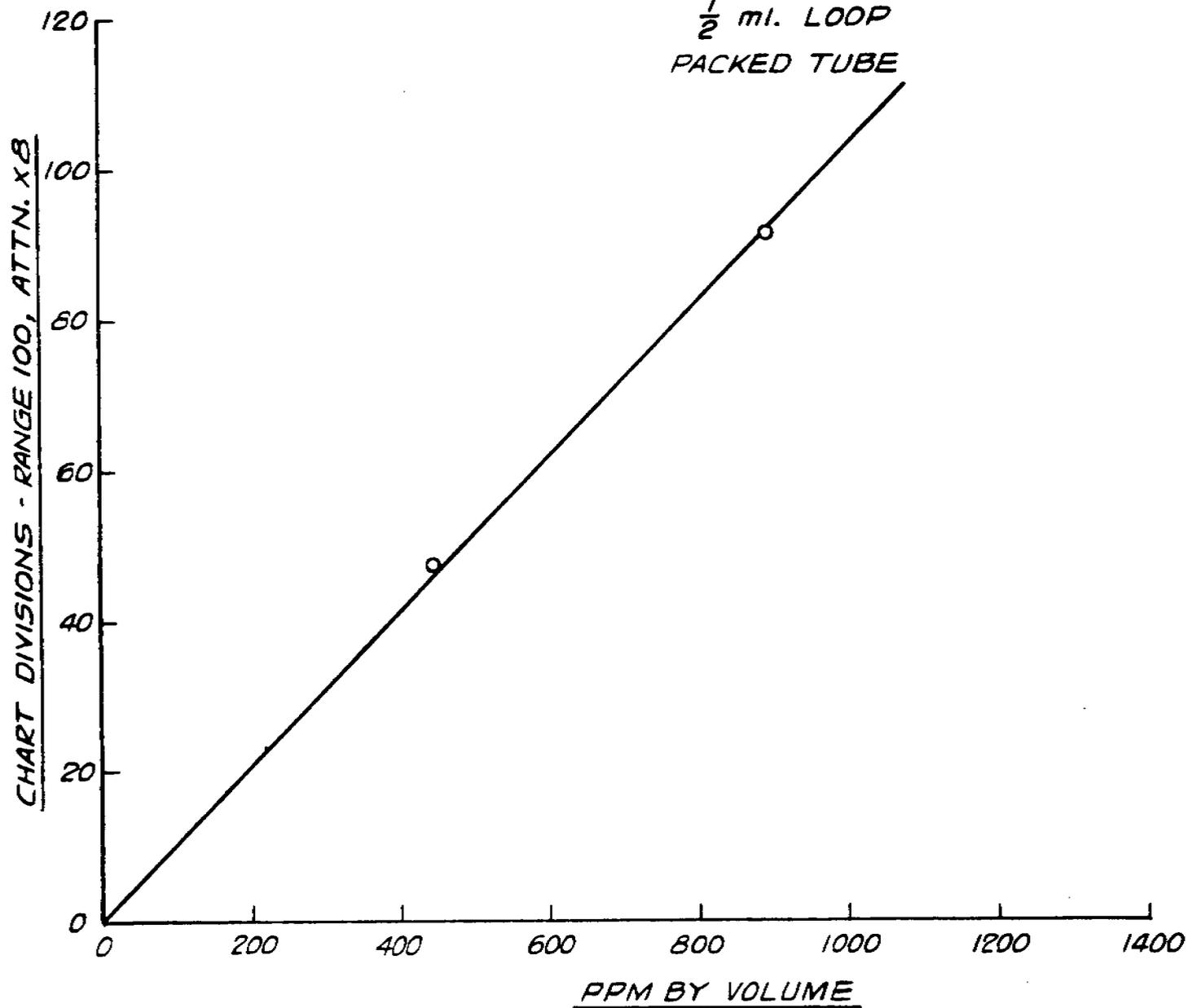
FIGURE 13
ISOBUTANE IN AIR
 $\frac{1}{2}$ MI. LOOP
PACKED TUBE



G-13791

FIGURE 14
n-BUTANE IN AIR

$\frac{1}{2}$ ml. LOOP
PACKED TUBE



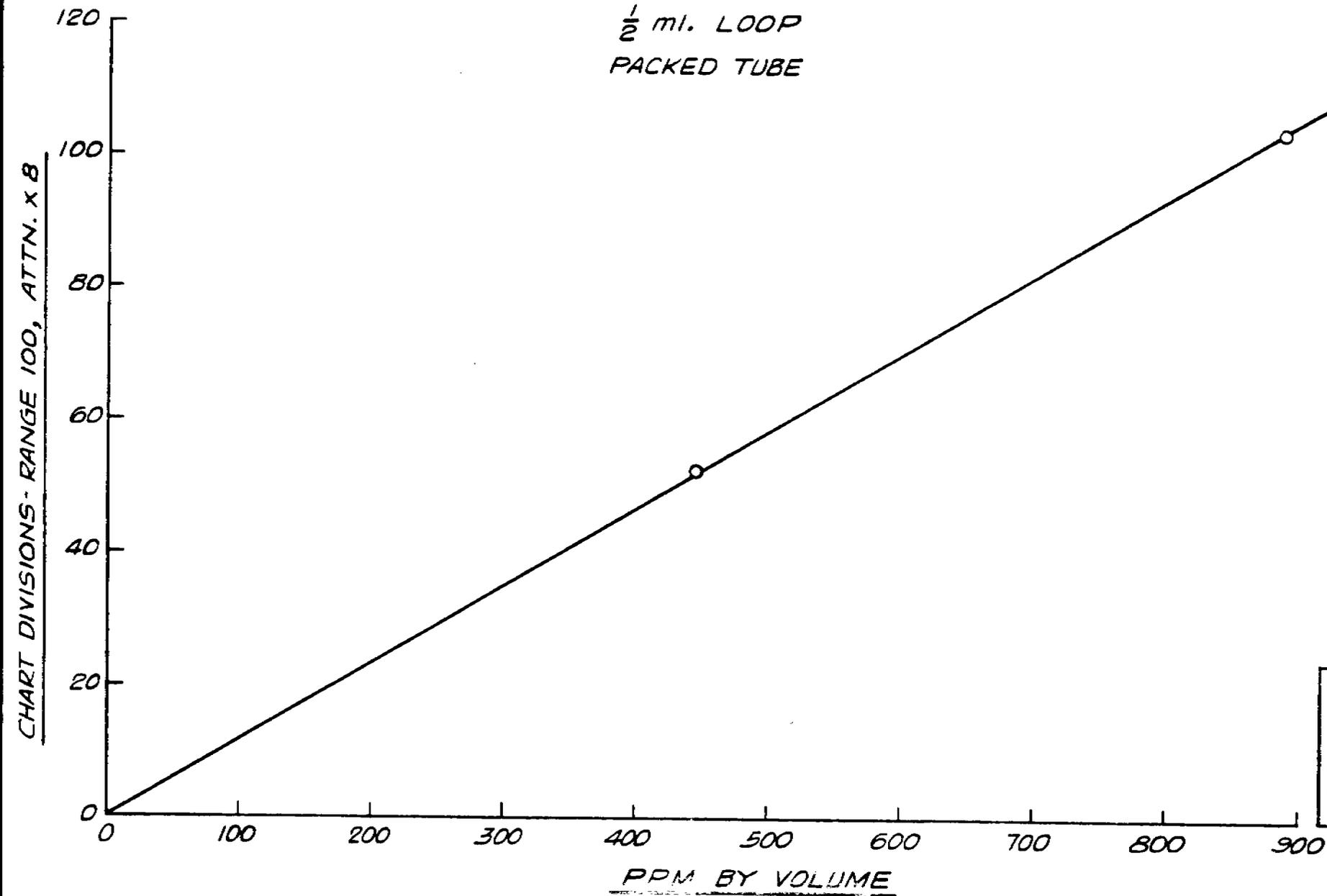
G-13792

FIGURE 15

BUTENE-1 IN AIR

$\frac{1}{2}$ ml. LOOP

PACKED TUBE



G-13793

TABLE X

DETERMINATION OF BUTENE-1 IN WATER

Butene-1, ppm by Weight	Per Cent Recovery Calculated from <u>Complete Analysis</u>	Per Cent Stripping Calculated from <u>Air Injection Procedure</u>	Per Cent Stripping Calculated from <u>Analysis on Restripping</u>
0.123	106	114	98
0.346	110	121	100

The concluding experimental work on this project was carried out with actual sea water samples obtained from Wrightsville Beach, North Carolina. The water was sampled at two locations: 1) 1,000 ft. out from the shore, and 2) at the suction pump near the site of a proposed Koppers Company pilot plant. These samples were believed to be typical of the sea water having normal contamination from sea-going vessel engine oil, exhaust, etc. and possible contamination from pipe lines, pump oil, etc. used to supply the water to the plant. These samples were stripped under the conditions established and the stripping gas analyzed both with the packed tube and with the empty tube. The trace hydrocarbon peak noted was the same as that obtained from stripping our laboratory distilled water and calculated to less than 1 ppb. by weight in the water. In order to be sure that no components in the sea water would hinder the stripping of the hydrocarbon from it, a propane and a Freon-12 solution were prepared in sea water from each location. These solutions were analyzed, stripped, and restripped as described previously and the stripping efficiency calculated as before. Based on the analysis of the stripping gas from the second stripping, the efficiencies are again 98 to 100 per cent (see Tables XI and XII).

TABLE XI

DETERMINATION OF PROPANE IN ACTUAL SEA WATER

Propane; ppm by Weight	Per Cent Recovery Calculated from <u>Complete Analysis</u>	Per Cent Stripping Calculated from <u>Air Injection Procedure</u>	Per Cent Stripping Calculated from <u>Analysis on Restripping</u>
0.128	93	72	100
0.289	93	75	100

TABLE XII

DETERMINATION OF FREON-12 IN ACTUAL SEA WATER

Freon-12, ppm by Weight	Per Cent Recovery Calculated from <u>Complete Analysis</u>	Per Cent Stripping Calculated from <u>Air Injection Procedure</u>	Per Cent Stripping Calculated from <u>Analysis on Restripping</u>
0.133	95	83	100
0.286	95	85	99

Another attempt was made to improve the calculation of the per cent stripping from the air analysis procedure. According to the manufacturer's experimental considerations, the conditions for operation of the detector unit at its maximum sensitivity were also the conditions at which the best linearity of response was obtained. Since the operating parameters of this method were not established to obtain maximum response, it was decided to adjust the fuel gas and carrier gas flow rates to the ratio recommended for maximum response per mole of hydrocarbon. Under the new conditions, the flow rate of nitrogen was about 70 ml. per minute and that of hydrogen, about 40 ml. per minute; the air flow rate was kept at 275 ml. per minute; the flame temperature was about 135°C. Several synthetic gas mixtures of Freon-12 in air and propane in air were prepared and analyzed under these conditions. Calibration curves were drawn as shown in Figures 16 to 19. Three solutions each of propane and of Freon-12 were prepared in 6 per cent brine and the analytical procedure carried out as previously described. The improvement in the results of the "per cent stripping calculated from air injection procedure" indicated that the best linearity of response was necessary when the analyses of two mixtures of widely different concentrations were to be used in the same calculation. As shown in Tables XIII and XIV, the per cent stripping calculated by both methods is in good agreement, particularly when it is considered that 1) an additional 1 to 2 per cent is often found on restripping, and 2) there is the possibility that a small amount of material may be adhering to the walls of the solution reservoir.

