Woods Hole
Oceanographic
Institution

MOTION SENSITIVITY OF FLAME IONIZATION DETECTORS

By
Ronald Carl Gularte

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TECHNICAL REPORT

Prepared for NOAA under Grant 2-35252 Office of Sea Grant Programs.

WOODS HOLE, MASSACHUSETTS 02543

WHOI-72-52

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Approved for Distribution Earl E Hays

Earl E. Hays, Chairman
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SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
OCEAN ENGINEER

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

and the

WOODS HOLE OCEANOGRAPHIC INSTITUTION

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ABSTRACT

A portable gas chromatograph, using a single flame ionization detector, was constructed. The unit was tested for response to surge, sway and heave accelerations up to 0.3g. Also the detector's response was studied for roll and pitch up to 25 degrees with periods ranging from 3 to 20 seconds. The effect on the detector's response of variation in hydrocarbon concentrations in the parts per million range was investigated and response increased with increasing concentration. Samples containing 1, 10, 100, 1000, and 10,000 parts per million dodecane were analyzed, and under the higher accelerations trace distortion was evident for concentrations below 10 parts per million. Stationary isothermal chromatograms of a normal alkane sample (nC_6 - nC_{32}) were compared with those obtained under the various test conditions and no detectable difference in peak area (which represented approximately 1 microgram of the particular hydrocarbon) or retention time was evident. The limits of detection for the Aerograph detector were found to be 21.8×10^{-6} mg/sec for a 30 degree roll, 29.1×10^{-6} mg/sec for 20 degree pitching and 21.8×10^{-6} mg/sec for a 0.6g heave acceleration. For the range of translational and angular accelerations that might be expected on a platform at sea, it was found that medium resolution gas chromatography using a flame ionization detector can be conducted, but in the trace analysis region, trace distortion can be expected.

ACKNOWLEDGEMENT

I wish to thank Albert J. Williams III under whose guidance this thesis evolved. Also George R. Harvey, Oliver C. Zafiriou, and William G. Steinhauer for their chemistry, loan of apparatus and chemical supplies for this project. I would also like to express my thanks to F. Claude Ronne who is responsible for the photography. And finally to my wife for typing the manuscript.

Acknowledgement is given to NOAA Office of Sea Grant Programs for support of this work under Grant 2-35252.

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I. INTRODUCTION AND DISCUSSION OF PROBLEM

A) Need for Analysis at Sea

There is an obvious need for real time monitoring of the marine environment, as evidenced by much dialogue within the literature (1).* Most efforts, to date, have been aimed at monitoring relatively simple physical and chemical parameters. The majority of the real time chemical measurements have been of inorganic substances. Most organic measurements have been obtained by removing a representative sample and returning it to the laboratory for analysis. With this approach there is always the possibility of sample degradation or contamination during transport. Therefore, comprehensive, real time, in situ hydrocarbon analysis is needed.

Those organic substances which should be monitored include key contaminants which one might expect to be present in the marine environment such as petroleum products, chlorinated hydrocarbons and polychlorinated biphenyls. It is believed that the most urgent need at this time is for the capability of monitoring petroleum products in the near shore environment. This is particularly important in establishing "base line" data in areas where there is a high probability that petroleum reserves might be developed. This choice is also justified because most of the documented oil damage to the environment has occurred in this region; also, these are areas of high spillage probability, and furthermore, the near shore regions

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*Numbers in parenthesis indicate references given in the bibliography.

are primary areas for waste disposal. There are numerous organic and inorganic substances which could be monitored; the greatest need exists for the monitoring of petroleum derived products.

A monitoring system should also satisfy those legal requirements necessary for enforcing pollution legislation. What is envisioned as a potentially important oceanographic tool is an essentially self-contained, automated instrument system which will continuously monitor the sea surface for the presence of organic compounds. Upon detection a sample would be removed, preserved and a "real time" chemical analysis performed.

B) Present Detection and Identification Methods

A number of techniques exist which have reportedly been used for monitoring hydrocarbons remotely, especially when the oil exists on the sea surface as a slick. None of these remote techniques are at present specific for individual hydrocarbons.

With respect to *in situ* monitoring, oil on the sea surface has been detected by sampling vapor and using an adsorptive-resistive detection element (2). Also the change in reflectivity of the sea surface due to the presence of an oilslick has been used as a detection scheme (3). Specific identification, at present, has been possible only by removing a sample and returning it to the laboratory for analysis. Offshore oil exploration is being conducted with hydrocarbon "sniffers" (4). With these methods, to date, only the lower boiling point hydrocarbons (C_1 through C_4) are being detected.

C) Requirements for Marine Analysis

In order for a particular analytical method to operate successfully at sea it must be capable of producing, inexpensively and unambiguously, those data that will allow the identification of organics in the marine environment.

Because there is a high probability that the technique will be used on a moving platform, it will have to be either insensitive to motion or its response to such motion understood and somehow compensated for either electrically or mechanically. In the latter case a gyro-stabilized platform could be used to compensate for rotational moves, but it is difficult to eliminate the vertical motions. The extent of the motion sensitivity is important as it will undoubtedly determine the limits of detection for the particular instrument. The range of values selected for this particular study were based on the estimated natural response of platforms to a random sea. For the mobile platforms used in oceanographic research, roll periods from 5 to 8 seconds can be expected. Roll angles in excess of 45 degrees have been reported, but anything over 30 degrees would probably result in work stoppage. Linear accelerations of approximately 0.5g are close to those reported, but linear amplitudes greater than those used in this experiment would be expected at sea.

The next most important required characteristic is sensitivity. High sensitivity is important because determination of trace components from small samples (in the parts per million and possibly the parts per billion range) will be required.

It is recognized that performing complex manual tasks at sea can seriously impair the accuracy of the results, and therefore, the technique should be amenable to automation. There is also the desire to have the unit operate unattended for extended periods of time. This would require a method that needs little or no sample pretreatment. Also, the data that are produced should be in a format which can be easily stored and telemetered if necessary. Other requirements include low power consumption, reliability, ruggedness and safety. Finally the system should produce the greatest amount of useful information (both qualitative and quantitative) that can be interpreted with the least amount of effort and complexity.

D. Chromatography

Of the available high resolution analytical methods which can be applied to unresolved whole oil samples (chromatography, mass spectrometry and thermal analysis), it is suggested that chromatography gives the greatest amount of useful information with the least amount of complexity. Specifically gas-liquid-chromatography (GLC) is capable of producing information which is relatively easy to interpret and has been found useful in identifying oil pollutants (5, 6). It is assumed that oils are so chemically different that their contents constitute a chemical "fingerprint" which will lead to their identity. The technique is sensitive enough to permit analysis of small samples obtained from a surface film, or which might be dissolved in the water column or found in sediments. It is a physical method for the separation and identification of a mixture of chemical compounds and lends itself to automation.

1) Gas-Liquid-Chromatography

Essentially gas-liquid-chromatography is a physical separation technique, in which the components to be separated are distributed between two phases. One of these phases is a liquid, which is held stationary on finely divided solid particles; the second phase is a gas which acts to transport the solute through the fixed liquid. In 1952 James and Martin described a gas-liquid partition technique in which the solutes were distributed between a moving carrier gas, nitrogen, and a non-volatile liquid phase, silicone oil, immobilized on a finely divided solid, Celite (7). In 1941, Martin and Synge in describing their Nobel prize work on liquid-liquid partition chromatography, clearly state the principle of gas-liquid chromatography (8).

As stated above, the mixture of chemical compounds is moved physically past a stationary phase. The various components of the mixture migrate from the moving phase into the stationary phase and back again into the moving phase. This process is repeated many times during the course of travel of the mixture through what is called the column. If the components have different adsorptivities, the more strongly adsorbed compounds will lag behind the others and, in sufficient time, a separation of the components of the mixture can be achieved. After separation, the components enter a detector.

2) Flame-Ionization-Detector

A detector which is highly sensitive to organic compounds and widely used is the Flame-Ionization-Detector. The flame ionization detector was first described in 1958 (9, 10). At that time it was reasoned that the thermal energy in a hydrogen flame should be sufficient to induce emission of electrons from organic and inorganic molecules having a sufficiently low work function. The electric current that flows between the two electrodes above the detector flame is thus related to the trace molecule concentration. Even to date the phenomena of ion production in the flame has not been unequivocally determined. One explanation by Stern points out that the low work function of carbon, 4.3V, could explain the large ion concentrations observed (11). On the other hand Calcote has presented evidence that the mechanism of ion formation in flames results from chemiionization rather than thermal ionization. According to Calcote, "chemiionization differs from the thermal ionization in that the product molecules retain the energy released by strong exothermic reactions which lead to ionization" (12). Whatever the actual ionization mechanism, positive and negative ion concentrations in hydrocarbon flames have been estimated at 10^{10} to 10^{12} ions/ml. (13).

Studies have been performed on polarizing potentials, and at low voltages the ion current is proportional to applied voltage, i.e., the electrode gap acts as a fixed resistance. At high voltages all ions are collected to produce a fixed current corresponding to the flat portion of the current-voltage ionization curve for gases (13). The electrode voltage is adjusted to obtain the saturation current for optimum performance. This voltage is a function of electrode spacing, higher voltage being required for larger interelectrode distances. If 200V or greater are used, a saturation condition will be achieved regardless of detector design.

Figure 1 is a schematic diagram of the commercial flame-ionization cell used. The column effluent, a dilute binary mixture of solute in nitrogen, is mixed with hydrogen fuel and burned at the tip of the quartz jet in an excess of air. Optimum performance is particularly dependent on the ratio of hydrogen to carrier gas flow rate. (This ratio determines the flame temperature of H_2 - air flames; about 2100°C (13).) A 2:1 ratio of nitrogen to hydrogen is suggested by Ongkiehong for better sensitivity and reduction in noise level (16). Condon, et al, recommend a 1:1 ratio of nitrogen to hydrogen for general use (17). It is generally agreed that the air flow should be ten times the nitrogen flow rate. The air flow should be sufficient to sweep the water vapor from the detector chamber. An excessive supply of air may lead to turbulence in the flame zone with resultant noise. Hydrogen burning at the jet produces a background signal of the order of 10^{-14} amperes, depending on the flow rate and the impurity content (13). The ions are collected at the electrodes, the probe being negative and the positive electrode, which is a cylinder located above the concentric with the flame, being the ion collector.

The detector is a transducer which is used to sense and measure the amounts of the components present in the carrier gas leaving the chromatographic column. That is, the detector indicates the presence and amount but not the identity of the components. Identification, in most cases, requires the interpretation of a complete chromatogram. The universal detector does not exist today, and a compromise must be made among the desirable characteristics for each particular case.

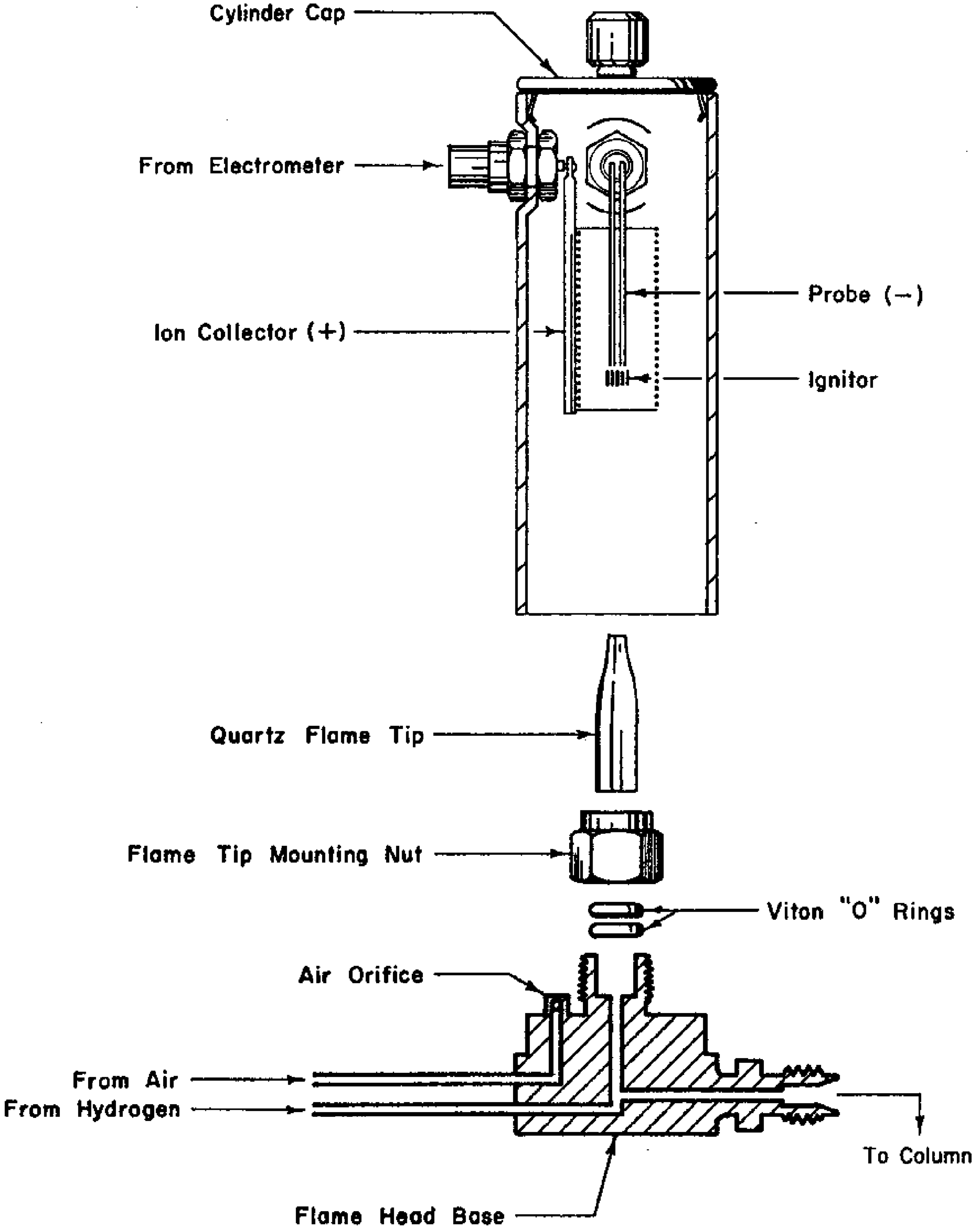


FIGURE 1: SINGLE FLAME CONFIGURATION (15)

Sensitivity is probably the most important characteristic of any detection system. High sensitivity in chromatographic detectors permits the determination of trace components in small samples of complex mixtures.

Another characteristic of the sensor and associated electrical equipment is the limit of detection. The lower limit is the minimum concentration which the detector will sense reliably. The upper limit is usually the point where the detector begins to respond nonlinearly with respect to concentration.

Another desirable characteristic is stability. Short term instability, or noise, limits the reliability of low level signals during trace analysis. Long term instability, or base line drift becomes a problem with separations that require extended periods of time. Random noise or even periodic noise can result if the detector is sensitive to motion. Fluctuations in gas flow, temperature and position can result in instability. Stability will govern reproducibility and the need and frequency of calibration. With respect to response time, the time constant of the detector must be small enough so that the separate components will be detected individually.

To assume reliability, simplicity in construction, maintenance and calibration are desirable. The unit should be rugged enough to withstand vibration and shock. Finally the detector should be safe to operate and inexpensive.