TABLE XIIIDETERMINATION OF PROPANE IN SYNTHETIC BRINE
(Maximum Sensitivity)

Propane, ppm by Weight	Per Cent Recovery Calculated from <u>Complete Analysis</u>	Per Cent Stripping Calculated from <u>Air Injection Procedure</u>	Per Cent Stripping Calculated from <u>Analysis on Restripping</u>
0.054	100	98	100
0.107	99	94	100
0.200	100	100	100

FIGURE 16

PROPANE IN AIR

$\frac{1}{2}$ mi. LOOP

PACKED TUBE

MAXIMUM SENSITIVITY

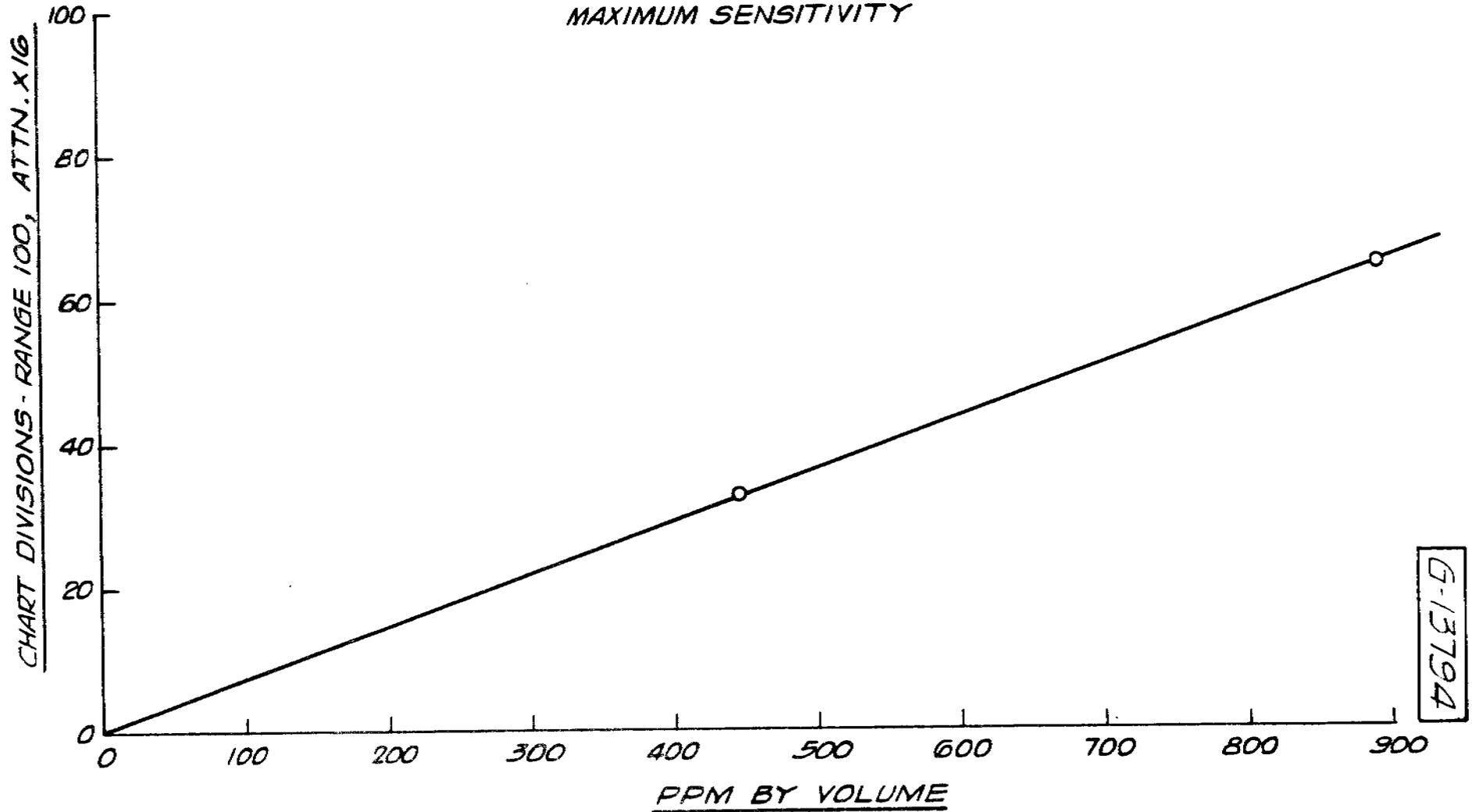


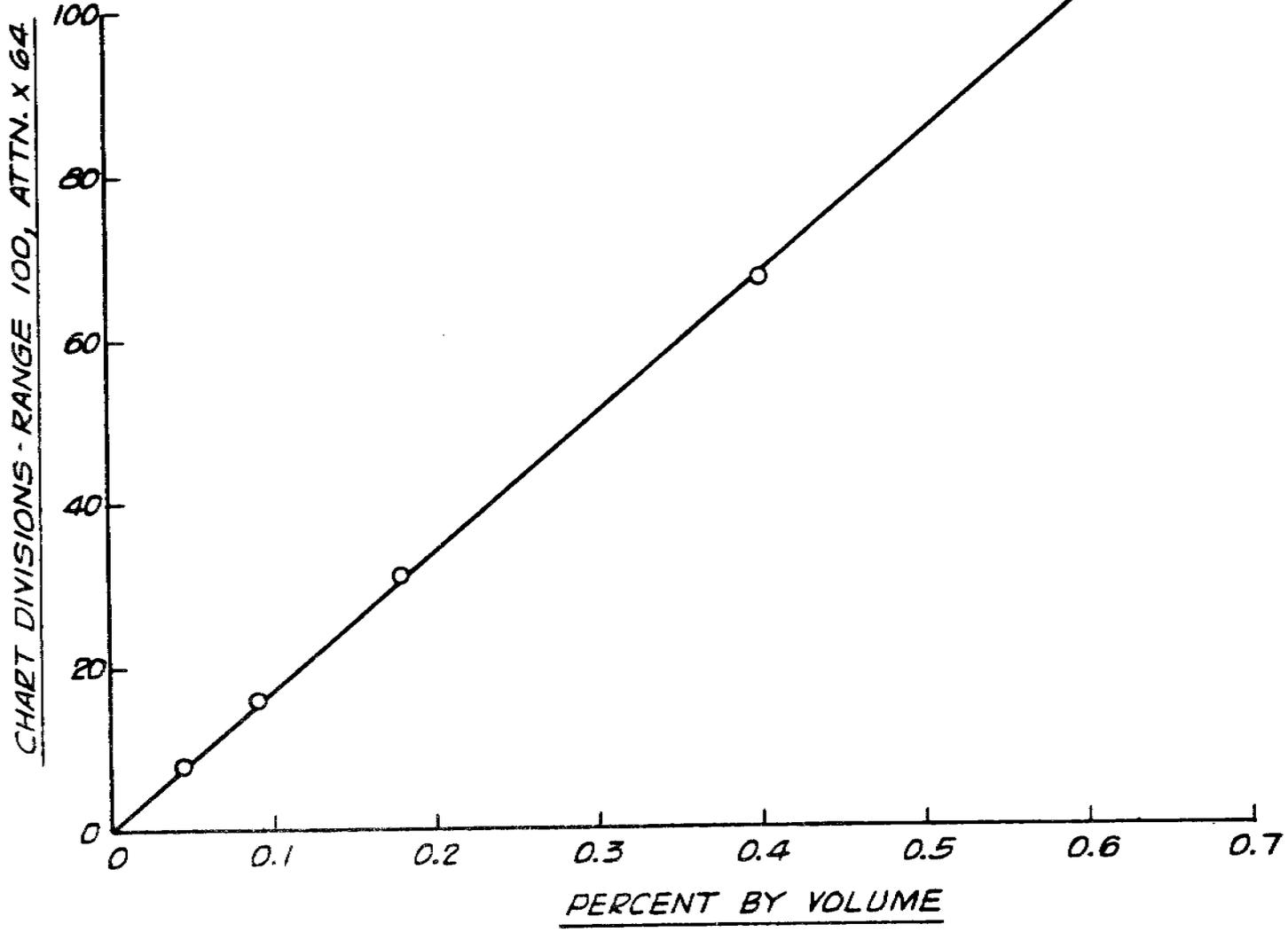
FIGURE 17

PROPANE IN AIR

$\frac{1}{2}$ ml. LOOP

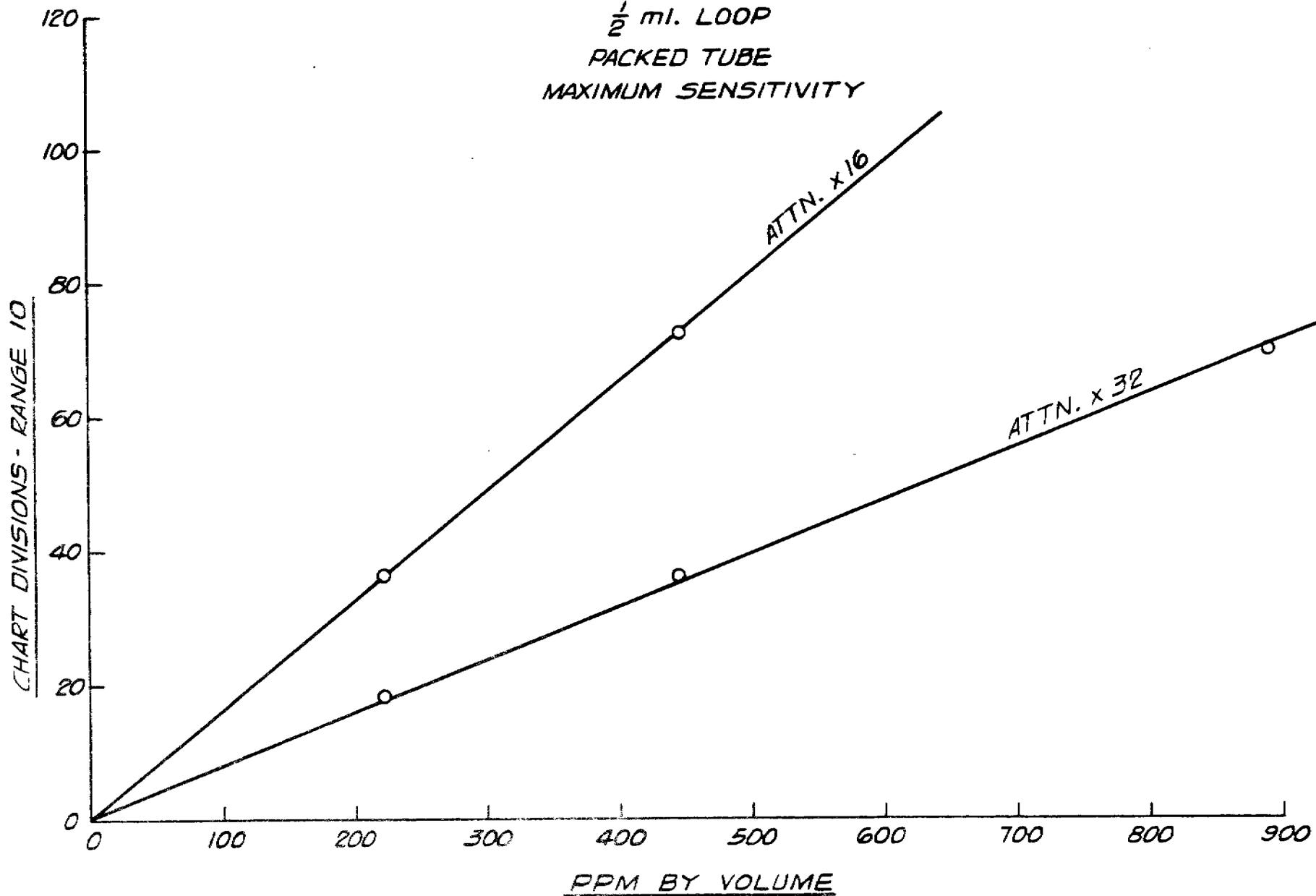
PACKED TUBE

MAXIMUM SENSITIVITY



G-13795

FIGURE 18
FREON-12 IN AIR
 $\frac{1}{2}$ ml. LOOP
PACKED TUBE
MAXIMUM SENSITIVITY



G-13796

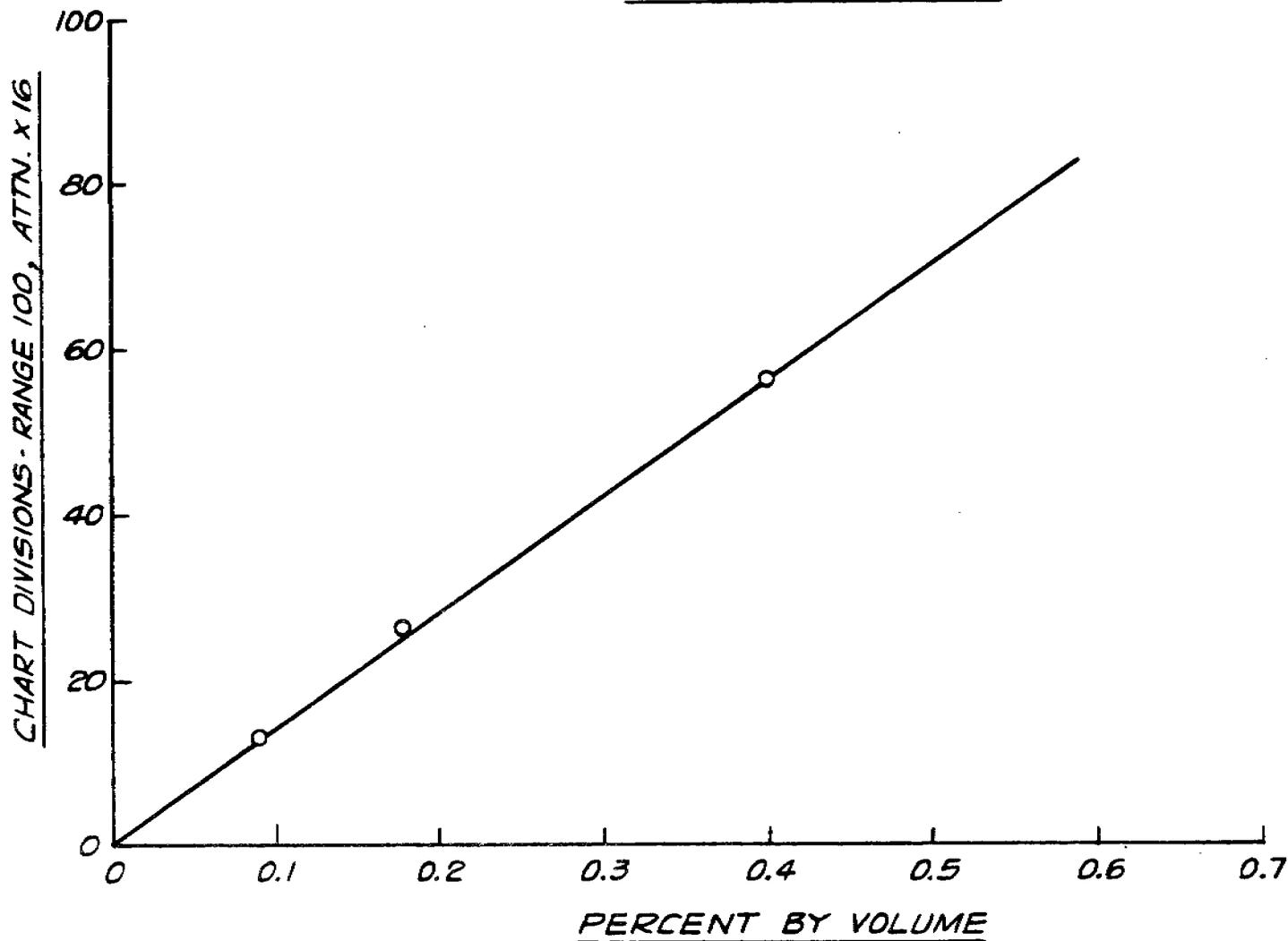
FIGURE 19

FREON-12 IN AIR

$\frac{1}{2}$ ml. LOOP

PACKED TUBE

MAXIMUM SENSITIVITY



G-13797

TABLE XIV

DETERMINATION OF FREON-12 IN SYNTHETIC BRINE
(Maximum Sensitivity)

<u>Freon-12, ppm by Weight</u>	<u>Per Cent Recovery Calculated from Complete Analysis</u>	<u>Per Cent Stripping Calculated from Air Injection Procedure</u>	<u>Per Cent Stripping Calculated from Analysis on Restripping</u>
0.064	98	93	100
0.152	98	94	98
0.590	98	92	100

Phase 5

Design of a prototype instrument for on-stream analysis.

At the conclusion of the experimental work on the development of this analytical method, the instrumentation and flow system established were found to be free from operational difficulties and to furnish reliable information in a brief period of time. Specifications for the various components of the system and for the design of the prototype analyzer were prepared by Koppers Research Department engineers. Their schematic diagram and list of specifications are attached (see Appendix I).

B. Construction, Testing and Installation of the Analytical Unit