E) Summary of Problem

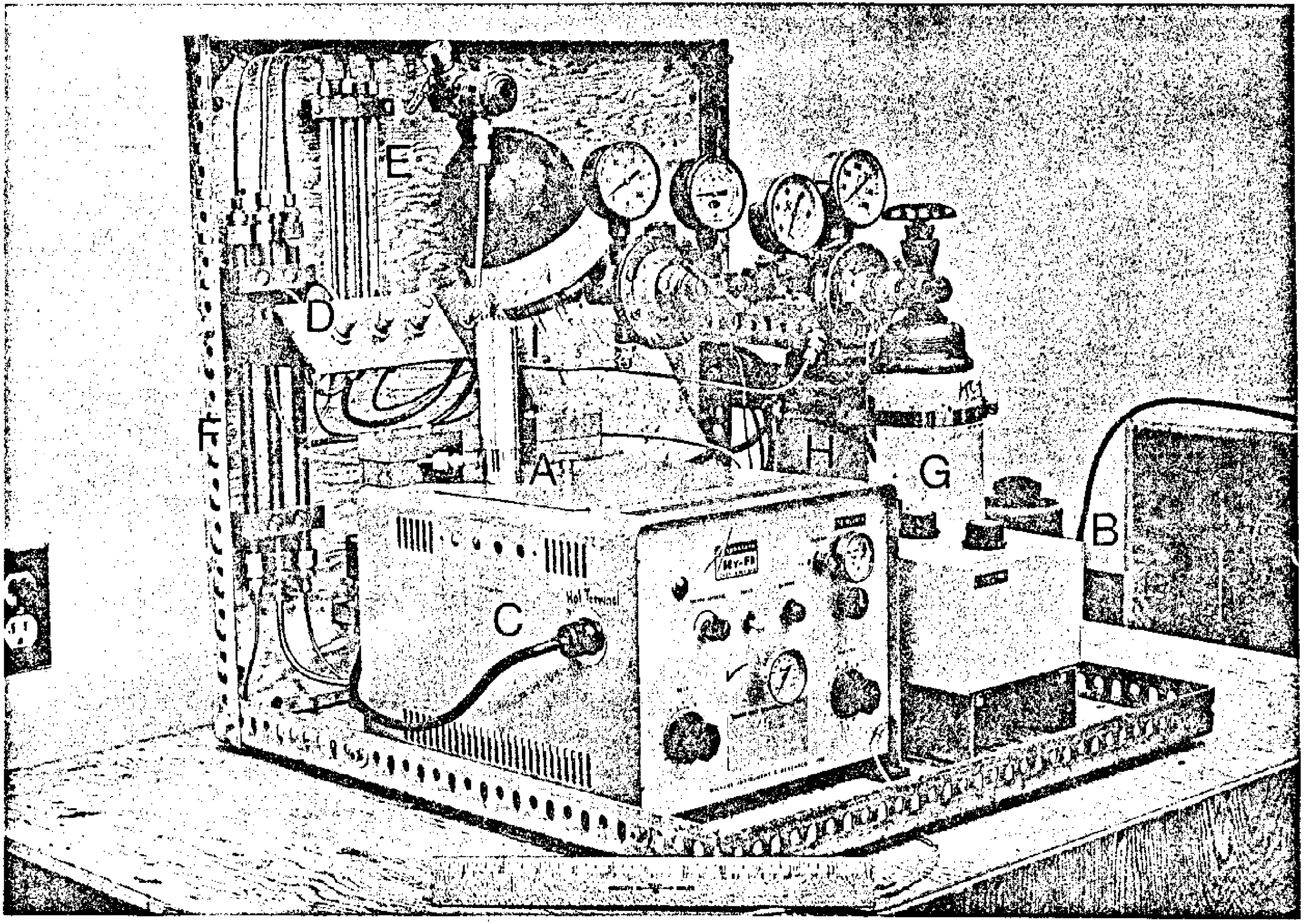
What is needed is a high resolution chemical analysis technique that will operate in a marine environment. By high resolution is meant the separation and identification of hydrocarbons in the parts per million and possibly the parts per billion range. The marine environment requires that the unit operate satisfactorily on a moving platform. The technique that satisfies the above criteria, with the possible exception of the motion sensitivity, is chromatography or more specifically, gas-liquid-chromatography. The exception arises in the particular type of detection used. To satisfy the sensitivity requirements, the flame-ionization-detector is required, and it was believed to be motion sensitive.

Therefore, it was important to determine if the detector is indeed motion sensitive and to what extent. Also of interest were any other problems that might be associated with trying to use a conventional flame-ionization-detector on a moving platform.

F) Summary of Thesis

An operational portable gas chromatograph, using an Aerograph flame ionization detector, was constructed. The unit is shown in photographic plate 1. A description of its construction is given in Section II - B. Modifications required to eliminate the detector's electrical motion sensitivity are discussed in Section III - A.

The translational tests (sway and heave) and the resulting detector's response to linear accelerations is described in Section III - D-2. The rotational testing procedure and the detector's response to angular acceleration is discussed in Part 3. Also, in this section, a description of the injection of different concentrations of hydrocarbons is given, and a comparison made between the stationary trace areas and those obtained while moving. For each



PHOTOGRAPHIC PLATE 1: PORTABLE GAS CHROMATOGRAPH of the motions studied, isothermal chromatograms for normal alkanes (nC_6 - nC_{32}) were obtained and these are given in Section III.

The sensitivity of the Aerograph detector was determined and the limits of detection for the motions studied are given in Section IV. In Section V the results are interpreted and modifications suggested for the use of flame-ionization-detectors at sea.

II. APPARATUS

A) Initial Considerations

To study the motion sensitivity, a means of subjecting a flame-ionization-detector to velocities and accelerations in various directions was required. The detector is defined as not only the flame cell, but also the related electronic equipment. Thus the FID consists of the flame cell, heater (to inhibit the condensation of water which results in noisy operation), the electrometer and the recorder. The detector also requires three gases each with a maximum pressure of about eighty pounds per square inch.

An approach using flexible gas lines and electrical leads could have been used and only the flame cell subjected to motion. However, spurious responses could result from surges in the accelerating gas lines. If only one particular direction of motion was involved, a suitable baffle arrangement probably could have been devised. But because the testing was to be translational in three directions as well as rotational, and it was anticipated that the unit would have to be moved from one piece of testing equipment to another, it seemed highly desirable to keep the detector as self contained and portable as possible. For the above reasons (and the electrical problems that will be discussed in Section III - A) it was decided to include the gas supplies and the electrometer with the detector and oven. The unit as it was used in testing is shown in photographic plate 1. The unit consists of the detector cell at "A", the electrometer at "B", the oven at "C", and the three gas supplies with associated regulators. Each gas has a fine metering valve (shown at "D"), a rising ball flowmeter (at "E") and a molecular sieve at "F". The only part of the detector which is not included with the unit in the photograph is the recorder which is shown in photographic plate 2. A dual channel recorder was used to compare the response with the actual motion or acceleration.

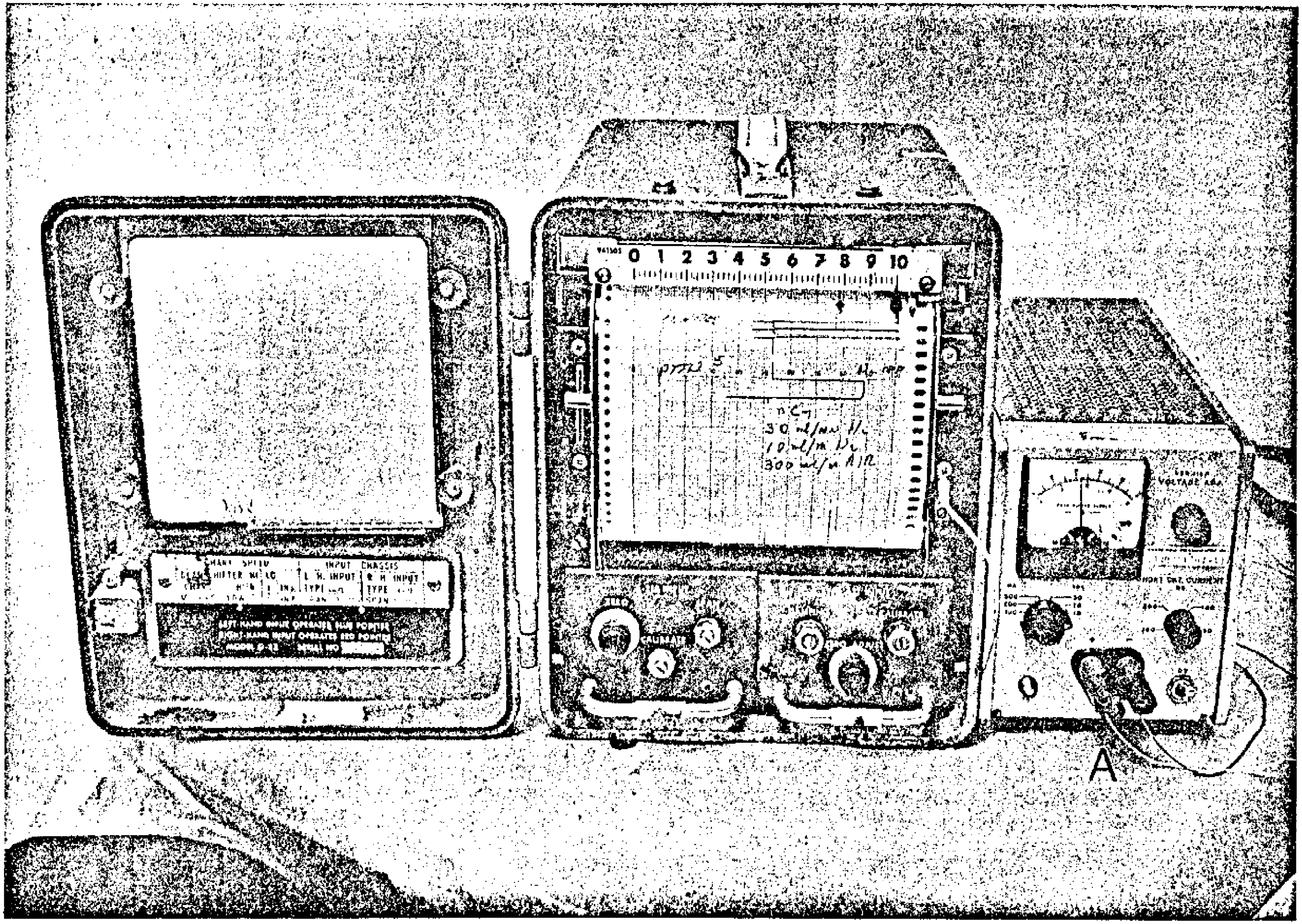
B) Portable Flame-Ionization-Detector

The flame-ionization-detector components are the flame cell, heater (which in this case is the column oven), electrometer, three gas supplies and a recorder. It was decided that the unit should be essentially self-contained and portable. Due to the constraints placed by the testing equipment, the space was limited to a two foot cube. The complete unit is shown in photographic plate 1.

A Wilkens Instrument and Research Model 550-B oven and detector was used. This is a single column single frame unit. The detector cell is shown in Figure 1; a single quartz tip is used. A cylindrical brass screen collector surrounds the flame; inside the collector is a combination probe and ignitor. The configuration of the probe in this particular unit results in the cell being asymmetrical. A ring probe would eliminate this asymmetry and possibly reduce the sensitivity of the cell to roll and pitch orientation.

1) Detector Cell Modification

Another design weakness (which was anticipated and corrected) was the securing of the ion collector in the Aerograph detector. The collector is shown at "A" in Figure 2. The collector was attached to the post shown at "B". This post was soldered to the penetrator at "D". In handling the detector housing it was observed that the pin



PHOTOGRAPHIC PLATE 2: DUAL CHANNEL RECORDER

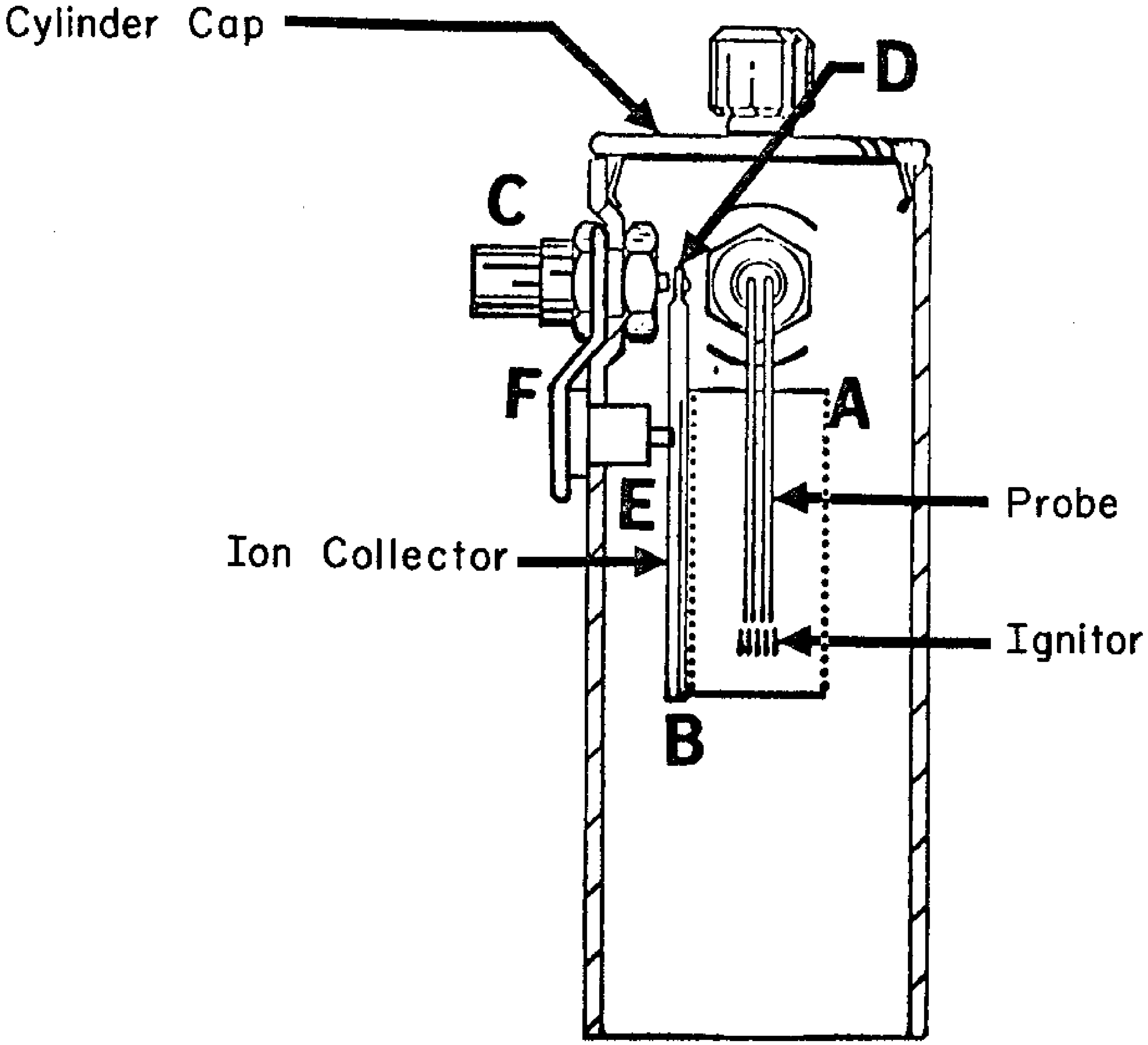


FIGURE 2: MODIFIED DETECTOR CELL

(shown at "D") would rotate and allow the ion collector to come in contact with the probe. If this were to occur during the operation of the instrument, the results would be catastrophic. As there is a 300 volt potential between the collector and the probe, some means had to be provided to prevent the collector from coming in contact with the probe. A ceramic standoff was modified to accept the rod that supports the ion collector. A one-quarter inch hole was drilled one-half inch below the penetrator shown at "C". The standoff was inserted into the one-quarter inch hole at "E" and was held in place by a brass back-up support which is shown at "F". The standoff is essentially supported as a cantilever from the detector housing. The assembled modified detector is shown in photographic plate 3.

A Carle electrometer (Model No. 9001) was used and is shown at "B" in plate 1. In the detector cell when ions are produced in the flame zone, a small current flows between the collector and the probe. The electrometer changes this small current into a voltage that is recorded on the chart recorder. The interfacing of the electrometer with the Wilkens Instrument and Research detector is discussed in the next section. As can be seen in the photograph, the electrometer was mounted as close to the detector as possible. It was discovered that any flexing of these leads with respect to the detector caused capacitive charges which produced transient currents. This problem is discussed and the corrective measures are described in Section III - A.

2) Interfacing Electrometer with Detector

The Carle electrometer was interfaced with the Aerograph Model 550-B oven and detector. The Carle gas chromatograph was equipped

PHOTOGRAPHIC PLATE 3: MODIFIED DETECTOR

with a differential dual flame ionization detector; this configuration is shown schematically in Figure 3. Both positive and negative ions can be collected with equal efficiency which permits operation of the unit as a differential detector compensating for reference background in the dual column system. By using this configuration only one electrometer is required; the schematic for the Carle electrometer is shown in Figure 4.

Comparing the configurations of the Carle and Aerograph detectors (Figures 3 and 1) shows that only minus 300 volts need be supplied to the Aerograph detector as opposed to both plus and minus 300 volts for the Carle. Both plus and minus 300 volts were brought from the electrometer to a selector switch on the control panel (shown at "G" in photographic plate 4) so that either plus or minus 300 volts could be applied to the detector probe. Also an on-off switch (shown at "H") was used to prevent electrical shock when handling or adjusting the probe.

The Aerograph detector has an ignitor (a match is used with the Carle detector). From the Aerograph electrometer schematic diagram, it was determined that 3.4 volts is used for ignition. In this particular case two 1.5 volt dry cell batteries in series were used. These batteries were isolated because they are connected to the -300 volt line. A button (shown at "I" in photographic plate 4) is provided to impress the three volts across the ignitor coil.

3) <u>Gas System</u>

Three separate gases are required for the detector. Two eleven cubic foot tanks are used for hydrogen and nitrogen; these are shown

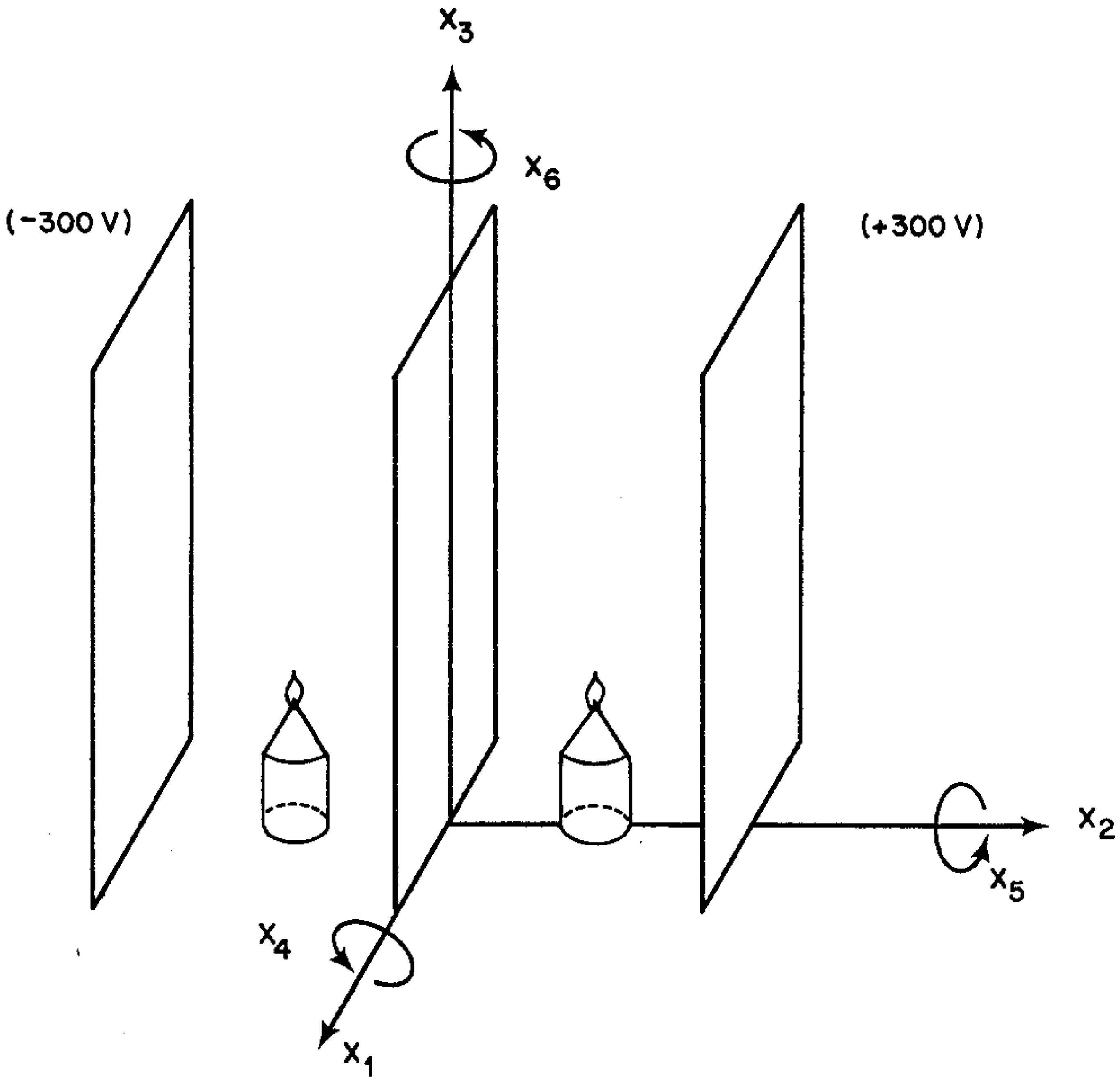
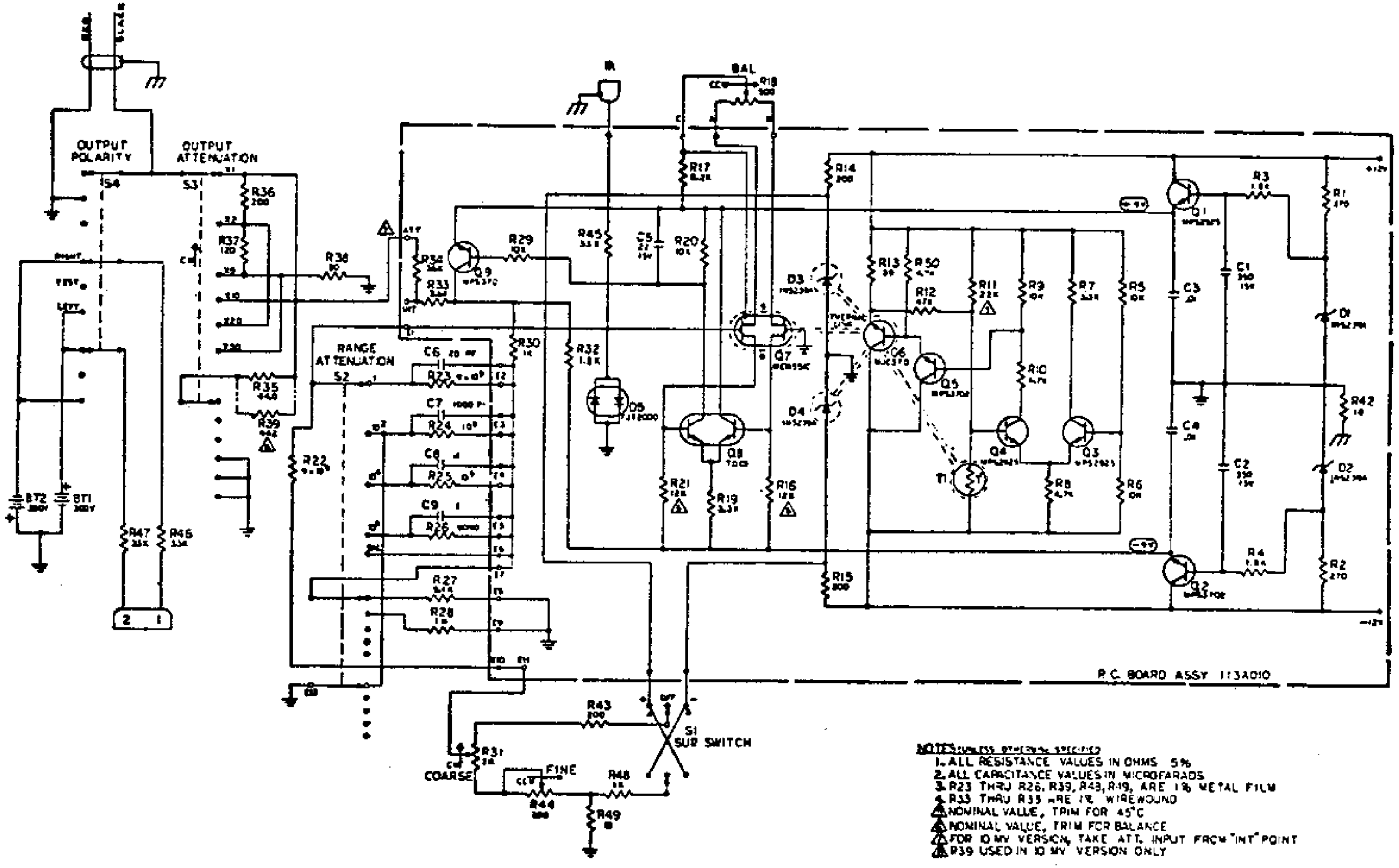
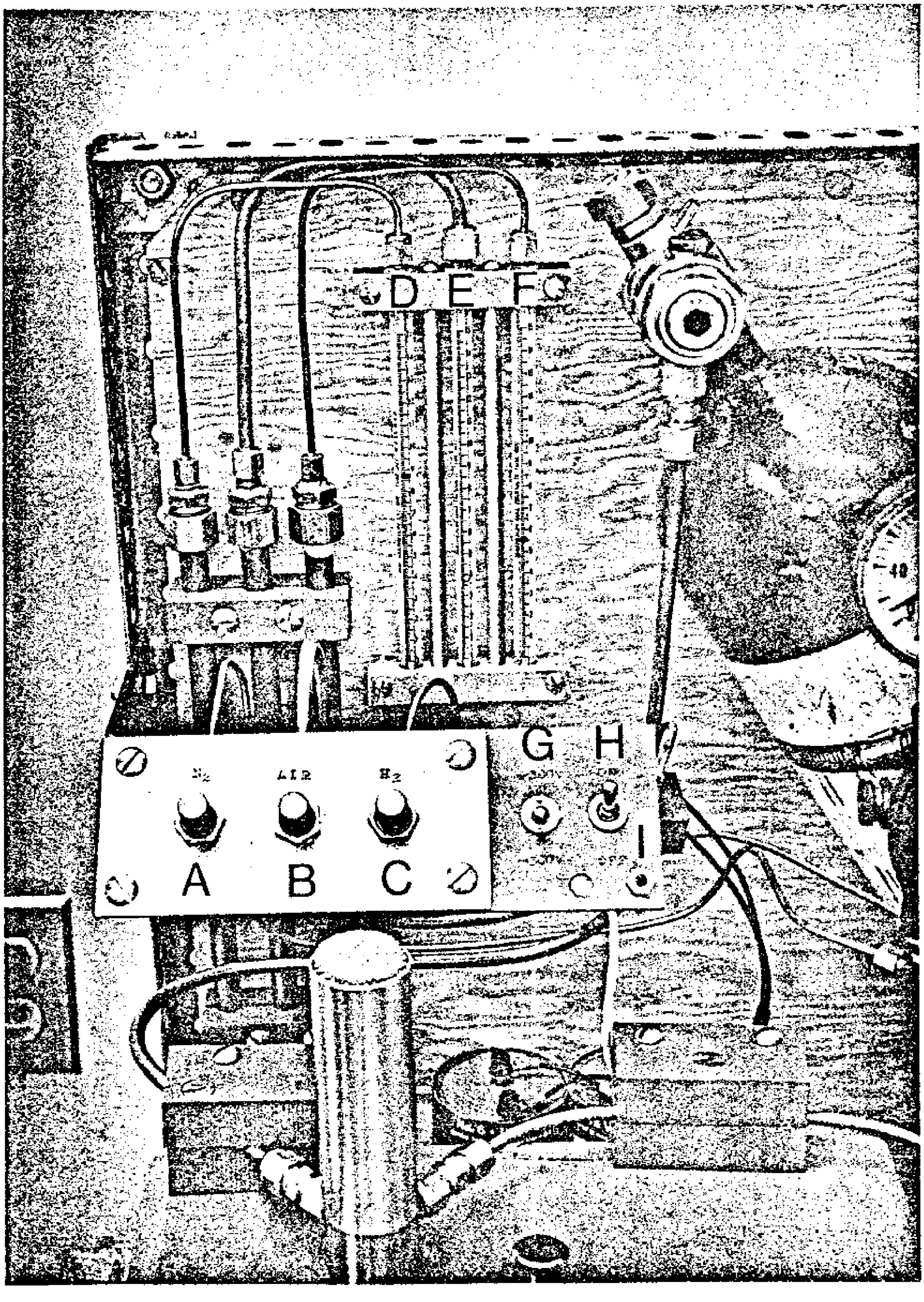


FIGURE 3: DUAL FLAME CONFIGURATION



NOTES: UNLESS OTHERWISE SPECIFIED
1. ALL RESISTANCE VALUES IN OHMS 5%
2. ALL CAPACITANCE VALUES IN MICROFARADS
3. R23 THRU R26, R39, R43, R49, ARE 1% METAL FILM
4. R33 THRU R35 ARE 1% WIREWOUND
△ NOMINAL VALUE, TRIM FOR 45°C
△ NOMINAL VALUE, TRIM FOR BALANCE
△ FOR 10 MV VERSION, TAKE ATT. INPUT FROM "INT" POINT
△ R39 USED IN 10 MV VERSION ONLY

FIGURE 4: ELECTROMETER SCHEMATIC (18)



PHOTOGRAPHIC PLATE 4: GAS SYSTEM

at "G" and "H" respectively in Plate 1. A thirty cubic foot cylinder is used for the air supply. Normally ten times as much air is used as the other gases, but a tank of this size would have been much too large for the two foot cube into which all the detector components were required to fit. The overall size of the unit was dictated by the testing equipment that was to be used. Pressure regulators are required on all three gases. On the air, a single stage regulator reduced the high pressure air in the tank (2000 psig maximum) down to 45 psig at the fine metering valve (shown at "B" in the photographic Plate 4). A single stage regulator was used with the air supply because the flow rate may easily vary ten per cent without causing problems. Two stage regulators are used on the nitrogen and hydrogen to reduce the tank pressure (2000 psig maximum) to about 20 psig at the inlet of the fine metering valve. The metering valve for the nitrogen and hydrogen are shown at "A" and "C" in the Plate 4. The nitrogen and hydrogen tanks could have been mounted in any position, such as horizontally or diagonally as the air tank is mounted.

After leaving the fine metering valves, each of the gases passes through a tube flowmeter. Matheson number 600 tube flowmeters with pyrex balls are used for the nitrogen and hydrogen. The height of the ball is read in centimeters and the flow rates obtained from calibration curves supplied by the manufacturer. The nitrogen flowmeter is shown at "D" and has a range of 5 to 100 milliliters per minute. The hydrogen flowmeter has a range of from 10 to 120 milliliters per minute, and is shown at "F". For the air flow a Matheson Model No. 602 is used with a stainless steel ball for 100 to 900 milliliters per minute. A tantalum ball can also be used with this flowmeter and increases the range about fifty per cent.

After leaving the flowmeters, each of the gases passes through a filter (shown at "F" in the photographic Plate 1). These filters are fabricated from one half inch copper tubing and are about 14 inches in length and are filled with Linde 5A molecular sieves. This material is granular and therefore a sterile cotton plug is employed at each end to prevent particles from entering the fine tubing. These filters remove hydrocarbons and particulate alkali salts which produce unwanted ions when they pass through the flame. The filters can be opened and the molecular sieves replaced. The filters are placed in a vertical position so that the granular material fills the entire cross section of the filter body. Also, to prevent low frequency standing waves it is desireable to keep the length of pipe in any particular direction at a minimum. One-eighth inch copper refrigeration tubing was used for the nitrogen and hydrogen gas systems and one-quarter inch for the air line. All components in the gas systems were vapor degreased with trichloroethylene and the utmost care taken to keep stray organics from entering.