The prototype instrument described above was used as a basis for the design of the hydrocarbon analyzer. After solicitation of bids and consultation with several instrument manufacturers, the contract for construction of the analyzer was awarded to Research Appliance Company, Allison Park, Pennsylvania on September 25, 1963. The completed analytical unit was delivered to the Monroeville Research Center on December 31, 1963. A front view of the instrument is shown in Figure 20. Features which are included in the analyzer that were not investigated as a part of the development of the prototype instrument are:

- (1) Compact installation in a console.
- (2) A timing device which permits either automatic sampling at intervals from 10 minutes to 12 hours or manual operation. A second timing device which permits varying the sampling period from 1/2 to 15 minutes.
- (3) The recorder chart drive operates only during the automatic or manual sampling periods.

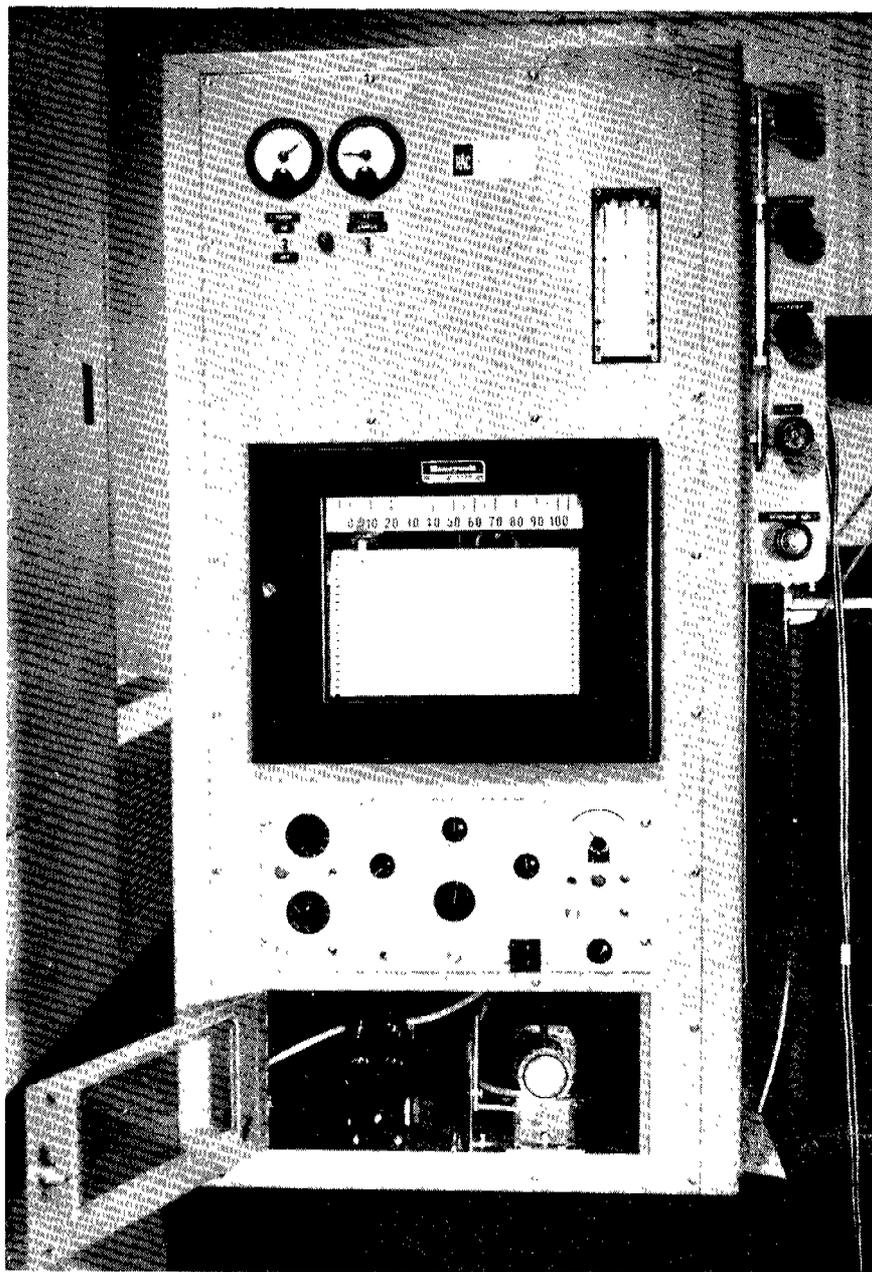


FIGURE 20

ANALYTICAL INSTRUMENT TO DETERMINE THE VOLATILE
HYDROCARBONS IN WATER BY GAS STRIPPING
AND HYDROGEN FLAME IONIZATION DETECTION

- (4) The stripping unit and associated water lines are enclosed in the console and can be maintained at a minimum temperature of 30°C.
- (5) Provision is made for introduction of a standard reference gas to the sampling system for periodically checking the instrument calibration.

The analyzer was installed in the Monroeville Research Center and all components and controls were checked for proper functioning. The recorder was rewired to permit continuous functioning of the amplifier. The recorder chart drive switch was disconnected to prevent activation of both solenoids simultaneously when the switch was thrown to the "on" position. A needle valve was installed in the gas line from the stripper to the gas sampling valve to prevent flow of standard gas through the stripper when checking the standard gas response. Drawings of the system and the electrical circuitry are shown in Appendix I, drawings C-66782 and F-22671 respectively.