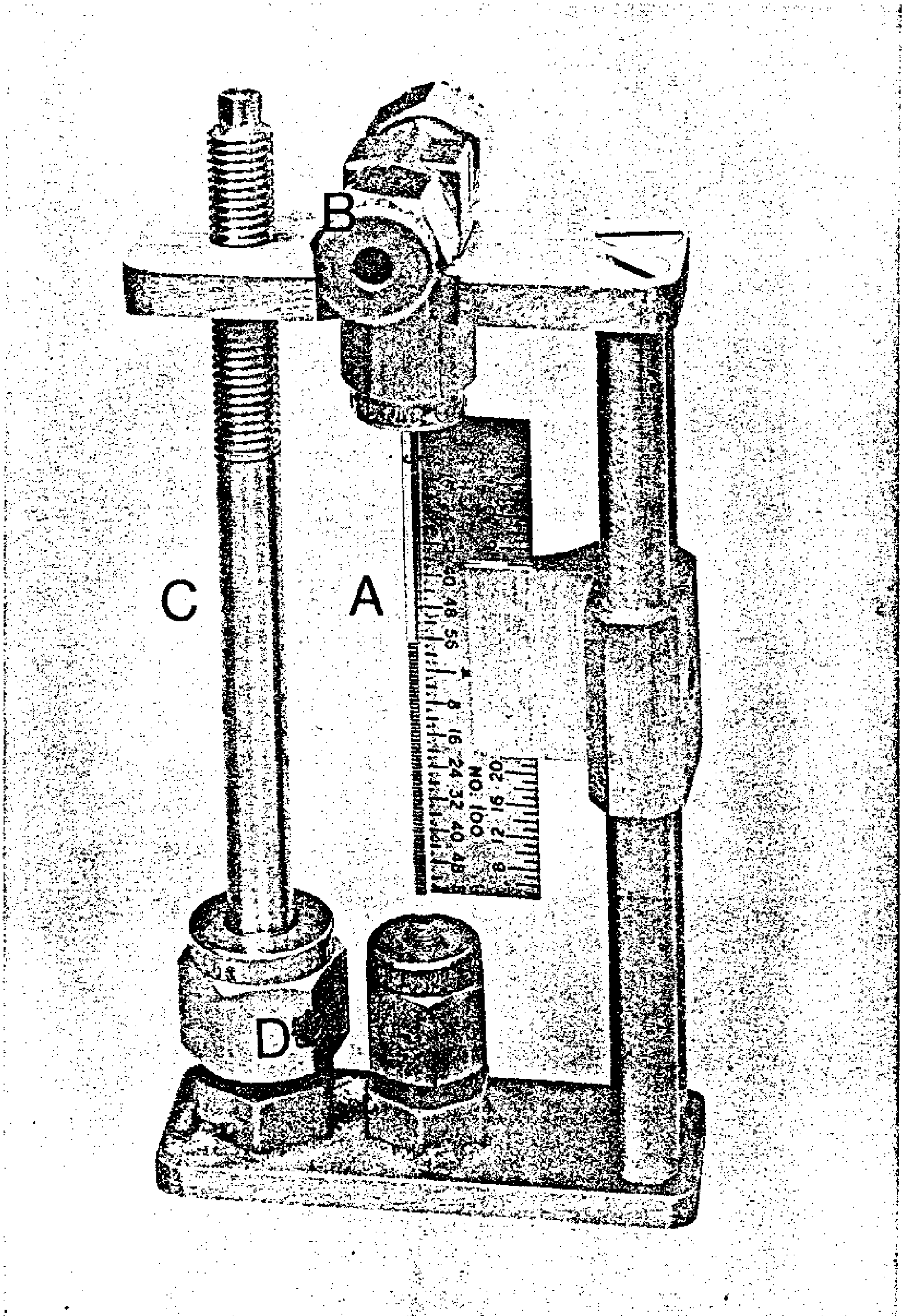
C) Constant Signal Source

In order to test the detector's response to acceleration at different hydrocarbon concentrations, a means was required to produce and maintain different concentrations in the flowing carrier gas for extended periods of time.

A method used by Desty, et al, required the use of capillaries having diameters from 50 to 450 microns (19). They were able to obtain constant signals in the parts per billion range for extended periods of time. No carrier gas was used in this method because the open end of the capillary was positioned in the mixing chamber of the detector. The liquid in the capillary evaporates slowly into the mixing chamber. From the dimensions of the capillary and the rate at which the liquid level fell, the rate of diffusion was determined. To change the mass flow rate at a given temperature, the capillary had to be changed.

The principle used above was first described by Stefan for determining gaseous diffusion coefficients (20). A constant rate of diffusion can be achieved in an open ended cylinder if the height of the liquid is held constant. The rate of diffusion is directly proportional to the cross-sectional area and inversly proportional to the distance from the liquid to the top of the cylinder. If the cross section is reduded to prevent convection cells in the stagnant column, low diffusion rates can be obtained, but if too small a cross section is used, a problem arises with too rapid a drop of the meniscus. Thus a cylinder bore must be chosen which will give the desired rate of diffusion at a particular temperature and maintain a relatively constant liquid level.

The following method was used in this experiment to produce constant mass flow rates in the parts per million range for extended periods of time. It consisted of using various diameter capillaries (from 400 microns to 1400 microns in diameter, and approximately 7.5 centimeters long) and passing the carrier gas over the open end. The mass flow rate was changed by varying the carrier gas flow rate and by



PHOTOGRAPHIC PLATE 5: CONSTANT SIGNAL SOURCE varying the temperature of the capillary.

The unit is shown in the photographic Plate 5. The capillary containing the hydrocarbon is shown at "A". The carrier gas passes through the fitting (at "B") and over the top of the capillary. Because of the expansion of the hydrocarbon with changes in temperature and the loss of fluid by evaporation, a means of adjusting the height of the meniscus was provided. The threaded piston (at "C") is rotated, which causes it to move up or down (depending on the direction of rotation) displacing fluid in the reservoir (at "D") and changing the meniscus height. The scale (at "E") is used to read the height. The unit was placed in the column oven and a mirror used to read the scale.

A series of valves and a bypass line was used with the capillary to switch the constant signal on and off. The carrier gas could be passed over the capillary to obtain a constant signal or the capillary could also be bypassed to obtain a reference base line. Then knowing the sensitivity of the detector, the mass flow rate could be determined. With the above method, a particular rate of diffusion was achieved by keeping the temperature constant and varying the carrier gas flow rate or by selecting a particular flow rate and changing the temperature and adjusting the liquid height.

A problem arose when using the capillary with an oven temperature below one hundred degrees centigrade. On the particular detector used, the column oven serves as the detector oven and with the lower oven temperatures, water condensed in the detector cell, causing noisy operation. It was not possible to increase the air flow rate to eliminate the problem. Therefore, an additional heater was provided for the detector cell when the capillary was used.

III. EXPERIMENTAL PROCEDURE

A) Electrical Motion Sensitivity

Initial testing indicated that a considerable amount of the motion sensitivity of the detector was due to electrical noise. A typical example for different attenuations is shown in Figure 5. This experiment was conducted with the detector leads furnished by the manufacturer and with the flame extinguished. The detector was subjected to a cyclic translational acceleration of approximately one-sixth gravity in one direction and one-eight in the opposite direction.

For the particular electrometer used, only 10^{-11} amperes are required for full scale deflection (10 mV) when the attenuation is set at unity. Figure 5 shows that the electrical noise is not significant above attenuations of 50. Medium resolution analysis is performed with attenuations in the 10^3 and 10^4 range and therefore for normal analysis the electrical motion sensitivity is not a serious problem. However, in this study the motion sensitivity of the flame was to be determined, however small, and therefore this electrical problem had to be eliminated. During trace analysis (parts per million range) the lower attenuations are used. With this detector one microliter of one part per million hydrocarbon results in a peak about one-half millivolt maximum with an attenuation of unity. The electrical noise would certainly obscure a signal of this magnitude.

The strategy for the elimination of the electrical noise was to start at the detector cell with shielding and work back toward the electrometer. The first line considered was the high impedance lead from the collector in the detector cell to the electrometer. Several

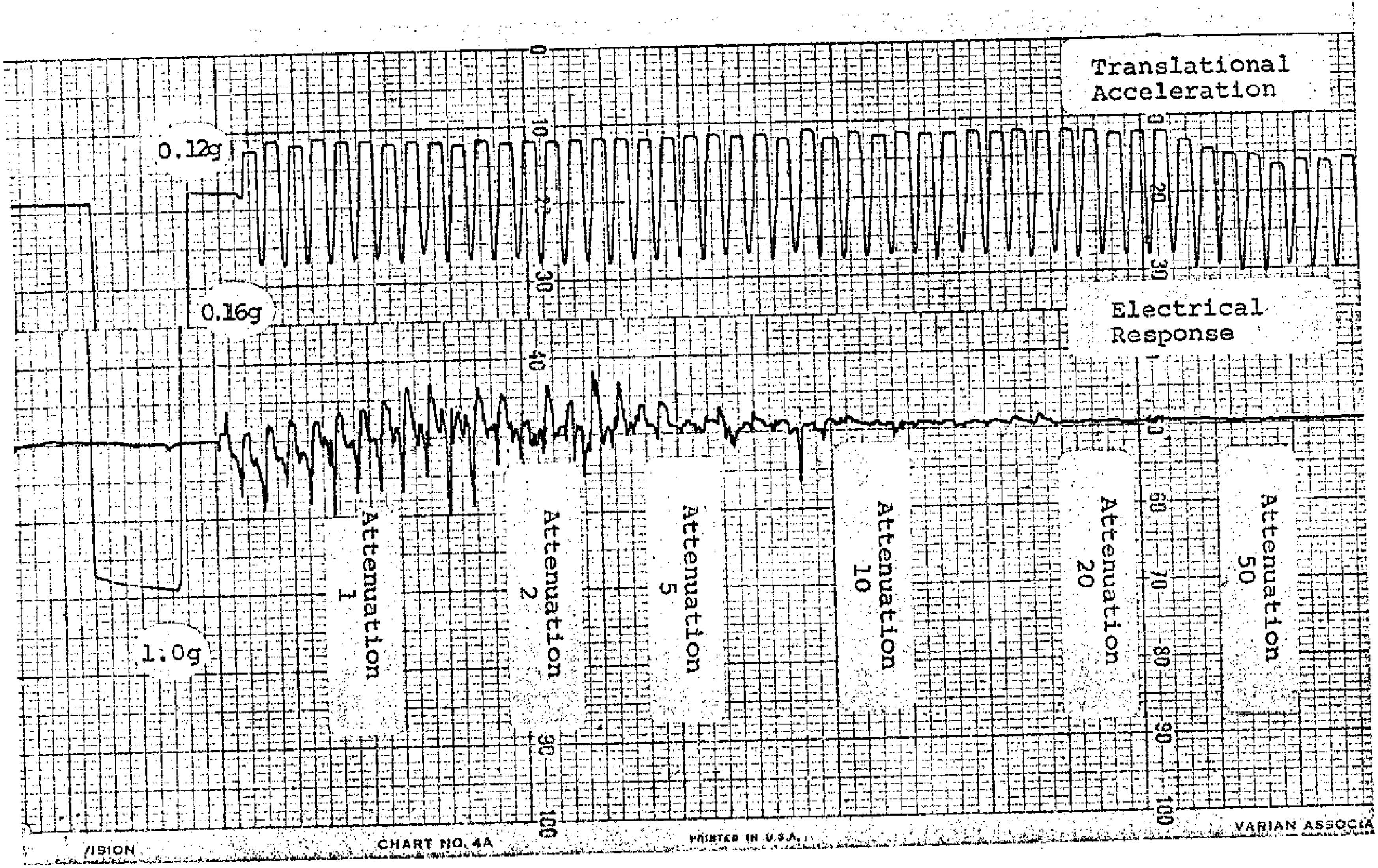
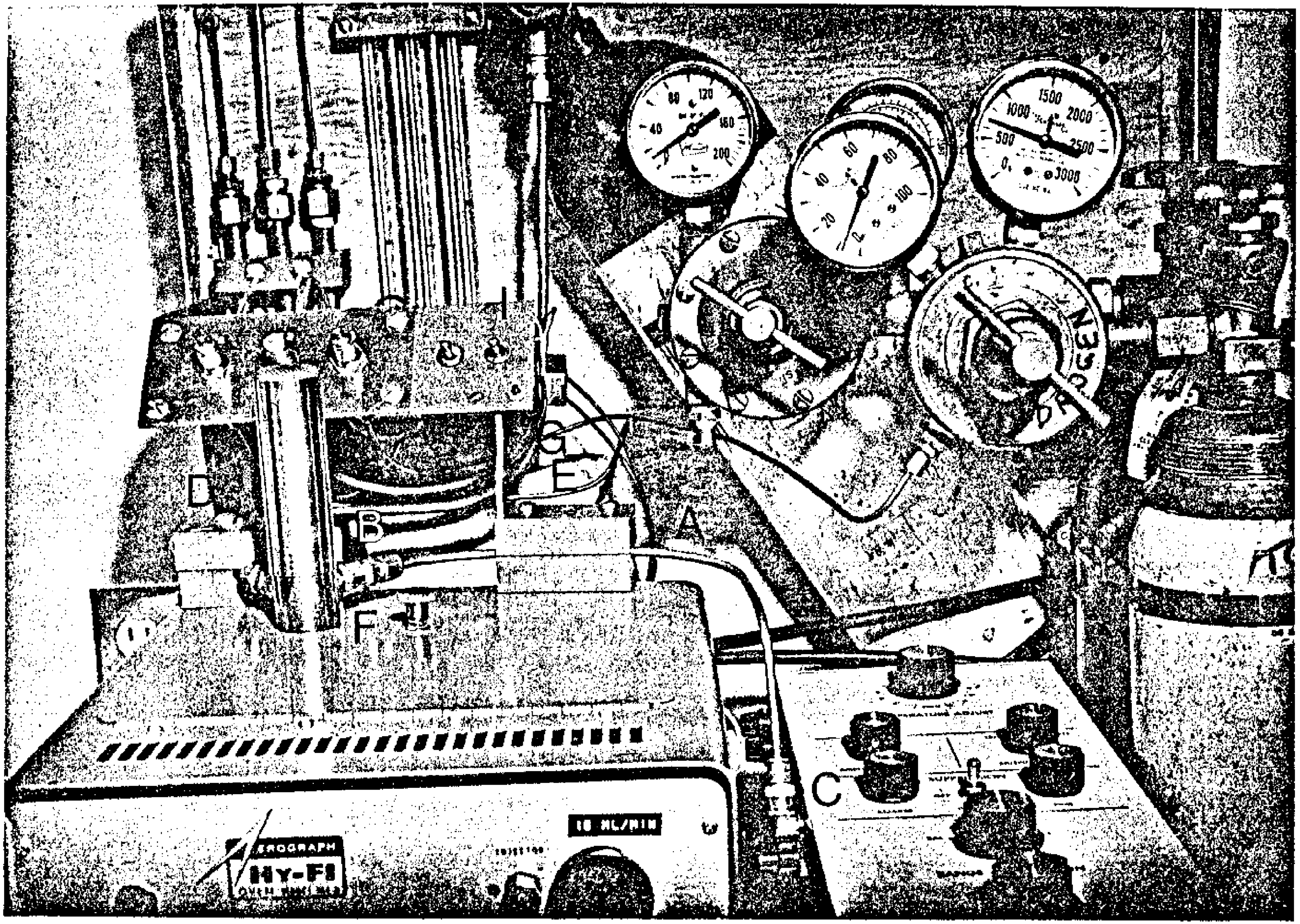


FIGURE 5: INITIAL ELECTRICAL MOTION SENSITIVITY (TRANSLATION)

methods of shielding were attempted without success. The major contributor to the electrical motion sensitivity was found to be the movement of the high impedance lead with respect to the adjacent equipment. Initially the lead was taped to the oven which reduced the noise level but not to a tolerable level. Finally the lead was encosed in three-sixteenths copper refrigeration tubing. This is shown at "A" in the photographic Plate 6. A modified Swagelok fitting was used to secure the lead to the detector cell (this is shown at "B"). A modified BNC fitting secured the shield to the electrometer as shown at "C". Thus positive mechanical as well as electrical contact was achieved; the same approach was applied to the combination probe and ignitor lead. It was found that any motion of the copper conduit with respect to the oven housing resulted in electrical disturbance. This was corrected by using "stand-offs" between the housing and the tubing. These are shown at "D" and "E". Finally the electrometer was disassembled and any wires causing an electrical disturbance when tapped, were secured. Also it was found that a slight amount of motion between the detector cell and the oven housing was causing noise. This was corrected with the small wedge shown at "F". With the above modifications the electrical motion sensitivity was reduced to the level shown in Figure 6. Prior to the running of any series of tests the electrical motion sensitivity was checked.

B) Electrometer Check-out

The following procedure was used to insure that the electrometer was performing satisfactorily. The electrometer and the recorder were plugged into a Sola constant voltage transformer for approximately



PHOTOGRAPHIC PLATE 6: WIRING MODIFICATIONS

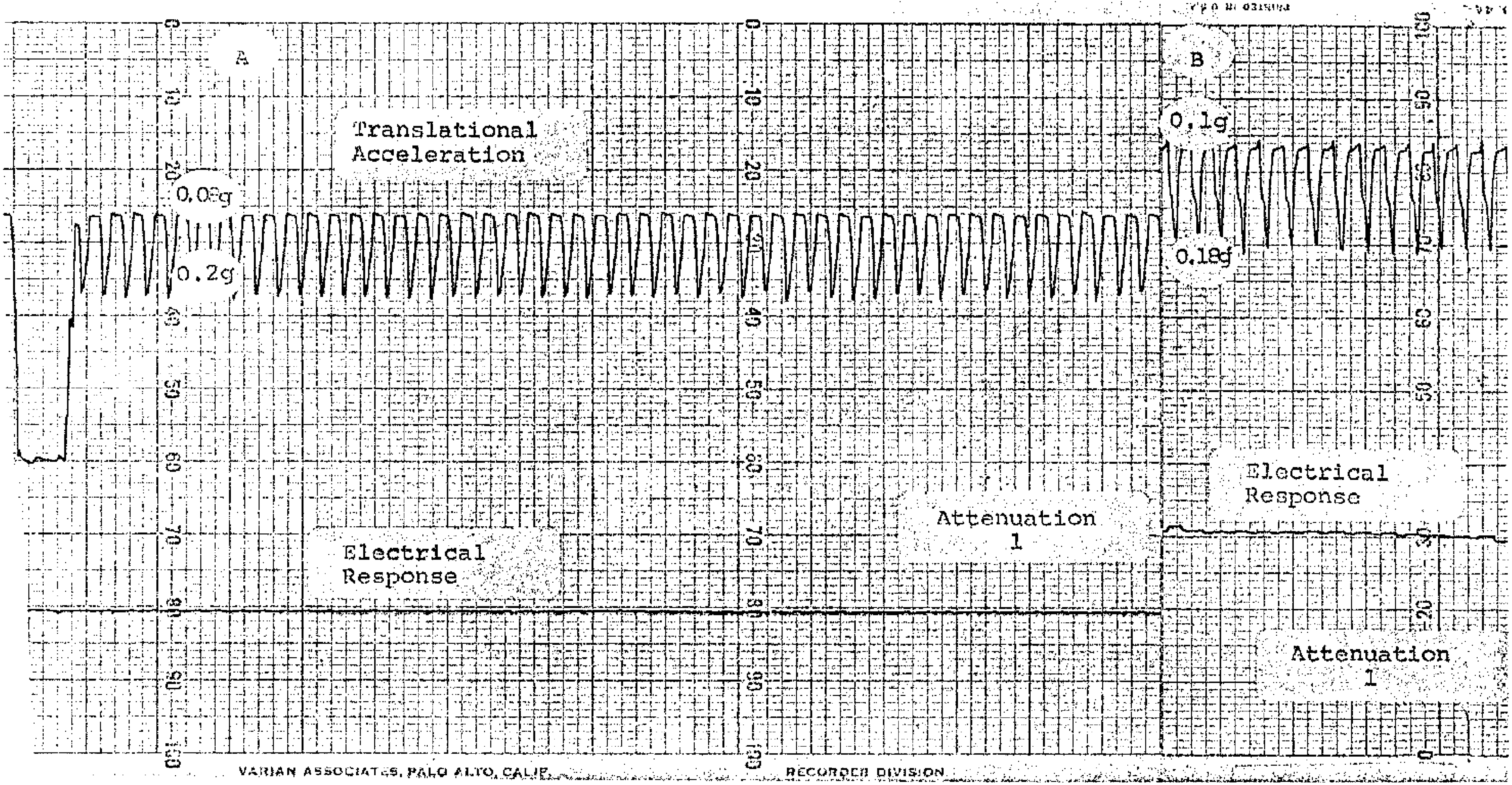


FIGURE 6: EXAMPLES OF CORRECTED ELECTRICAL MOTION SENSITIVITY (TRANSLATIONAL).

one-half hour to warm up the electrical components before beginning the check out procedure. The cables were disconnected from the detector housing and covered with aluminum foil to block any stray electrical pickup which might show up as noise. The leads from the electrometer were disconnected at the recorder and the recorder input shorted. The recorder was then zeroed at midscale. The shunt was removed and the electrometer output leads connected; the range and output attenuation on the electrometer were both set to 1. Next the amplifier balance was adjusted so that the recorder pen was at midscale, which in this case is electrical zero on the recorder. This base line was observed for several minutes and one per cent drift or noise was considered acceptable. Additonal verification of electrical zero was achieved by changing the attenuation from 1 through 50 and if deflection was observed, the amplifier was re-adjusted until no deflection was observed when the attenuator was switched. Finally the recorder was zeroed and the pen positioned 100 per cent of full scale using the suppression voltage. The attenuator was adjusted successively 2, 5, and 10 with the pen moving to 50 per cent, 20 per cent, and 10 per cent for each of the respective attenuator positons. With respect to response, which was less than a second for full scale on the recorder used, the response between switchings should be less than 0.5, 0.8, and 0.9 respectively for the three attenuations.

At this point the electrometer was considered fully operational. The amplifier balance was not adjusted after this point and all base line adjustments were accomplished using the suppression voltage.

C) Detector Check-out

With the electrometer operational the performance of the detector was verified as follows. The leads from the electrometer to the detector were secured. The following flow rates were achieved: 1) 20 milliliters per minute of nitrogen, 2) 20 milliliters per minute of hydrogen, 3) and approximately 300 milliliters per minute of air. The attenuation was placed on "balance" and the flame ignited by impressing 3 volts D.C. across the element which is incorporated in the detector probe. The voltage was applied with the button shown at "I" in photographic Plate 4 and was removed when a "pop" was heard. The pen was zeroed on the recorder using the suppression voltage. This was necessary because ions are formed in the hydrogen flame and the current that flows is bucked with a suppressor current. The range and output attenuation were set to 1. The unit was allowed to run for about 30 minutes. The tolerable noise was less than 0.2 millivolt or less than two minor divisions on the recorder; the drift was kept below one minor division or 0.1 millivolt. If the above criteria were not achieved, the detector was removed and cleaned in ethanol. When adjusting the ignitor, the switch (shown at "H" on Plate 4) was used to remove the -300 volts to prevent operator shock. Also the placement of the ignitor coil with respect to the flame was checked; the exact placement is not critical as long as the coil is not in or directly above the flame as this results in thermionic noise. Upon satisfaction of the above criterion, the detector was considered operational.

D) Testing Procedure

1) Detector Orientation

The orientation of the Aerograph detector cell with respect to the axes tested is shown in Figure 7. The X_1 axis (which is perpendicular to the console shown in the photographic Plate 1) was chosen as the roll axis and X_4 as the roll angle. X_2 is the pitch axis and X_5 is the pitch angle. The X_3 axis is then the direction for heave.

The environmental variables that were measured with respect to translational motion were the amplitude and acceleration along the X_2 axis. In roll (X_4) and pitch (X_5) axes the magnitude of rotation and the period were measured. With respect to the range and number of values each variable assumed, in translation an amplitude of one foot was used, and because of the geometry of the shaker table drive, accelerations of 0.1 of gravity in one direction and 0.375 of gravity in the other were achieved. With the roll and pitch tests, the angles used were 5, 10, and 20 degrees in both the clockwise (-) and counterclockwise (+) directions. Periods ranged from five to twenty seconds. In heave, maximum amplitudes of one foot and periods of 1.5 and 2 seconds were achieved.

2) Translational Tests

The translational tests were performed on a shaker table. The drive mechanism is shown in the photographic Plate 7. It was fabricated from a unit originally manufactured by Precision Scientific Co., Chicago, Illinois. Modifications included lengthening the table travel to two feet by replacing the bars shown at "A" in Plate 7. A one-sixth horsepower motor and gear reduction (1750 rpm in; 87.5 rpm out) was mounted

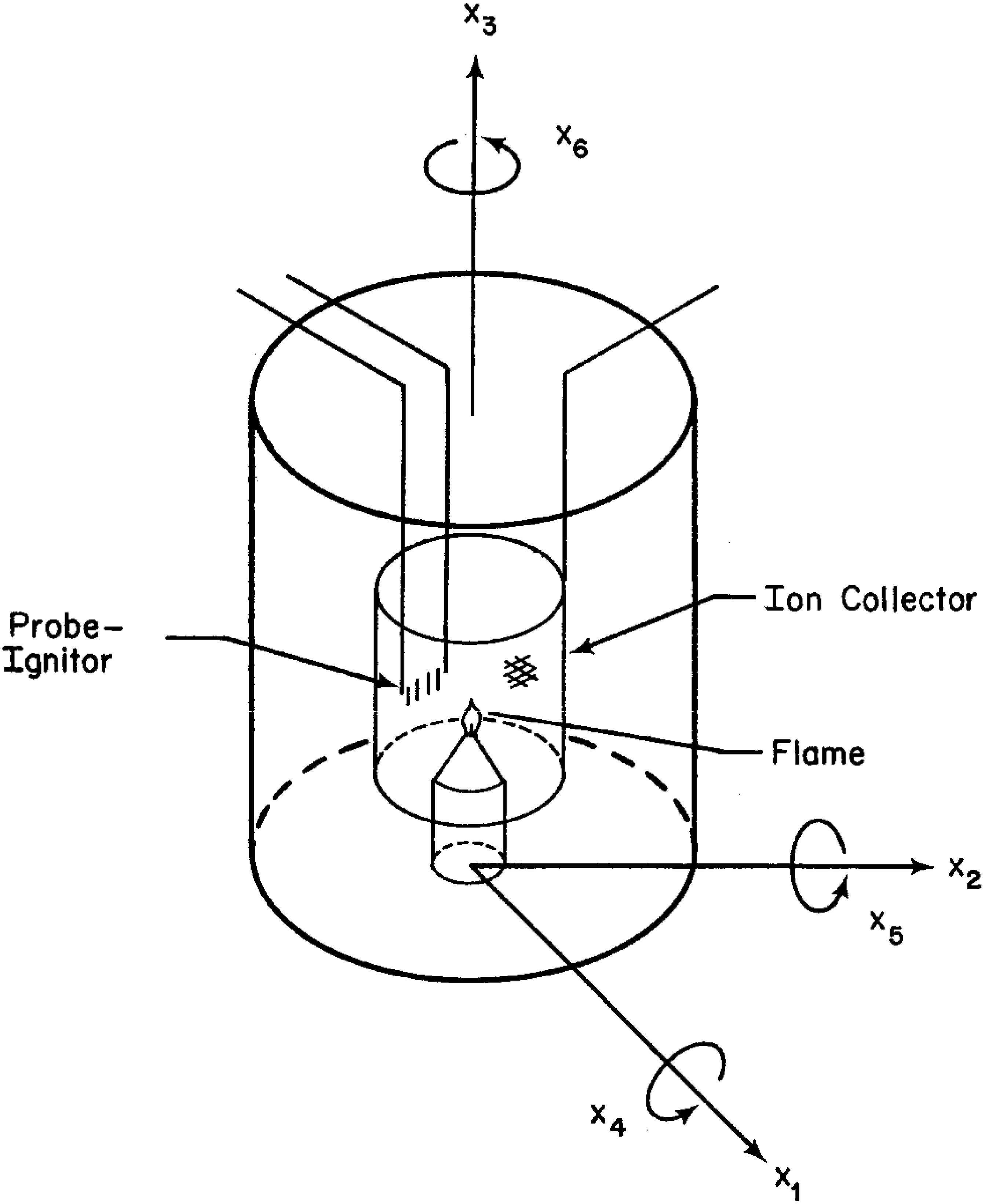
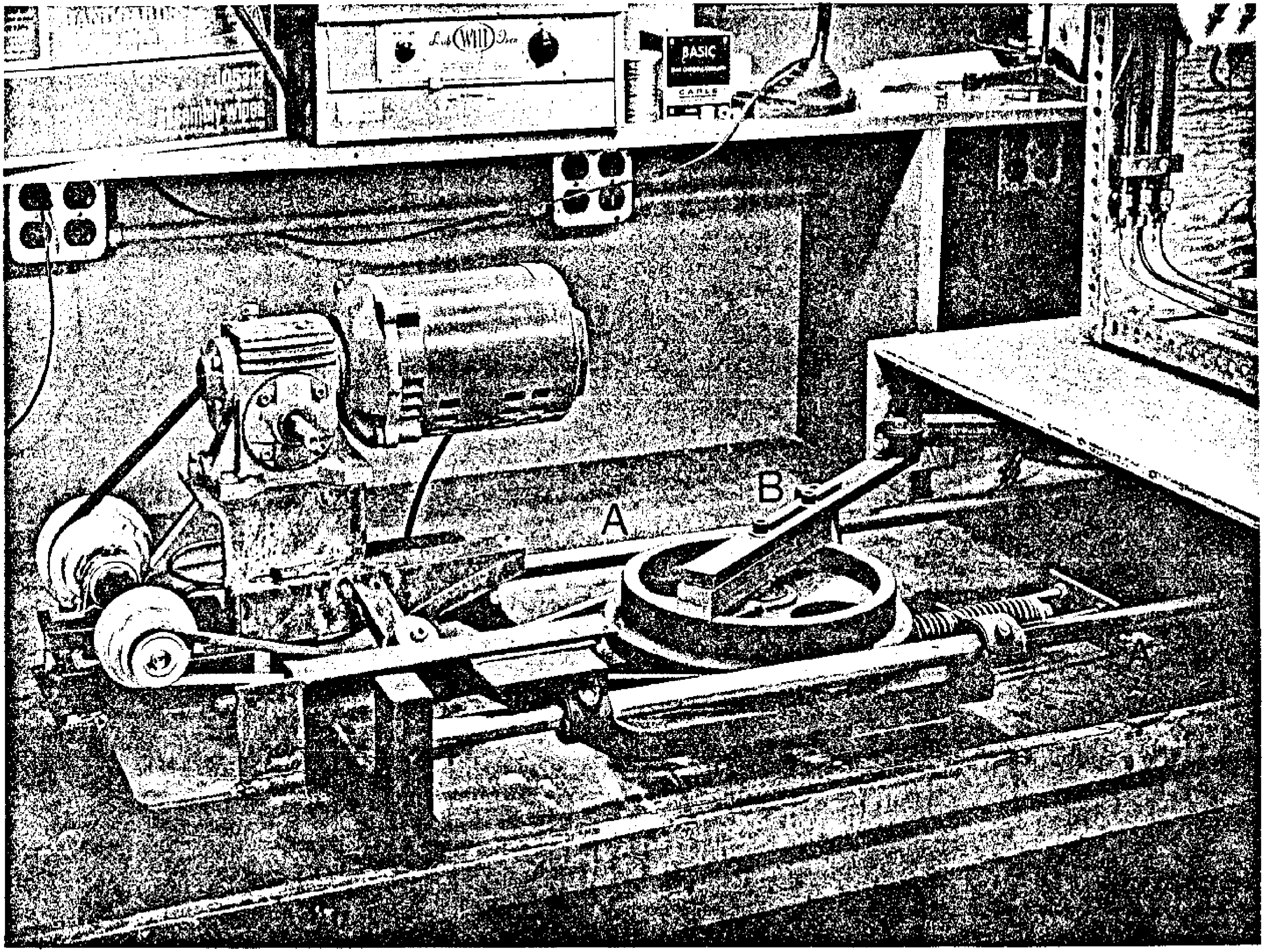


FIGURE 7. SINGLE FLAME ORIENTATION



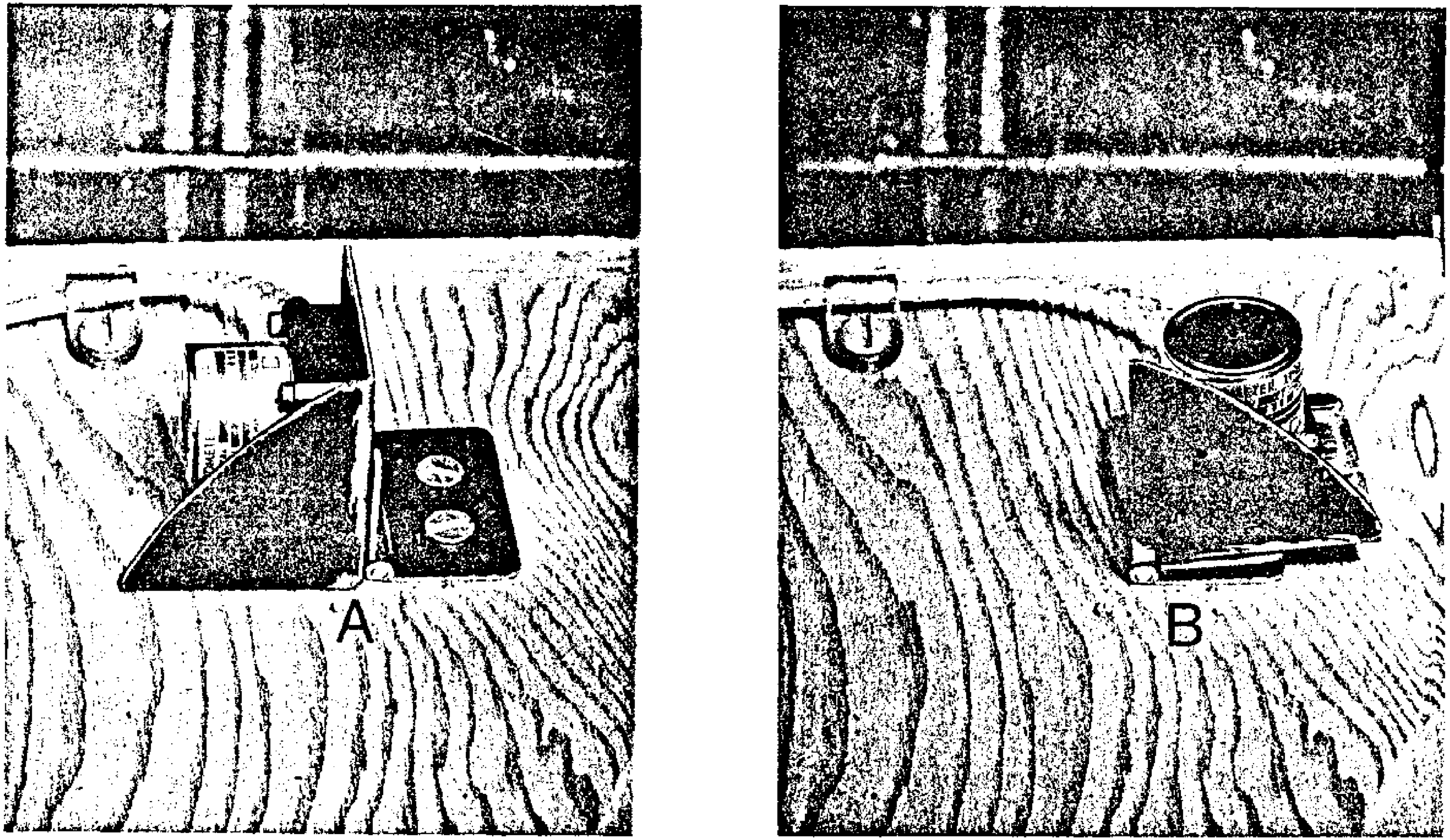
PHOTOGRAPHIC PLATE 7: SHAKER TABLE DRIVE MECHANISM as shown in the photograph. Multiple sheave pulleys were used to effect discrete changes in period. This configuration allowed a range of periods between 1 and 10 seconds in 16 increments. A means of varying the stroke from nine to twelve inches was installed and is shown at "B".