The gas stripper was adjusted to 260 rpm. to make a preliminary check of water flow in the system. Interference was detected by the recorder which varied proportionately with the speed of rotation of the stripper. The source of interference was traced to rotation of the magnet used to drive the stripper. A section of 2-inch pipe mounted over the magnet was found to be the most satisfactory shield for the rotating magnetic field, reducing the interference to a minimum.

The instrument was calibrated with synthetic gas blends of n-butane in nitrogen over the range of 0 to 900 ppm. by volume. Conditions for operation of the detector unit were adjusted for maximum sensitivity to give the best linearity of response. The flow of nitrogen was adjusted to 80 ml. per minute, of hydrogen to 40 ml. per minute and of air to 275 ml. per minute. The response for a standard gas mixture of n-butane in nitrogen was determined for these conditions. Subsequently, this standard gas mixture was analyzed at the beginning of each day's runs and slight flow adjustments were made to obtain the original response value. Preliminary synthetic mixtures of butane in nitrogen were prepared. Known volumes of these mixtures were then transferred by means of a gas-tight hypodermic syringe to calibrated bulbs containing nitrogen. One-half ml. samples of these final blends were then injected into the carrier gas stream of the ionization detector unit by way of the transfer system and the gas sampling valve (see Drawing No. F-22611-V).

The calibration curves are shown on the attached graphs. Figure nos. 21 and 22 show the response for butane over two concentration ranges on the same electrometer range setting (input) but on different attenuations (divided output). The standard gas mixture was found to contain 152 ppm. by volume n-butane in nitrogen from the appropriate calibration curve.

Aqueous blends of butane were prepared by injecting a known volume of butane into a calibrated bulb containing known volumes of air and water. The mixture was agitated for a 10-minute period and was then allowed to stand at least 10 minutes to attain equilibrium. Stripping unit conditions of operation were established as follows: water flow rate, 50 ml. per minute;

FIGURE 21

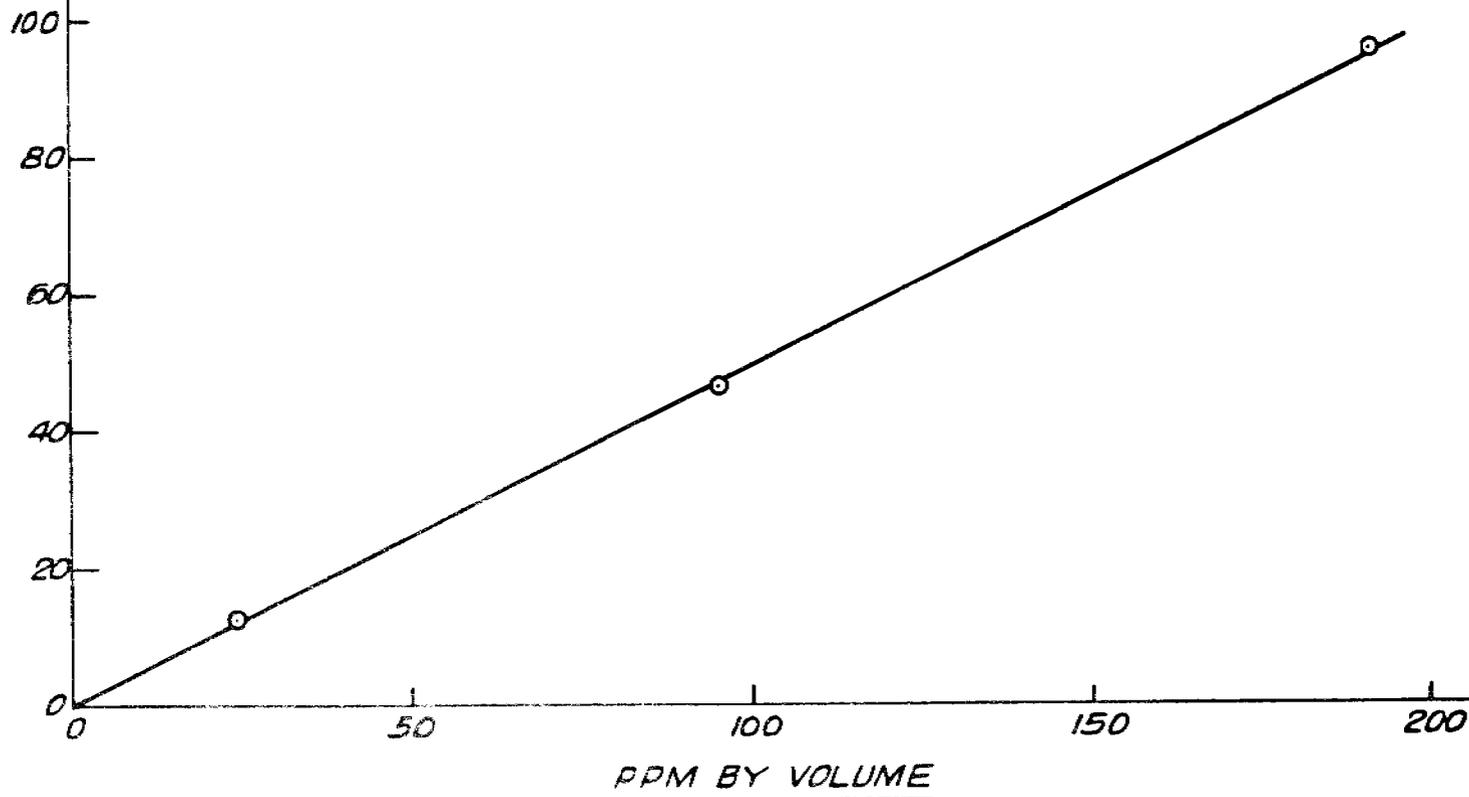
n-BUTANE IN NITROGEN

$\frac{1}{2}$ ml. SAMPLE LOOP

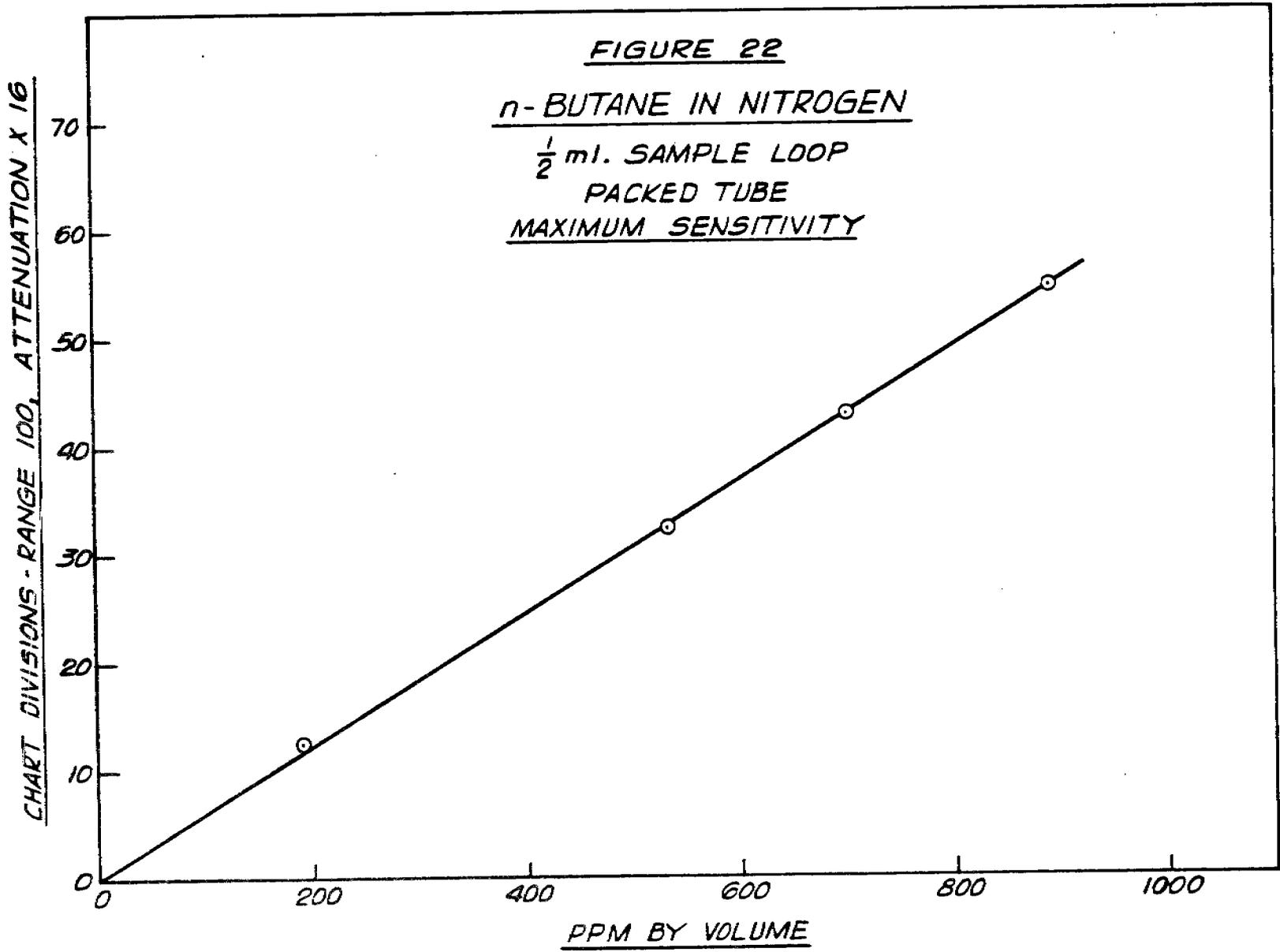
PACKED TUBE

MAXIMUM SENSITIVITY

CHART DIVISIONS - RANGE 100, ATTENUATION X 2



G-14079



5-14080

nitrogen stripping gas rate, 50 ml. per minute; and disc rotating speed, 260 rpm. The detector unit was operated under the same conditions as previously described. Aqueous blends of butane were prepared over the range of 0.05 to 2.0 ppm. by weight. These solutions were stripped in the gas stripping unit and the stripping gas analyzed. The stripped solutions were then restripped and the stripping gas analyzed. The results of these analyses are shown in Table XV.

TABLE XV

DETERMINATION OF BUTANE IN WATER
(Maximum Sensitivity)

<u>Butane,</u> <u>ppm by Weight</u>	<u>Per Cent Stripping</u> <u>Calculated From</u> <u>Analysis on Restripping</u>
0.187	100
0.322	98
0.826	97
1.16	98
2.23	98

From data presented in Part A of this report, the stripping efficiency of the prototype analyzer was found to be 98 per cent minimum.

The instrument was delivered to the Research and Development Test Station, Wrightsville Beach, North Carolina, where it was installed in the analytical laboratory. Personnel designated by the Manager of the Research and Development Test Station were trained to operate the unit.

V. CONCLUSIONS

The gas stripping unit described in conjunction with a hydrogen flame ionization detector has been found suitable for the applications discussed in the introduction to this report. The analytical method developed for these applications along with the instructions for operating the analytical instrument has been incorporated in the procedure manual (see Appendix II).

An analytical unit has been installed at the Research and Development Test Station, Wrightsville Beach, North Carolina, to measure the hydrocarbon content in potable and reject brine streams emanating from saline water conversion pilot plants.