An accelerometer (±0.5 g's) was mounted on the shaker table as shown in the photographic Plate 8. It was mounted on a hinged bracket for easy calibration. That is, the accelerometer in the position shown at "A" in the photograph has the acceleration axis aligned with the motion of the table and will record the acceleration of the table. In the position shown at "B" the acceleration axis is vertical and the unit is subjected to the acceleration of gravity and thus calibrated. A vernier voltage source was also required for the operation of the accelerometer and is shown at "A" in the photographic Plate 2. Any constant voltage source would have sufficed.

a) Sway

The detector was mounted on the shaker table as shown in the photographic Plate 1. Since the detector is moving with respect to the stationary air mass, the Aerograph detector was found to be sensitive to air currents. This problem was alleviated by replacing the cap provided by the manufacturer with a stack (shown at "I" in the photograph) which was packed with glass wool. This would not be a problem on a large platform in which the air mass and the instrument would be moving together.

The samples were introduced either by the microliter syringe or by using the capillary as described in Section II - C. The electrical noise had to be significantly reduced (as described in Section III - A)



(IN USE) (CALIBRATION)

PHOTOGRAPHIC PLATE 8: ACCELEROMETER MOUNT before any testing in the lower attenuations could be achieved. Subsequent to this, a series of tests were performed to determine if linear accelerations would have any effect on the ratios of the gases suggested in the literature for optimum sensitivity (13). The nitrogen and hydrogen were maintained at a 1:1 ratio and the air flow varied. It was found that a considerable amount of periodic flame response occurred at high flow rates (in excess of 500 ml/min). This is possibly due to the air causing turbulence in the detector cell of the molecular sieve may not be efficient at such high flows with hydrocarbons being swept through the filter. Tests with varying carrier gas flow rates and hydrogen flow rates indicated that the 10:1 ratio of air to hydrogen and a 1:1 ratio between nitrogen and hydrogen were satisfactory. This finding is in agreement with that reported in the literature for stationary analysis. Most of the subsequent testing was run with 30 ml/min of hydrogen and 300 ml/min of air and from 15 to 30 ml/min of the carrier gas.

Next the capillary was installed in the oven of the "Aerograph" and tests run to determine the response of the detector to a steady mass flow rate of hydrocarbons under linear accelerations. An example of the response obtained is shown in Figure 8. The mass flow rate was varied and the response increased with increasing concentration and the configuration of the response remains essentially the same. In this figure the lower trace is the output of the detector to a constant signal (a constant number of milligrams per second entering the detector). In this dual channel recorder, the lower trace leads the upper by one-half division (this is required so that the pens can cross each other,

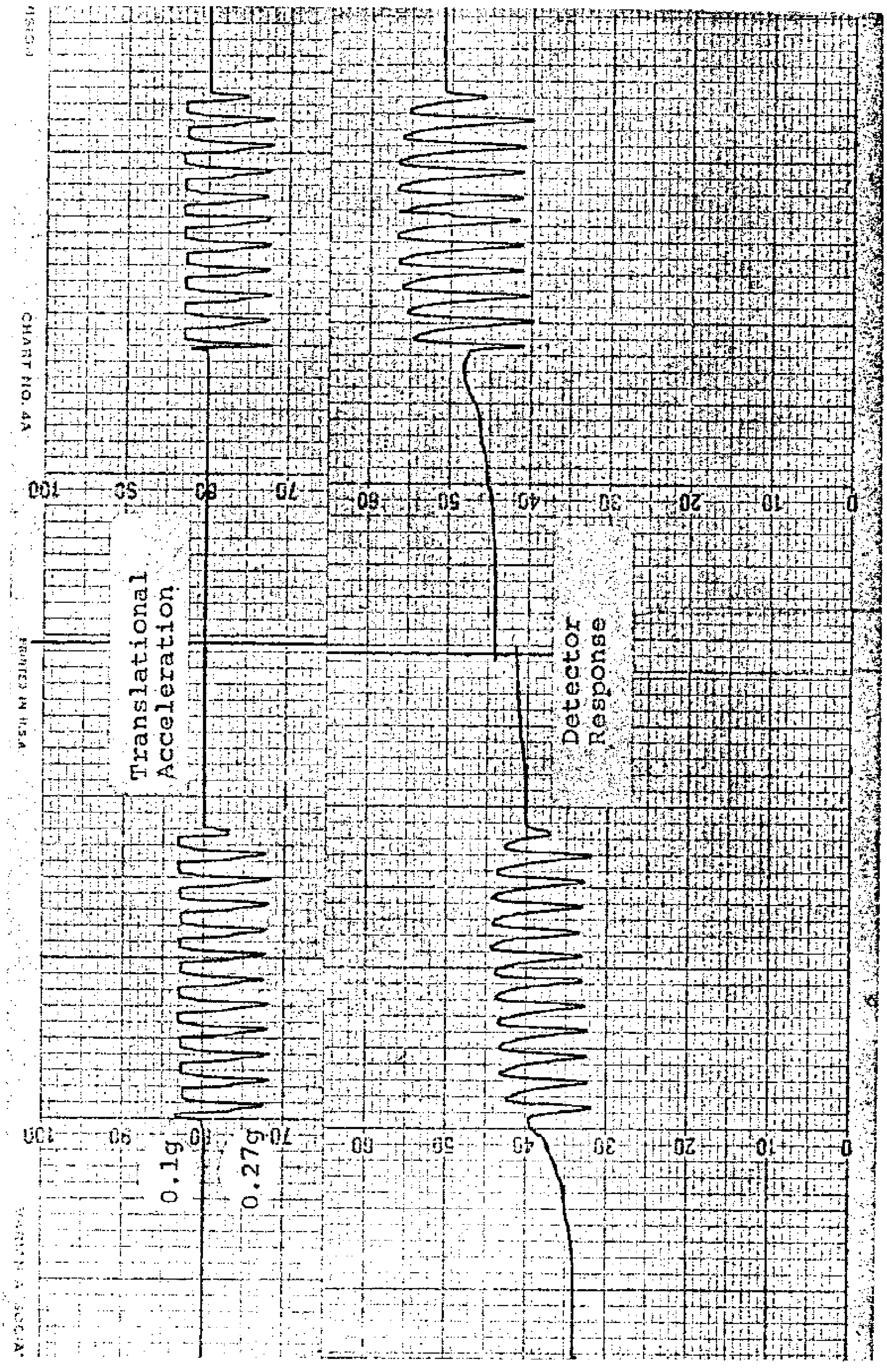


FIGURE 8: TYPICAL DETECTOR RESPONSE TO TRANSLATIONAL ACCELERATION

and was corrected graphically by moving the lower trace one-half division to the left). The upper trace is the output from the accelerometer. The reason for the asymmetrical output is that a "bell-crank" was used in an attempt to obtain a sinusoidal acceleration, which is usually satisfactory if the connecting link is long enough; the link was not long enough in this case.

What is important here however, is that the response is in phase with the acceleration and is essentially the same shape. Therefore, the response appears to be a linear function of acceleration at this frequency. Also, at these low attenuations the response increases with increasing concentrations.

Next an isothermal chromatogram of a sample, containing alkanes having 6 to 32 carbon atoms was obtained both while the unit was stationary and while subjected to cyclic linear accelerations. The resulting chromatograms are shown in Figure 9 and 10. They were run at an attenuation of 1000. It can be seen from these chromatograms that the areas are essentially the same allowing for the injection technique causing the amounts injected in the two cases to not be exactly equivalent. Assuming one microliter was injected, each peak represents one microgram of the particular hydrocarbon represented.

b) Heave

For heave the detector was suspended vertically on springs. The amplitude could be varied by the magnitude of the forcing function and the period by adding additional weight to the unit.

The ususal tests were performed to determine the amount of electrical and flame noise (without any hydrocarbons). These were

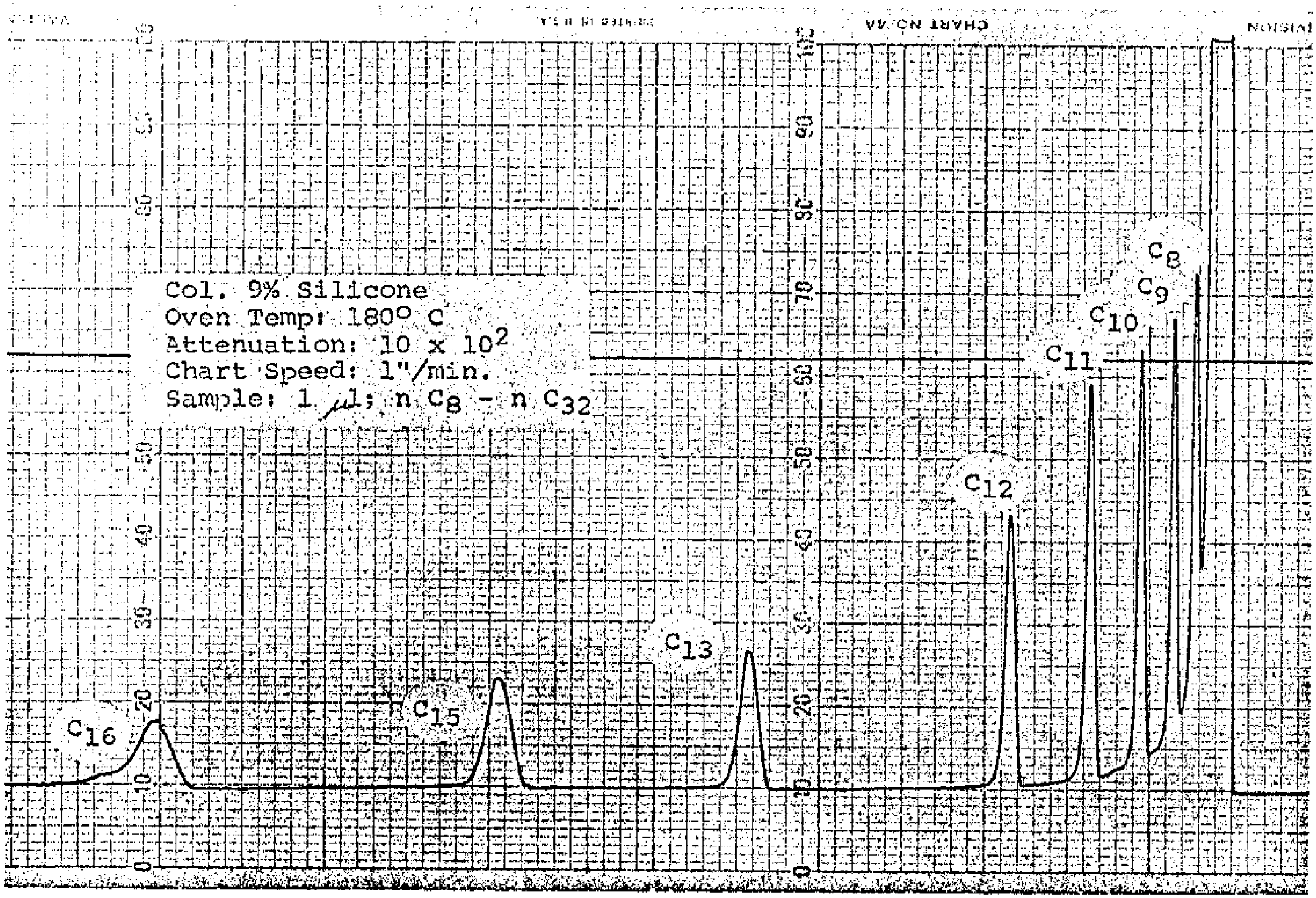


FIGURE 9: STATIONARY ISOTHERMAL CHROMATOGRAM

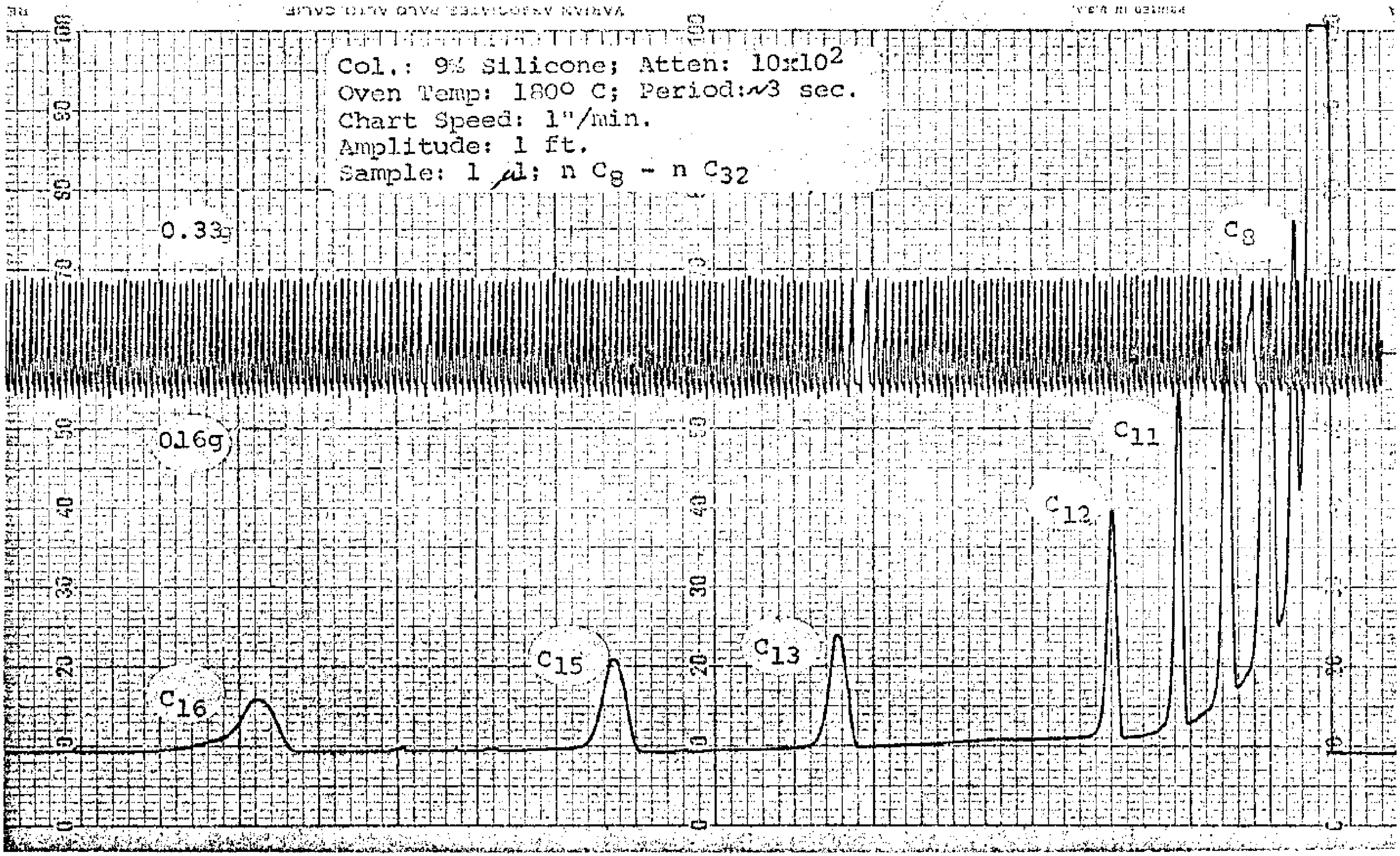


FIGURE 10: ISOTHERMAL CHROMATOGRAM WITH DETECTOR SUBJECTED TO TRANSLATIONAL ACCELERATION.

found to be essentially negligible.