VI. ACKNOWLEDGMENTS

Acknowledgment is gratefully extended to Miss Margaret D'Andrea for gas chromatographic analysis of air samples, to Mr. H. A. Trautman and Mr. W. R. Kurvach for preparation of the drawings, to Mr. H. H. Tuche for assistance with the magnetic interference problem and to Mr. H. P. Esselman for assistance with the installation of the analyzer at Wrightsville Beach, North Carolina.

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APPENDIX I

SPECIFICATIONS FOR APPARATUS USED IN
THE DETERMINATION OF DISSOLVED FREON, PROPANE
AND BUTANE IN WATER

SPECIFICATIONS FOR APPARATUS USED IN
THE DETERMINATION OF DISSOLVED HYDROCARBON IN WATER

<u>ITEM</u>	<u>DESCRIPTION</u>
<u>Flowrator</u>	<p><u>Use</u> - To meter nitrogen flow to gas stripping unit</p> <p><u>Manufacturer</u> - Fischer & Porter Company</p> <p><u>Model</u> - Precision Bore Flowrator</p> <p><u>Tube No.</u> - 08F-1/16-12-4</p> <p><u>Float</u> - 0.0625 inch diameter</p> <p><u>Float Material</u> - Type 316 S.S.</p>
<u>Sigmamotor Pump</u>	<p><u>Use</u> - To pump water samples into gas stripping unit</p> <p><u>Manufacturer</u> - Sigmamotor Inc.</p> <p><u>Model</u> - T-8 with a Model E Zero-Max. speed changer with vernier adjustment. Pump to be fitted with #205 T-6 heavy springs, head to accommodate 1/4" I.D. x 1/16" wall polyurethane tubing</p> <p><u>Motor</u> - 1/8 H.P., 115 volt, 60 cycles, 1 phase</p>
<u>Gas Stripper</u>	<p><u>Use</u> - Contactor for removing dissolved hydrocarbon from water samples with nitrogen sweep gas (see Assembly Dwg. No. C-66723-V and Detail Dwg. No. B-511123-V)</p> <p><u>Manufacturer</u> - Mitchell Plastics, Pittsburgh, Pa., as per Koppers specifications</p> <p><u>Materials of Construction:</u></p> <p style="padding-left: 20px;"><u>Body and Base</u> - Lucite</p> <p style="padding-left: 20px;"><u>Shaft</u> - Delrin</p> <p style="padding-left: 20px;"><u>Shaft Bearings</u> - Teflon</p> <p style="padding-left: 20px;"><u>Shaft Disc</u> - Mylar</p> <p style="padding-left: 20px;"><u>Disc Spacers</u> - Lucite</p> <p><u>Overall Dimensions</u> - 4-1/4" x 2" diameter</p> <p><u>Drive Wheel</u> - Lucite with soft iron cores sealed inside with Lucite cement</p> <p><u>Drive</u> - Speed-Mate, Model 3A250M, CCW rotation, 0-260 rpm., 60 cycles, 1 phase</p> <p><u>Features</u> - shaft rotates a permanent magnet which controls the drive wheel in gas stripper. A 3-5/8 inch section of 2-inch pipe was mounted over the magnet to remove interference from the rotating magnetic field.</p>

ITEMDESCRIPTIONGas Sample Valve

Use - To divert flow of gas from vent to sample loop and secure a measured volume of gas

Manufacturer - F & M Scientific Corp.

Model - GV-10

Sample Volume - 0.5 cc.

Note - This valve is manually or automatically operated to secure a sample of gas for analysis, and is rated for 1000 samplings before the "O" ring seals need to be replaced. For automatic monitoring of the water sample stream, this valve is controlled by timer actuated solenoids.

Flame Ionization Detector and Electrometer

Use - Transmits an electrical signal which is proportional to the concentration of hydrocarbon in the gas stream. This signal is amplified and relayed to a millivolt recorder.

Manufacturer - F & M Scientific Corp.

Model No. - 1609

Special Features:

1. Line-operated electrometer with sensitivity of 4×10^{-12} amps full scale.
2. Collector electrometer area 100 sq. mm.
3. Applied voltage to collector electrode - 130V.
4. Automatic flame re-igniter.
5. High-temperature operation from ambient to plus 400°C.
6. Flow meters for air, carrier gas and hydrogen flows.

Power Requirements:

Voltage - 110

No. Phases - 1

Current - (A.C.) 20 amps.

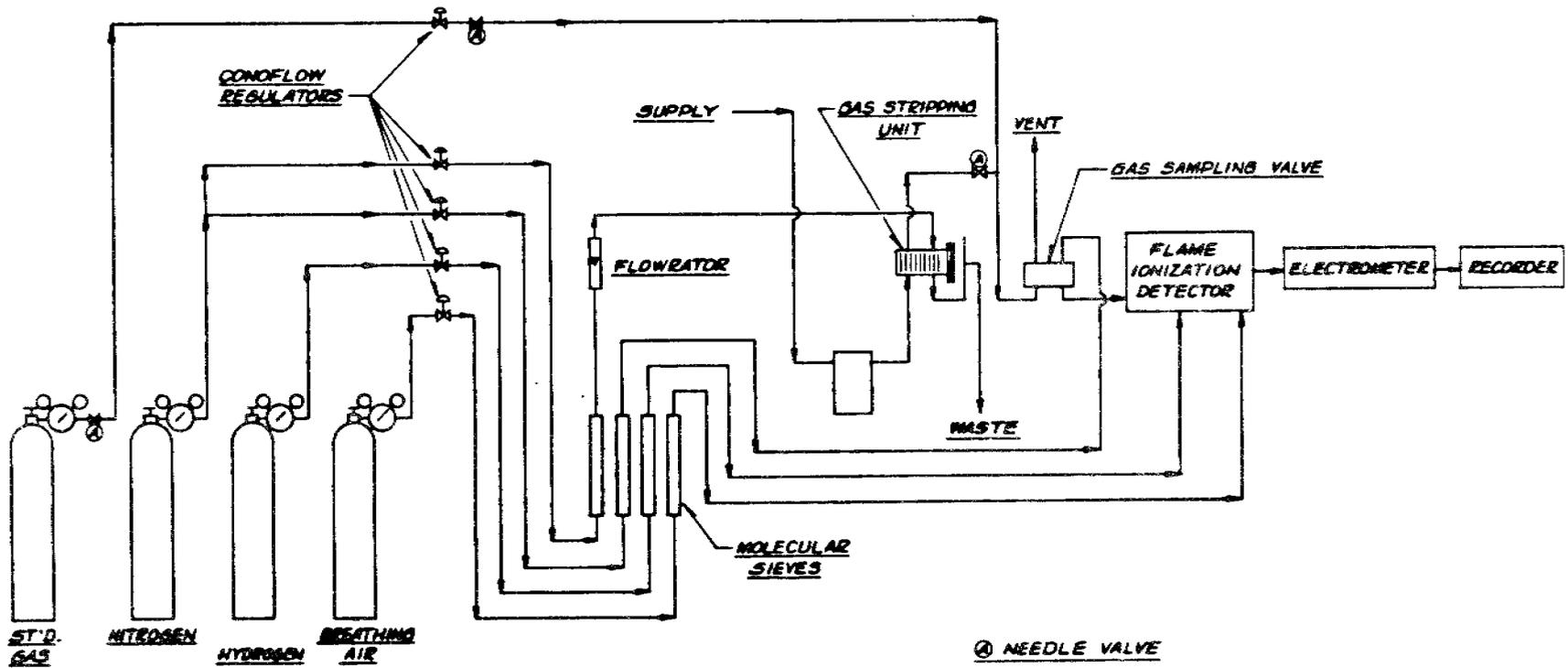
Cycles - 50-60

Recorder

Use - To record millivolt signal received from flame ionization detector

Manufacturer - Minneapolis-Honeywell
Regulator Company, Brown
Instruments Division

Model No. - 15307856-01-05-0-000-030-07-136,
Electronic 15 Chromatography
Recorder



REV	DESCRIPTION	DATE	BY

DESIGNED BY W. KURMACH 1-10-64
 CHECKED BY William R. Holder
 APPROVED BY



HYDROCARBON
 ANALYZER
 FLOW DIAGRAM

ACTIVITY No.	SCALE 3/4" = 1 FT.
C-66782	



SKETCH SHEET

NAME

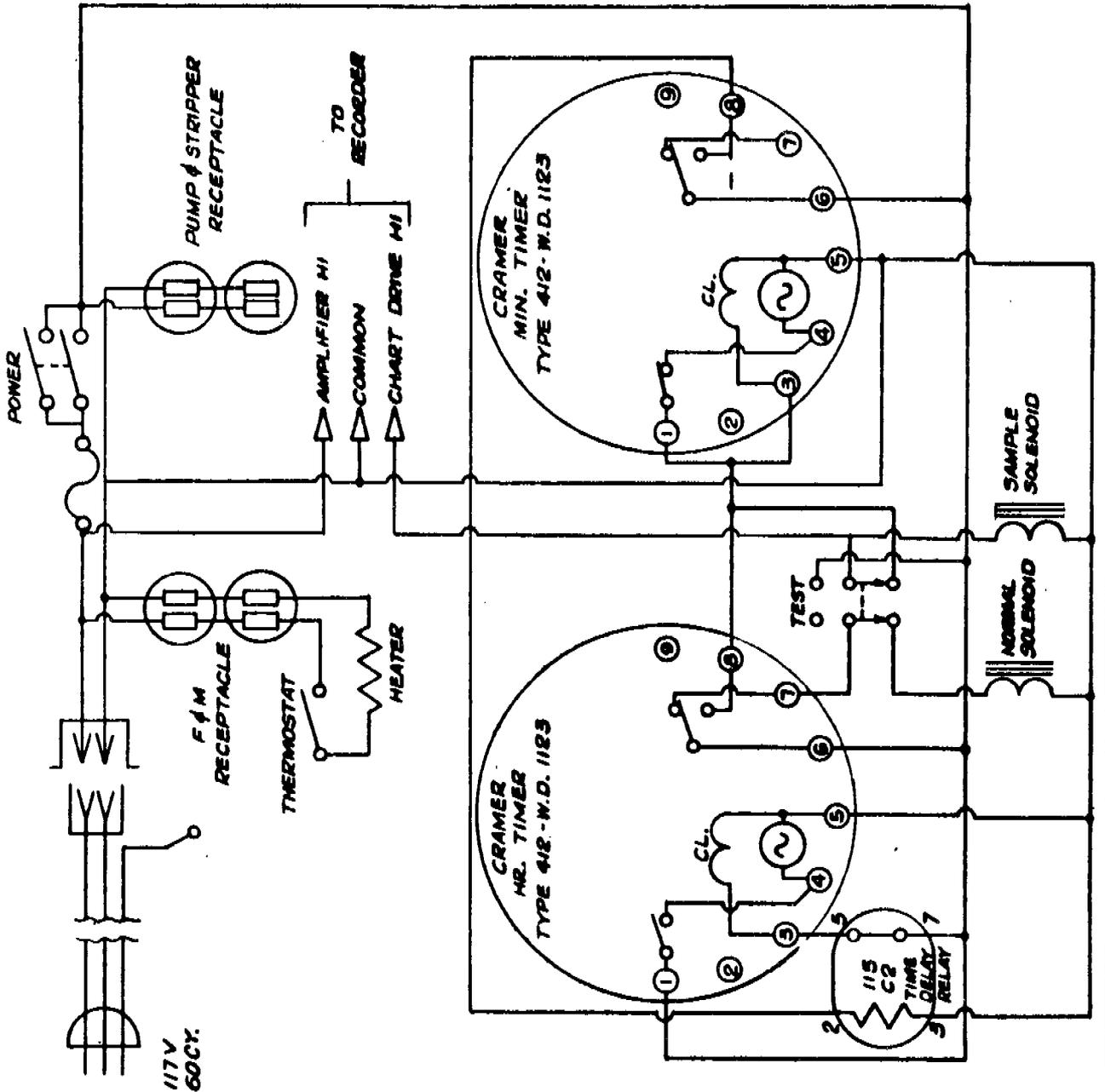
DATE

DRAWN *W. KURYACH*

1-14-1964

CHECKED

William R. Hedon



REV.	DESCRIPTION	CHKD. BY	DATE

ACTIVITY No.

TITLE **HYDROCARBON ANALYZER - SCHEMATIC WIRING DIAGRAM**

F-22671



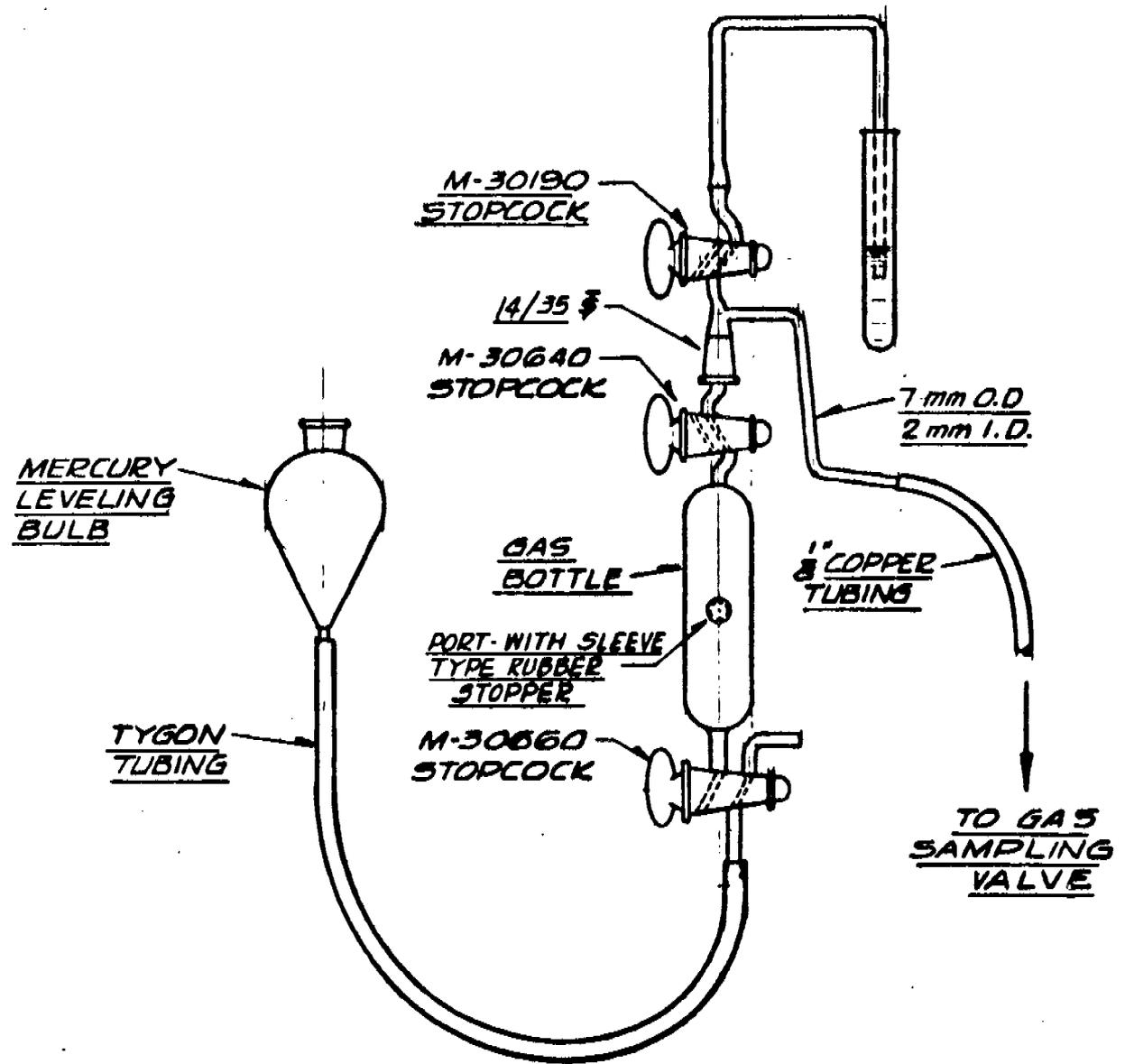
SKETCH SHEET

NAME

DATE

DRAWN H. TRAUTMANN 3-20-63

CHECKED William R. Holden

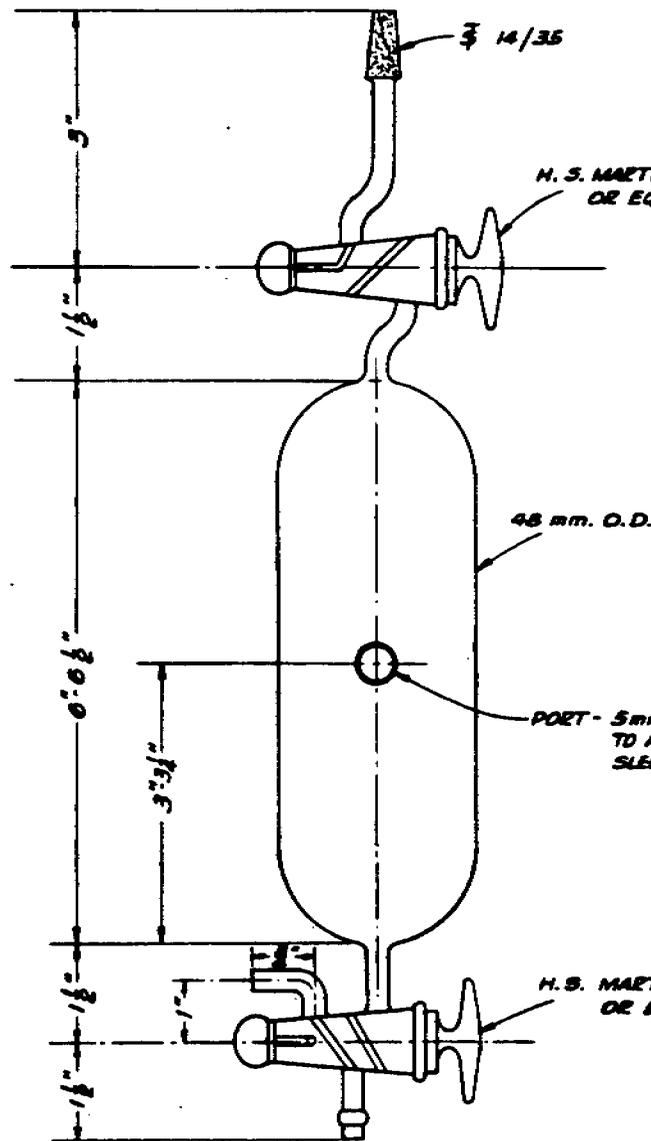


△	GENERAL REVISIONS-5-25-1964	
REV.	DESCRIPTION	CHKD. BY DATE

ACTIVITY No.

TITLE APPARATUS FOR CALIBRATING DETECTOR

F-22611-V



SPECIFICATIONS:

- 1 TO BE CONSTRUCTED FROM PYREX NO.7740 or KIMAX (KG-33) GLASS.
- 2 ALL STOPCOCKS TO BE PRECISION-GROUND, VACUUM TYPE, WITH EVACUABLE BOTTOM END SEAL; PLUGS TO BE SOLID WITH 4-mm. I.D. BORES.
- 3 ALL PLUGS AND BARRELS OF STOPCOCKS TO BE PROVIDED WITH UNIQUE, MATCHING NUMBERS; NUMBERS TO BE ENAMEL-OR DECAL-TYPE FIRED INTO GLASS.
- 4 ALL STOPCOCK TUBULATIONS TO BE MADE OF 10mm O.D. HEAVY WALL TUBING (Ca. 5.5-6 mm. I.D.).
- 5 ALL BOTTLES TO BE OVEN ANNEALED.

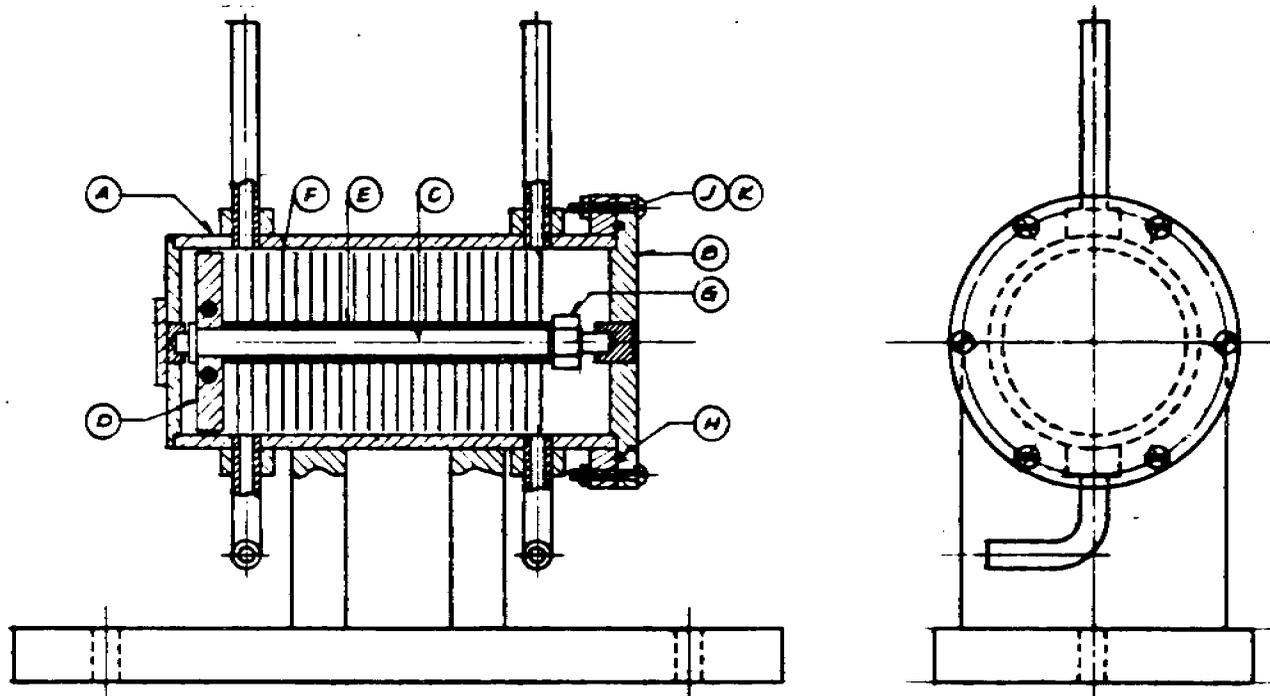
NOTE:
DRAWING NOT TO SCALE

REV.	DESCRIPTION	DATE BY-CHKD	APPROVED BY



**GAS SAMPLE
BOTTLE**

ACTIVITY No. SCALE NPS-10%
C-66801



F	22	DISC	B-511123-V				
E	23	SPACER	B-511123-V				
D	1	DRIVE WHEEL	B-511123-V	K	6	1/4-40 HEX HD. NUT	
C	1	SHAFT	B-511123-V	J	6	M-40 X 3/8 LG RD HDMS.	
B	1	COVER	B-511123-V	H	1	"O" RING	
A	1	BODY & BASE	B-511123-V	G	1	TEFLON NUT 1/2-20	
ITEM	NO. REQ.	DESCRIPTION	DWG. NO.	ITEM	NO. REQ.	DESCRIPTION	DWG. NO.