Using the capillary an essentially constant signal was produced. The system was oscillated and a typical response is shown in Figure 11. The response is similar to the horizontal acceleration, but is 180 degrees out of phase. The response at various accelerations was determined and used to determine the limits of detection, which are described in Section IV - B.

Tests were performed with the straight-chain hydrocarbon sample (nC_6 - nC_{32}). These were run at various heave accelerations. These results were compared with those obtained from a stationary chromatogram and no appreciable changes in area were noted. Examples are shown in Figures 12 and 13.

3) Rotational Tests

a) Roll

In order to rotate the detector it was placed in the stands shown at "A" and "B" in photographic plate 9. The unit was mounted so that the axis of rotation passed essentially through the tip of the flame which is enclosed in the detector cell shown at "C". A beam and outboard weights were used to obtain a large rotational moment of inertia. The beam and one of the outboard weights is shown at "D". Two springs were provided for a restoring torque. The period of oscillation could be changed by changing the moment of inertia (moving the outboard weights).

First the unit was rocked with the flame out, but with the electrical equipment operational. With the unit rolling, a slight amount of relative motion was possible between the detector cell and

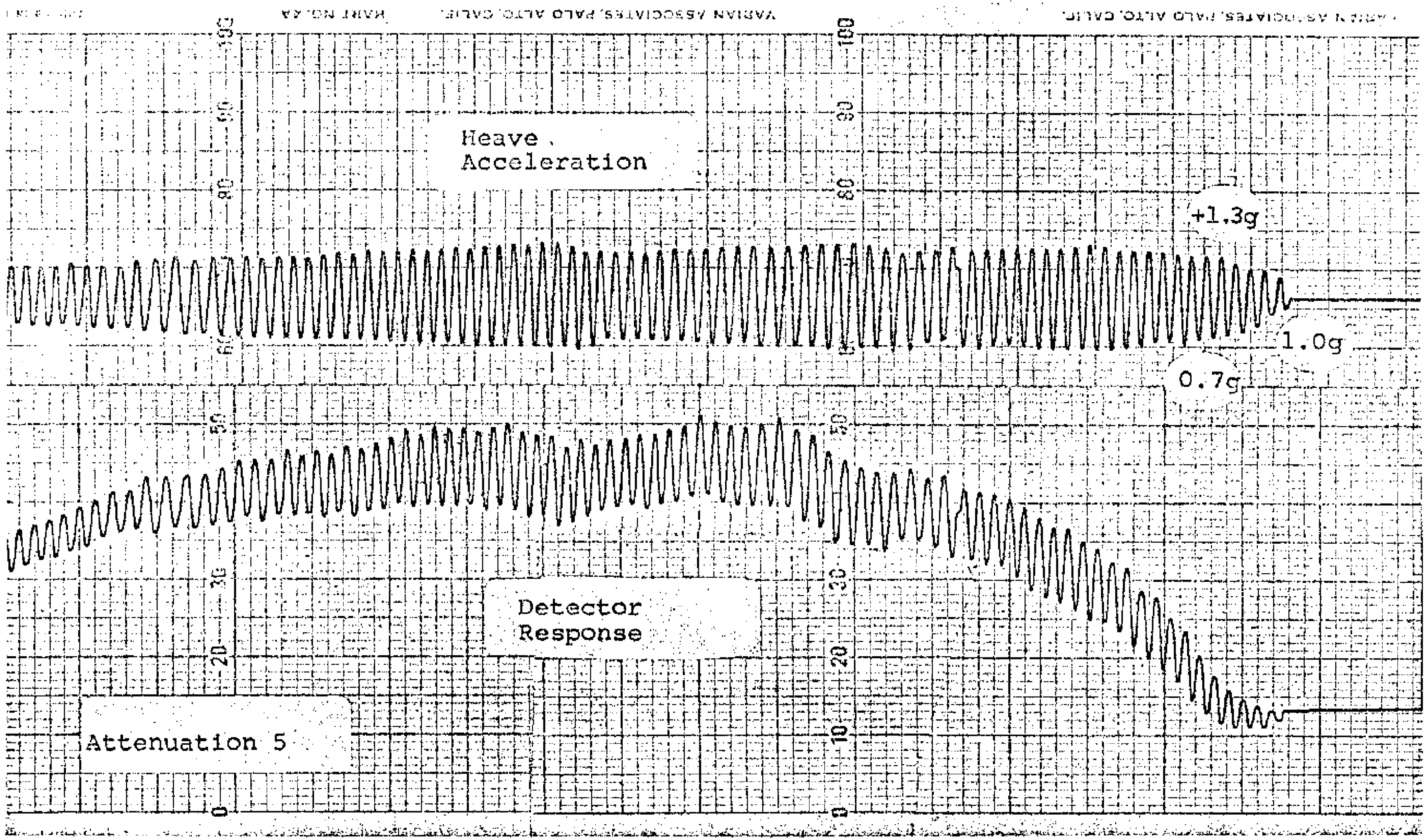
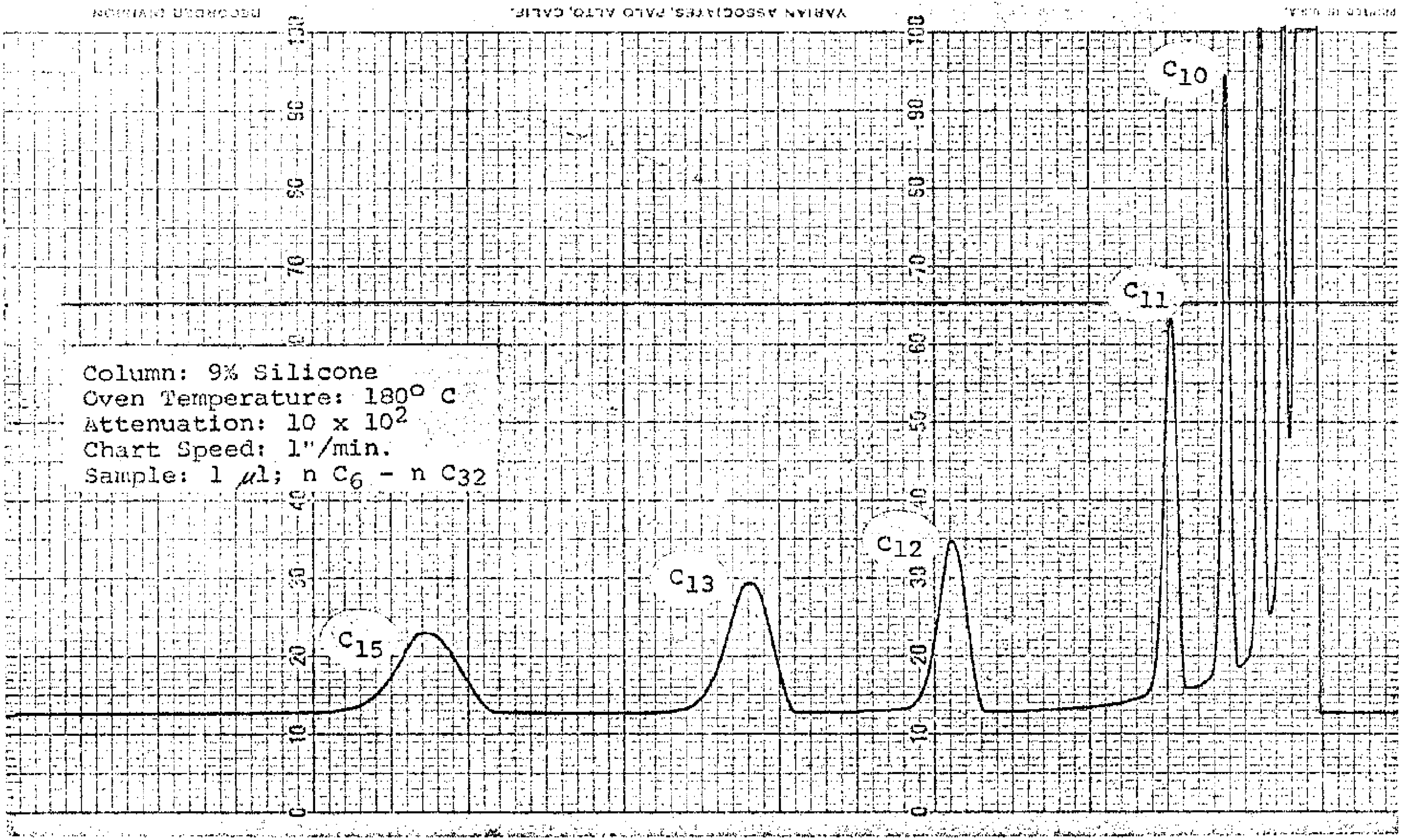


FIGURE 11: DETECTOR RESPONSE TO A CONSTANT SIGNAL WHILE SUBJECTED TO ONE-THIRD GRAVITY HEAVE ACCELERATION.



Column: 9% Silicone
Oven Temperature: 180° C
Attenuation: 10×10^2
Chart Speed: 1"/min.
Sample: 1 µl; n C_6 - n C_{32}

FIGURE 12: ISOTHERMAL CHROMATOGRAM WITH DETECTOR STATIONARY PRIOR TO HEAVING

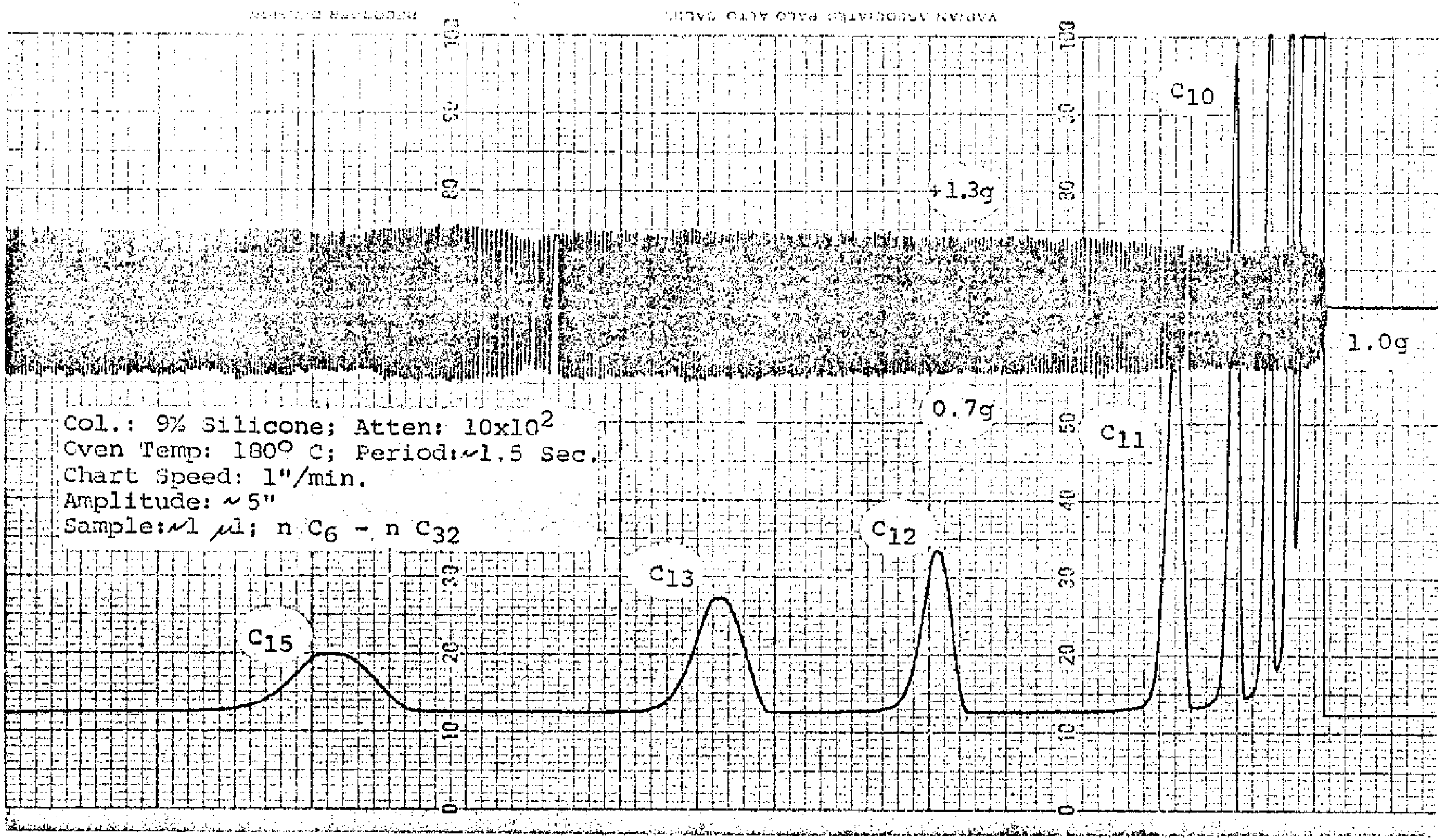
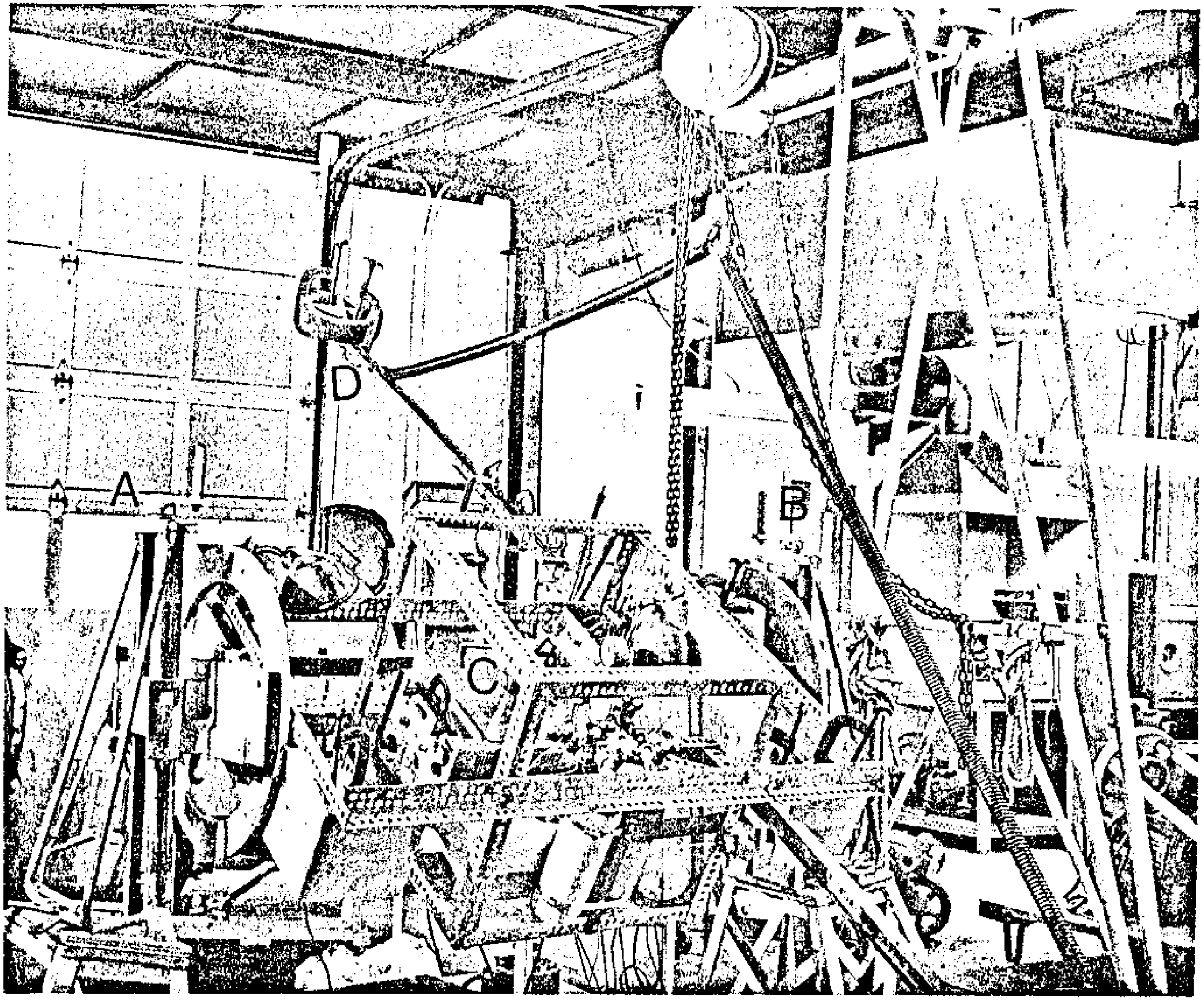


FIGURE 13: ISOTHERMAL CHROMATOGRAM WITH DETECTOR SUBJECTED TO A HEAVE ACCELERATION OF APPROXIMATELY ONE-HALF GRAVITY WITH A ONE AND ONE-HALF SECOND PERIOD.