REV.		DESCRIPTION		DATE		APPROVED BY		5-11-63 DRAWN BY H. TRAUTMANN CHECKED BY J. HANDEL APPROVED BY				STRIPPER ASSEMBLY		ACTIVITY No. _____ SCALE 1/2" = 1"	
								C-66723-V							

APPENDIX II

PROCEDURE MANUAL FOR ANALYTICAL INSTRUMENT
TO DETERMINE THE VOLATILE HYDROCARBONS
IN WATER BY GAS STRIPPING AND HYDROGEN FLAME
IONIZATION DETECTION

PROCEDURE MANUAL FOR ANALYTICAL INSTRUMENT
TO DETERMINE THE VOLATILE HYDROCARBONS
IN WATER BY GAS STRIPPING AND HYDROGEN FLAME
IONIZATION DETECTION

SCOPE

This method describes the procedure for the operation of the analytical unit for measurement of the volatile hydrocarbon content in potable water and reject brine streams emanating from saline water conversion pilot plants at the Research and Development Test Station, Wrightsville Beach, North Carolina. The analytical unit has been calibrated for the determination of n-butane over the range 0.05 to 2.0 ppm. by weight in water.

OUTLINE OF METHOD

The aqueous solution to be analyzed is fed at a known rate into a gas stripping unit. The stripping gas is vented through the sample loop of a gas sampling valve of a hydrogen flame ionization detector. At intervals the valve is actuated to inject a sample of the stripper gas into the carrier gas stream of the detector unit. The output from the hydrogen flame ionization detector is amplified and recorded. The amount of hydrocarbon in the water is calculated from calibration curves prepared from data obtained with synthetic mixtures.

APPARATUS

- (a) Analytical Unit for measurement of hydrocarbon content (Research Appliance Company, Allison Park, Pennsylvania). Constructed in accordance with the specifications of the Koppers Company, Inc., Research Department, Monroeville, Pennsylvania. A copy of the specifications is shown in Appendix I.
- (b) Copper Tubing, 1/4-inch O.D., 0.030-inch wall thickness, soft temper; 1/8-inch O.D., soft temper.
- (c) Glass Wool, Pyrex-brand.
- (d) Microliter Syringes, 0.5-, 1.0-, 5.0-, and 10.0-milliliter capacities with fixed needle and Teflon-tipped plunger (Hamilton Company, Inc., Whittier, California, Part Nos. 1750-N, 1001-N, 1005-N and 1010-N).
- (e) Pressure-Reducing Regulators, two-stage, for use with compressed nitrogen, air, and hydrogen gases (Linde Company, Type R-2028 for nitrogen, Type R-201 for air, and Type R-219 for hydrogen).
- (f) Pressure-Reducing Regulator, two-stage, for use with compressed standard butane-nitrogen mixture (The Matheson Company, Inc., Type 8-350).

- (g) Vacuum Pump, oil-sealed, motor-driven.
- (h) Sieve Screens, brass, U. S. Standard, 30- and 60-mesh sizes.
- (i) Soap Film Meter, calibrated from 0 to 50 ml. (Fisher Scientific Company, Catalog No. 3-711).
- (j) Crystallizing Dish, Pyrex-brand glass, 150-mm. diameter.
- (k) Oven, thermostatted, gravity-convection type, suitable for use up to 125°C.
- (l) Filtering Flask, with side tube, Pyrex-brand glass, 1-liter capacity.
- (m) Gas Sample Bottle, 225-ml. capacity, and Aqueous Solution Reservoir, 2000-ml. capacity, of the same special design, used in the development work (see Drawing No. C-66801). The aqueous solution reservoir has a 100-mm. diameter and 12-inch height to give the 2000-ml. volume in lieu of these respective dimensions on the drawing for gas sample bottle.
- (n) Leveling Bulb, 500-ml. capacity.
- (o) Glass Sampling System, special design (see Drawing No. F-22611-V).
- (p) Stand-pipe, stainless steel.
- (q) Serum Stoppers, to fit side-arm of gas sample bottles.
- (r) Powder Funnel.
- (s) Swagelok Fittings, brass, for use with 1/4-inch O.D. copper tubing (Crawford Fitting Company, Part Nos. 402-1, 403-1, and 404-1).
- (t) Stopwatch.
- (u) Swagelok Union, brass, for 1/8-inch copper tubing (Crawford Fitting Company, Part No. 200-6).
- (v) Polyurethane Tubing, 1/4-inch I.D., 1/16-inch wall thickness (Sigmamotor Inc.).
- (w) Tygon Tubing, 3/16-inch bore.
- (x) Graduated Cylinder, 100-ml. capacity.
- (y) Stainless Steel Tank, 6-inch diameter by 24-inch length, 1/4-inch pipe thread opening each end (A. C. Tank Company, Model D-2). This tank is used for transporting samples and as a reservoir for analyzing pilot plant samples.

- (z) Needle Valve, stainless steel, 1/4-inch pipe thread each end (Fisher Scientific Company, Catalog No. 10-588).

REAGENTS

- (a) Acetone, technical-grade (Enjay Company, Inc.).
- (b) Carbon Tetrachloride, technical-grade (J. C. Ackerman Company, Pittsburgh, Pennsylvania).
- (c) Chloroform, A.C.S.-grade (Fisher Scientific Company, Catalog No. C-298).
- (d) Molecular Sieve 5A, 1/16-inch pellets (Linde Air Products Company, 30 East 42nd Street, New York 17, New York).
- (e) Methylene Chloride, Fisher Certified (Fisher Scientific Company, Catalog No. D-37).
- (f) Fluorosilicone QF 1-0065 (Analabs, Catalog No. G19).
- (g) "CHROMOSORB P" (Fisher Scientific Company).
- (h) Mercury, metal, distilled, technical-grade (Fisher Scientific Company, Catalog No. M-139).
- (i) Nitrogen, compressed, prepurified, 99.99 per cent minimum purity (The Matheson Company, Inc.).
- (j) Hydrogen, compressed, prepurified, 99.9 per cent minimum purity (The Matheson Company, Inc.).
- (k) Breathing Air, compressed (Ohio Chemical and Surgical Equipment Company).
- (l) Gas Mixture, compressed, 100 ppm. n-butane, instrument-grade, in nitrogen, prepurified, analyzed (The Matheson Company, Inc.).
- (m) n-Butane, instrument-grade, 99.5 per cent minimum purity (The Matheson Company, Inc.).
- (n) Stopcock Grease, Dow Corning high vacuum.

PROCEDURE

A. Preparation of Column

1. Dissolve 5 grams of Fluorosilicone in about 100 ml. of methylene chloride contained in a 150-mm. diameter crystallizing dish. Then add 45 grams of Chromosorb P to the solution and mix the slurry.

2. Allow the major portion of the methylene chloride to evaporate by allowing the slurry to stand at room temperature. Swirl the contents of the crystallizing dish periodically to remix the slurry. Then remove the last traces of the solvent by drying the material for 2 hours in an oven at 120°C. Size the dried material through a 30- and on a 60-mesh screen.
3. Cleanse thoroughly the inside surface of an 8-inch length of 1/4-inch O.D. by 3/16-inch I.D. copper tubing by rinsing it first with acetone, then with carbon tetrachloride, and finally with chloroform.
4. Dry the tubing thoroughly by attaching it to a vacuum pump and aspirating air through it for about 30 minutes.
5. Plug one end of the tubing with a small amount of glass wool. Pour the impregnated Chromosorb P slowly through a powder funnel into the other open end while tapping the tubing to ensure uniform distribution of the packing. Close the packed tube with a small plug of glass wool.
6. Bend the packed tube as necessary for installation in the column compartment of the detector unit.
7. Attach Swagelok fittings to both ends of the tube.

B. Preparation of Apparatus

1. Attach the gas supplies to the inlets of the Conoflow regulators. The hydrogen cylinder should be independently well grounded.
2. Install the packed tube in the column compartment of the detector unit.
3. Turn all switches on the panels of the analyzer unit to the off position.
4. Connect the power cable to the connector at the bottom rear of the unit. Plug the other end into a 110-volt a.c. 60-cycle source. Be sure the analyzer unit is well grounded.
5. Throw on the master power circuit breaker on the flame ionization detector panel.
6. Adjust the block heater variable transformer to a setting of 30 to obtain a detector block temperature of 110°C. Throw the block heater switch to the on position.
7. Throw the electrometer switch to the warm-up position. Leave it there for at least ten minutes, then throw it quickly to the operate position. **ALLOW AT LEAST FOUR HOURS FOR ELECTROMETER STABILIZATION BEFORE OPERATING.**

8. Install the chart as described in the recorder instruction manual.
9. Fill and start the pen as described in the recorder instruction manual.
10. Turn on the recorder power switch to energize the amplifier. ALLOW AT LEAST 30 MINUTES FOR AMPLIFIER WARM-UP.
11. Adjust the zero controls as described in the recorder instruction manual. The electrometer range is set at 10,000 and the attenuator at ∞ for this adjustment.
12. Several minutes after performing step 5, turn the temperature selector switch to the detector position. A deflection of 18 chart divisions will indicate a detector block temperature of 110°C. Readjustment of the block heater variable transformer may be necessary to achieve this temperature.
13. With the packed column in position and the oven cover in place, turn on the blower switch.
14. Turn on the air, nitrogen and hydrogen supplies and with the Conoflow regulators adjust the gas flows as listed in Table I. Flowrator settings are read at the top of the ball.

TABLE I

APPROXIMATE GAS FLOW ADJUSTMENTS

<u>Gas</u>	<u>Cylinder Pressure psi.</u>	<u>Flowrator Setting</u>	<u>Flow ml./min.</u>
Hydrogen	30	8.70	40
Nitrogen carrier	40	13.35	80
Air	30	5.00 (a)	275

(a) Setting to obtain a flow of 275 ml./min. varies depending on the back pressure adjustment of the needle valve after the Conoflow regulator.

15. Rotate the meter relay adjusting knob counter clockwise until the red arm reads 0°C. on the flame temperature meter. The black needle will read near the temperature of the cell. Remember this black needle reading for step 17.
16. Turn on the igniter switch. Push the manual igniter button in and hold for several seconds. The black needle of the meter relay will go upscale. Determine if the flame is lit by removing

the cell cover and putting a thin strip of paper down into the cell, over the jet. The normal flame is not visible. If the flame will not light, observe the igniter wire while pushing the manual igniter button. The wire should glow red within two seconds if properly adjusted.

17. After the flame is lit, adjust the red arm of the meter relay to a value less than the temperature now indicated by the black needle, but above the cell temperature as measured in step 15. (The temperature of the thermocouple should go up by about 100°C . on igniting the flame. If it does not, move the thermocouple closer to the flame.)
18. Set the electrometer range at 10,000 and the attenuator at 8. With the coarse control knob and the fine control knob, adjust the recorder pen to the zero mark. Turn on the recorder chart drive by setting the hour timer at zero, the minute timer at 15, and turning on the power switch located on the panel beneath the timers.
19. After allowing sufficient time for complete equilibrium of the detector, the unit is ready for adjustment to the standard gas response.
20. Follow the instruction manuals furnished by the manufacturers of the detector, recorder, and pump for details of operation and recommended maintenance.

C. Adjustment of Standard Gas Response

1. Attach the standard n-butane-nitrogen supply to the inlet of the Conoflow regulator.
2. Close the needle valve in the gas line from the stripper to the gas sample loop to prevent standard gas flow through the stripper. This valve is located inside the rear door of the analyzer cabinet.
3. Adjust the Conoflow regulator and needle valve in the standard gas line to provide a flow of 50 ml. per minute through the gas sample loop. Use the soap film meter for this measurement.
4. Set the electrometer range at 100 and the attenuator at 2 and adjust the recorder pen to the zero mark.
5. Turn on the power switch beneath the timers and set the hour timer at 2 hours. (The pump and stripper may be unplugged during the remainder of this adjustment.)
6. Throw the manual test sample switch and hold for one minute, then release.

7. Repeat step 6 at 2 minute intervals for replicate analyses of the standard gas.
8. The average of four analyses should be within ± 1.0 chart division of the response for the n-butane concentration of the standard gas from the calibration curve (Note 1).
9. Minor flow adjustments of the nitrogen carrier and hydrogen gas flows may be required to obtain the desired response value. If flow changes are made, 10 to 15 minutes should be allowed for stabilization before repeating steps 6 through 8.
10. After the desired response value is obtained, wait 15 minutes and repeat steps 6 through 8 to be certain that stabilization of gas flows has been achieved (Note 2).
11. Turn off the standard gas supply and open the needle valve in the gas line from the stripper to the gas sample loop.
12. The analyzer is now ready for analysis of samples.

D. Calibration (Note 1)

1. Fill a calibrated gas sample bottle containing 1 ml. of mercury with air or nitrogen to atmospheric pressure.
2. Using the appropriate gas-tight syringe, inject a measured volume of n-butane through the serum stopper in the side arm of the bottle.
3. Mix the gases by turning the bottle end-over-end for several minutes.
4. Connect the bottle to the mercury leveling bulb and the injection system shown in Drawing No. F-22611-V.
5. Using this system, evacuate the sample loop and fill it to atmospheric pressure with the synthetic mixture.
6. Inject the sample with the manual test sample switch.
7. Adjust the electrometer range setting for the n-butane concentration range of interest, and attenuate the recorder range as necessary to keep the peak within the limit of the chart paper.
8. Repeat steps 5 through 7 for replicate analyses of the same synthetic mixture.
9. Repeat steps 1 through 8 with several mixtures over the concentration range of interest (Note 3).

10. Prepare a calibration curve by plotting response in chart divisions versus n-butane concentration (Note 4).

Model Calibration

1. Fill a calibrated gas sample bottle of 222.6 ml. volume containing 1 ml. of mercury with nitrogen to atmospheric pressure.
2. Using the 10 ml. gas-tight syringe, inject 5.90 ml. of n-butane through the serum stopper in the side arm of the bottle. The syringe should be flushed twice with n-butane before the final filling to 5.90 ml. with n-butane.
3. Mix the gases by turning the bottle end-over-end for several minutes.
4. Fill a second calibrated gas sample bottle of 217.0 ml. volume containing 1 ml. of mercury with nitrogen to atmospheric pressure.
5. Using the 1 ml. gas-tight syringe, inject 0.20 ml. of the mixture prepared in step 3 through the serum stopper in the side arm of the bottle. The syringe should be flushed twice with the gas mixture before the final filling to 0.20 ml. with the mixture.
6. Mix the gases by turning the bottle end-over-end for several minutes.
7. With the electrometer range setting at 100 and the recorder range attenuator at 2, follow steps 4 through 8 of the Calibration section to obtain the response in chart divisions.
8. Repeat steps 4 through 7 with several mixtures over the concentration range of interest. Examples are listed in Table II.
9. The gas mixture prepared in step 3 should be maintained at atmospheric pressure by replacing the gas removed from the sample bottle with mercury. This is accomplished by connecting a mercury leveling bulb to the sample bottle and maintaining equal levels of mercury in both the leveling bulb and the sample bottle.

TABLE II

MODEL CALIBRATION MIXTURES

<u>Volume of Nitrogen, ml.</u>	<u>Volume of Gas Mixture from Step 3</u>	<u>n-Butane Concentration, ppm by Volume</u>	<u>Electrometer Setting</u>	<u>Recorder Range Attenuation</u>
216.0	0.20	24	100	2
216.0	0.80	95	100	2
216.0	1.60	191	100	2
216.0	1.60	191	100	16
216.0	4.50	529	100	16
216.0	7.80	903	100	16

E. Analysis of Sample

1. Fill the stainless steel solution reservoir with distilled water and connect it to the Sigmamotor pump by means of 1/4-inch O.D. copper tubing. Use an 8-inch length of polyurethane tubing through the pump head. Use short (ca. 2 inches) sections of Tygon tubing to connect the reservoir and the stripper unit to the copper tubing. Flexible tubing can be used for the stripper exit line.
2. Check to see that the standard gas supply is off and the needle valve in the gas line from the stripper to the gas sample loop is opened.
3. Turn on the power switch beneath the timers to operate the pump and the stripper. Open the needle valves of the solution reservoir.
4. Pump the water into the stripper unit until the water level is at the halfway point in the stripper, and adjust the stand-pipe to maintain this level.
5. Adjust the pump rate to 50 ml. per minute. Use a graduated cylinder to measure the volume pumped per minute from the stripper exit line. This adjustment is made on the vernier of the Sigmamotor pump.
6. Adjust the Conoflow regulator and needle valve in the nitrogen stripping gas line to provide a flow rate of 50 ml. per minute. Use the soap film meter for this measurement.
7. Set the electrometer range at 100 and the recorder range attenuation at 2.
8. After 5 to 10 minutes of operation, throw the manual test sample switch and hold for one minute, then release. The trace hydrocarbon peak from ordinary laboratory distilled water should not exceed one chart division (Note 5).
9. Turn off the power switch beneath the timers and remove the distilled water reservoir (Note 6).
10. Fill the reservoir with the sample solution to be analyzed and connect it to the pump.
11. Open the needle valves and turn on the power switch (Note 7).
12. Allow the system to operate for 5 to 10 minutes before throwing the test sample switch to inject a sample of the stripping gas into the detector unit.
13. Repeat the analysis of the stripping gas at intervals of 2 to 4 minutes. Equilibrium will be attained in 10 to 15 minutes as indicated by duplicate peaks being recorded on the chart.

14. Adjust the electrometer range setting and recorder range attenuation to keep the peak on the chart paper and to conform to the settings used for the calibration curve for the particular range of concentration.
15. Calculate the n-butane content of the solution as described under CALCULATIONS.

CALCULATIONS

1. Measure the peak height of the n-butane band in chart divisions.
2. From the calibration curves previously prepared find the concentration of n-butane in the stripping gas sample analyzed in ppm. by volume.
3. From the ppm. by volume in the stripping gas, calculate the ppm. by weight in the solution as follows:

$$\frac{\text{Ppm. by volume in gas} \times 0.05}{E} = \text{Ppm. by weight in water}$$

where E = Ppm. by volume in stripping gas equivalent to 0.05 ppm. by weight in water for n-butane.

This equivalent is calculated as follows:

0.05 ppm. by weight in water =

$$\frac{5 \times 10^{-6} \times 10^{-2} \times W \times \left(\frac{22400 \times \frac{760}{P} \times \frac{273 + t}{273} \right) \times 100}{\text{M.W.} \times V} \quad \text{volume per cent in stripping gas}$$

where W = weight of water stripped per minute, expressed in grams;

V = volume of stripping gas used per minute, expressed in milliliters;

P = barometric pressure, expressed in mm. of mercury;

t = ambient temperature, °C.;

and M.W. = molecular weight of n-butane.

MODEL CALCULATIONS

Barometric pressure = 735 mm.

Ambient temperature = 23°C.

1:1 stripping rate

$$\begin{aligned} E_{n\text{-butane}} &= \frac{5 \times 10^{-8} \times 2.51 \times 10^6}{58} \text{ volume per cent in gas} \\ &= 0.00216 \times 10^4 \text{ ppm. by volume in the gas} \\ &= 21.6 \text{ ppm. by volume.} \end{aligned}$$

ACCURACY AND REPRODUCIBILITY

From data presented in Section IV, Part A of this report, the stripping efficiency of the unit was found to be 98 per cent minimum.

The reproducibility of the analysis at the lowest concentration studied is better than ± 5 per cent of the amount present, and at the highest concentrations it is better than ± 2 per cent of the amount present.

REFERENCESA. Corporate

1. Holden, W. R., Koppers Company, Inc., Research Department, Laboratory Notebook No. 1352 pages 53-84 (November 1962 through March 1963).
2. Holden, W. R., Koppers Company, Inc., Research Department, Laboratory Notebook No. 1623 pages 22-27 (January 1964).
3. Phillips, M. A., Koppers Company, Inc., Research Department, Laboratory Notebook No. 1277 pages 7-100 (scattered); No. 1386 pages 1-96 (scattered); No. 1453 pages 2-11 (June 1962 through March 1963).
4. McKinstry, W. E., Koppers Company, Inc., Research Department, Laboratory Notebook No. 1520 pages 55-65 (January 1964).

B. Literature

1. Instruction Manual for the Model 1609 Hydrogen Flame Ionization Detector, F & M Scientific Corporation, Avondale, Pennsylvania.
2. Instruction Manual for Electronic 15 Chromatography Recorder, Honeywell, Brown Instruments Division, Philadelphia, Pennsylvania.

3. Instruction Manual for Model S AZAR Speedomax G Recorder, Leeds and Northrup Company, Philadelphia 44, Pennsylvania.

NOTES

1. The standard gas mixture used to obtain the calibration curves attached to this method contained 152 ppm. by volume n-butane and gave a response of 75.5 ± 1.0 chart divisions. It is recommended that a new supply of standard gas mixture be on hand before the original mixture is depleted. The new mixture should be analyzed with the instrument adjusted to the response of the original mixture. This will avoid the preparation of new calibration curves.
2. If any adjustments of air, hydrogen or nitrogen gas flows are subsequently made, the standard gas response must be checked before analysis of samples.
3. For low concentrations (0-200 ppm.), prepare a preliminary synthetic mixture of about 2 per cent by volume of n-butane. From this mixture prepare blends of the required concentrations using the gas-tight hypodermic syringes.
4. If the detector unit is used under continuous operation, the standard gas mixture is analyzed at the beginning of each day's runs, and slight flow adjustments may be necessary to obtain the response shown on the calibration curve.
5. Should a solution of high hydrocarbon content have been run just prior to this analysis, the addition of 1 to 2 liters of distilled water may be necessary to completely purge the stripper unit and the lines.
6. The distilled water purging is necessary only for adjustment of water and stripper nitrogen flow rates when an insufficient quantity of sample is available for these adjustments and subsequent analysis.
7. When this analysis is to be made on a plant stream, connect the water stream to the pump, turn on the power switch, adjust the timers for frequency of sampling, and allow the system to purge until duplicate peaks are recorded.