PHOTOGRAPHIC PLATE 9: ROLL FIXTURE

the oven housing; this resulted in an appreciable amount of noise. This was corrected by wedging a piece of plastic between the housing and the cell. The wedge is shown at "F" in photographic plate 6. What is important here is that everything must be mechanically secure.

Subsequent to the electrical checkout, the flame was ignited, and without any hydrocarbon passing through the detector, the unit was rocked. The total disturbance due to any remaining electrical and background flame noise was less than a tenth of a millivolt peak-to-peak, which is an acceptable base line.

The capillary was then installed and various adjustments made in order to achieve a constant signal. Dynamic tests were then run with different concentrations for roll angles of plus and minus (counter-clockwise and clockwise) 5, 10, and 20 degrees as well as stationary tests at 20 degrees clockwise and 20 degrees counterclockwise. Typical roll responses were shown in Figures 14 and 15. As can be seen in these figures, the response is the sum of two sinusoidal responses which are slightly out of phase, one twice the frequency of the other. The upper trace represents the rotation as a function of time in both figures.

From these figures it can be seen that two cases exist. With smaller roll angles (Figure 14), the maximum response occurs when the detector is rotated to a counterclockwise (positive) orientation. A second maximum occurs at the maximum clockwise position. A minimum occurs during rotation from counterclockwise to clockwise and the absolute minimum during rotation from clockwise to counterclockwise.

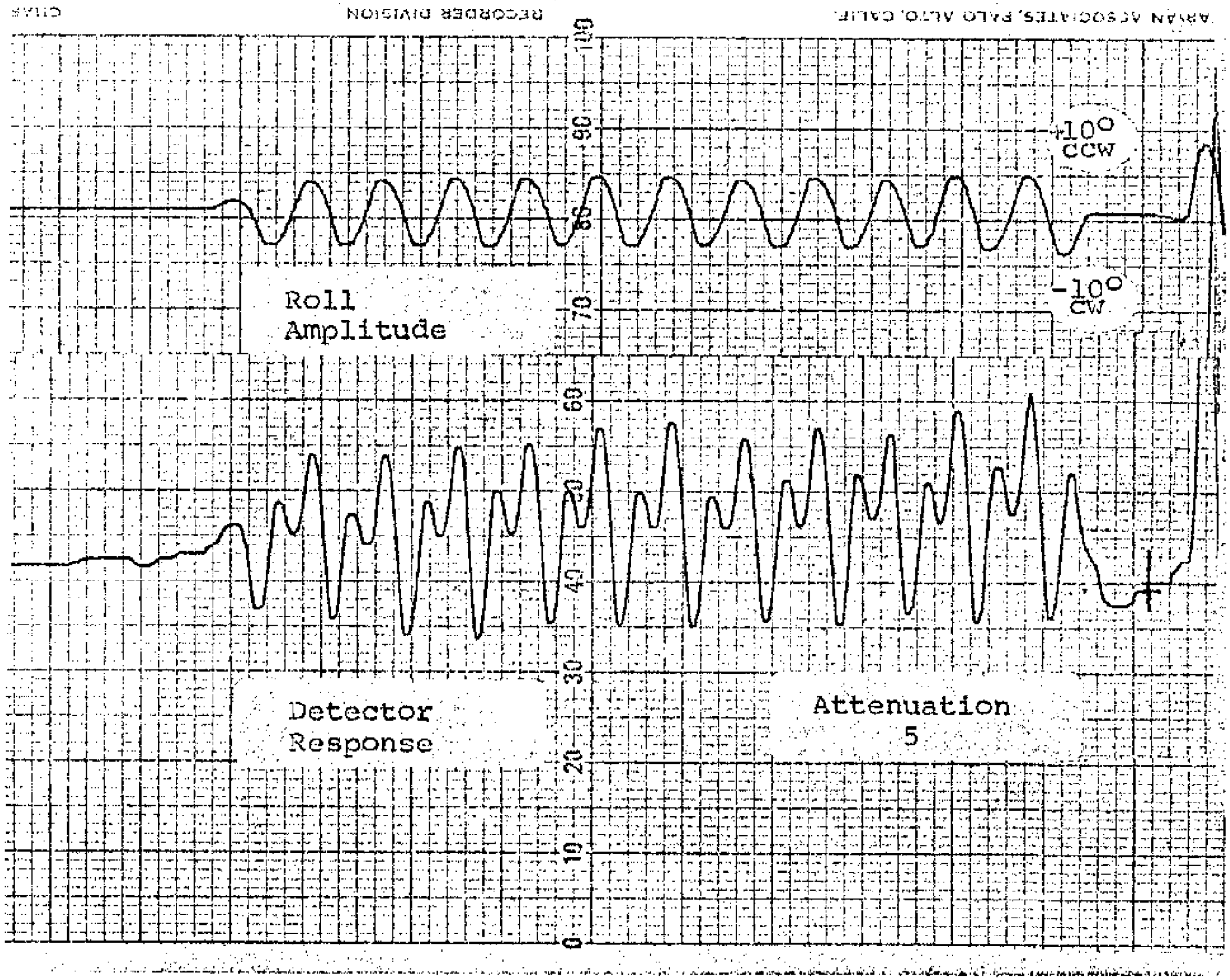


FIGURE 14: TYPICAL DETECTOR RESPONSE TO TEN DEGREE ROLLING MOTION.

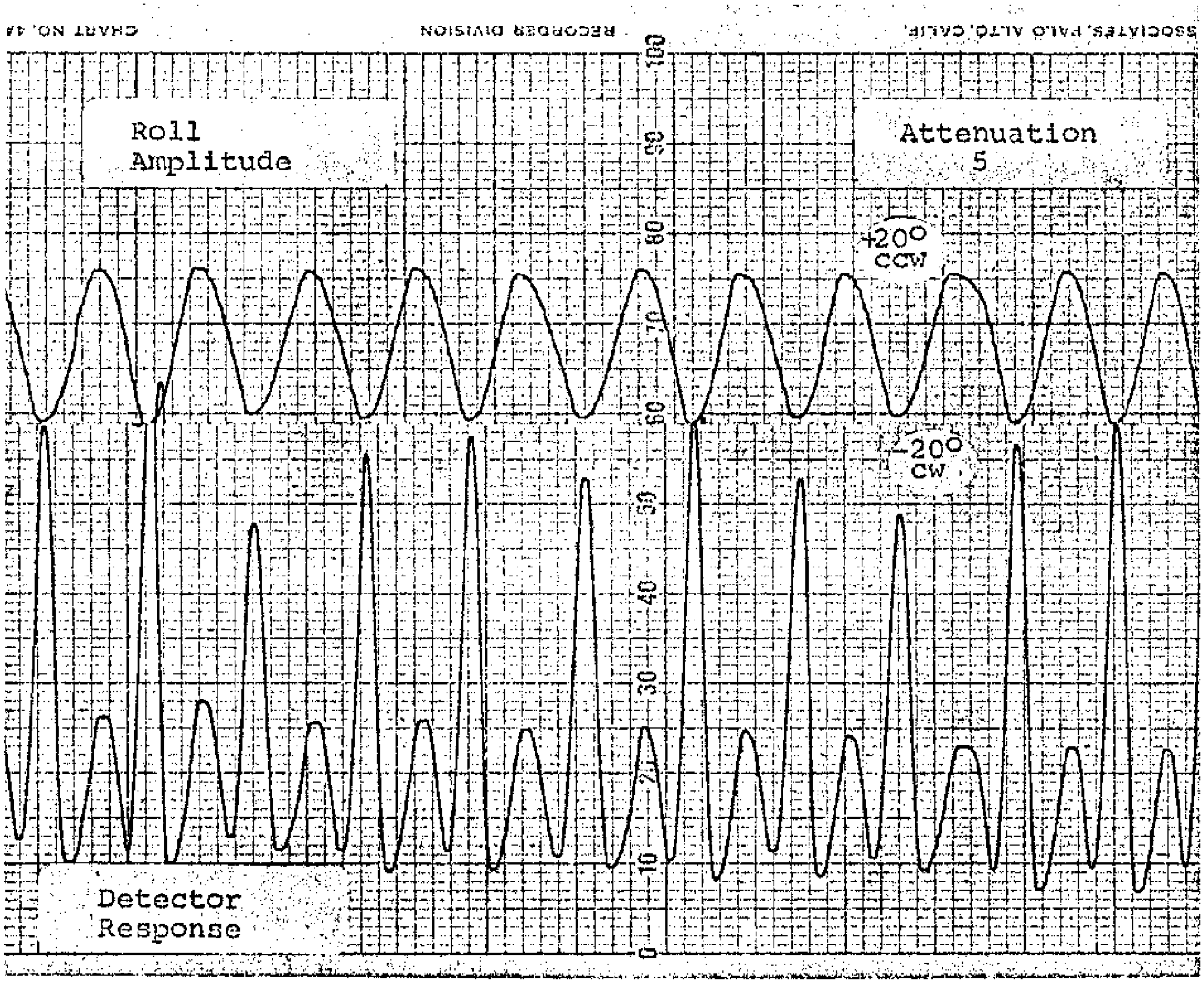


FIGURE 15: TYPICAL DETECTOR RESPONSE TO TWENTY DEGREE ROLLING MOTION.

Also important here is that both minima occur near the vertical detector orientation zero roll angle.

At higher roll angles (Figure 15) maximum response occurs at maximum clockwise rotation and the second maximum at the counterclockwise rotation. The minima occur at the same place in the higher roll angle as observed in the lower amplitudes, as should be expected. What appears to be happening here is a shift in maximum response from the counterclockwise to the clockwise orientation with increasing roll amplitude. Also evident from Figure 15, is the relative decrease in the counterclockwise maxima with respect to the clockwise maxima. That is, at the 20 degree roll the counterclockwise maxima are approximately one-third as great as that of the clockwise maxima as opposed to the clockwise maxima being only about two-thirds the counterclockwise maxima at ten degrees. Thus, the order is reversed and the relative magnitudes increased with increasing roll amplitude.

With respect to an explanation for this phenomena, it is suggested that the asymmetry of the detector becomes more influential at high roll angles. At low roll angles the ion capture is not effected by the linear probe and the symmetry of the collector is dominant. As the amplitude increases the asymmetry created by the probe dominates and the maxima shift to the clockwise orientation. This, it is suggested, is due to more of the ionized gas entering the higher electric field that exist in the neighborhood of the probe. The minima do not change since they occur when the detector is essentially vertical.

In summary, the response from a symmetrical detector would have maxima occurring each time the ionized gas approached the sides of the collector. The response curve would have two maxima for each roll period. It is suggested that the asymmetry of the detector cell caused by the linear probe is responsible for the relative differences in the maxima in the detector response. The asymmetry becomes a dominant factor in the maximum detector response at high roll amplitudes because more of the ions enter the higher electric field around the probe. The significant limit in a rolling situation is the peak-to-peak response.

Also, tests were performed at different periods to determine if the magnitude of the response was frequency dependent. A steady signal was produced and subjected to the different roll angles, with periods ranging from 5 to 20 seconds. The peak-to-peak response in millivolts was plotted against roll angle for the different frequencies. The results are shown in Figure 16. From this it can be seen that for periods ranging from 7.5 to 20 seconds the response is dependent upon the magnitude of the angle and not the frequency of oscillation.

The next series of tests consisted of injecting known quantities of hydrocarbon into a column and subjecting the unit to the same roll angles as stated above. The samples consisted of 1, 10, 100, 1,000 and 10,000 parts per million of dodecane diluted in carbon disulfide. A series of these are shown in Figures 17 through 19. Here approximately 10 ppm of dodecane was injected and sequentially subjected to a 5, 10, and 20 degree roll with a period of about five seconds. For the five degree roll (Figure 17) one can detect a slight distortion of the base line and the peak appears undisturbed. For the 10 degree roll the base line distortion is more prominent and some peak distortion is evident near the base and the maximum. For the 20 degree roll the base line has a configuration that is identifiable with Figure 19 and the

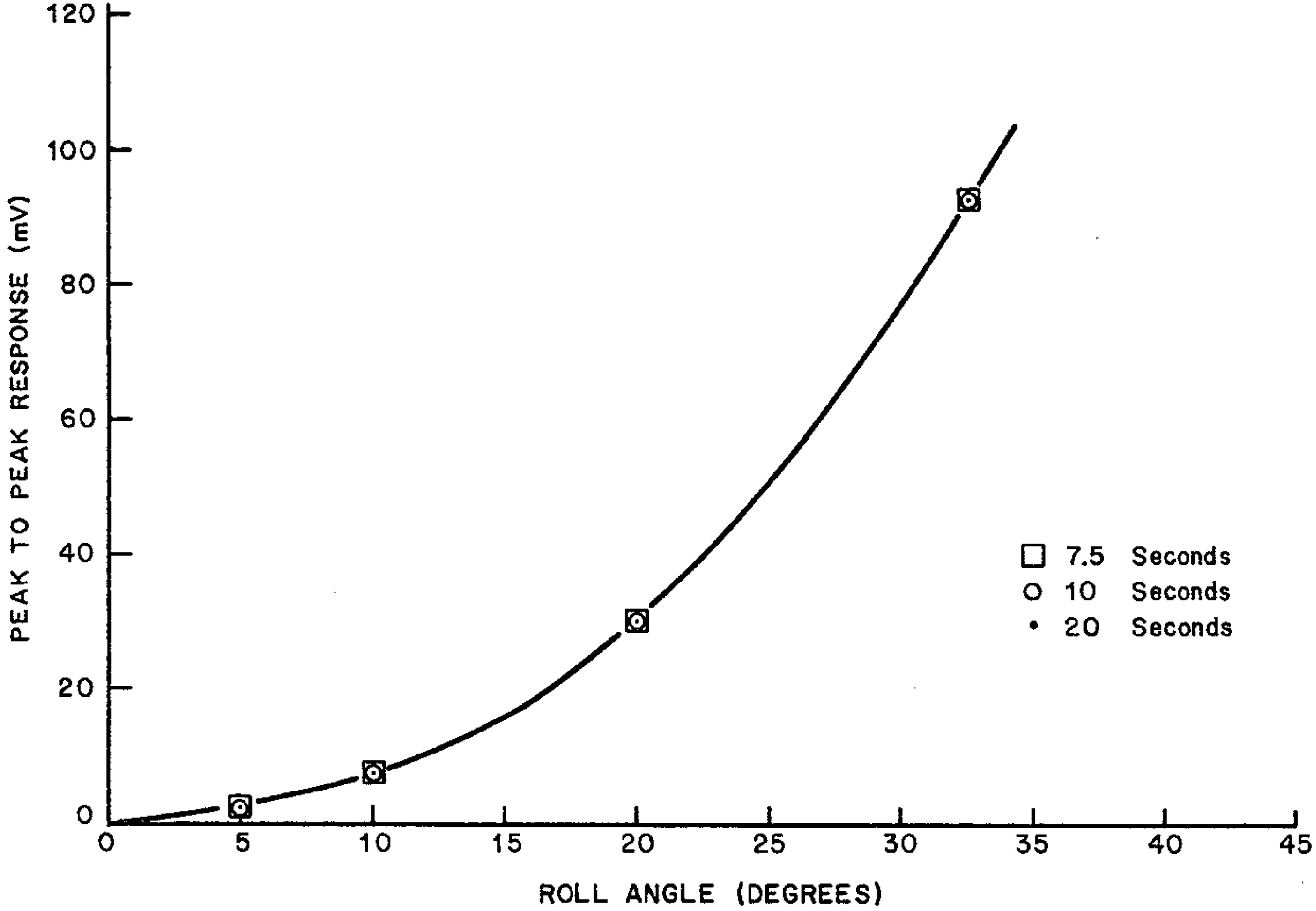
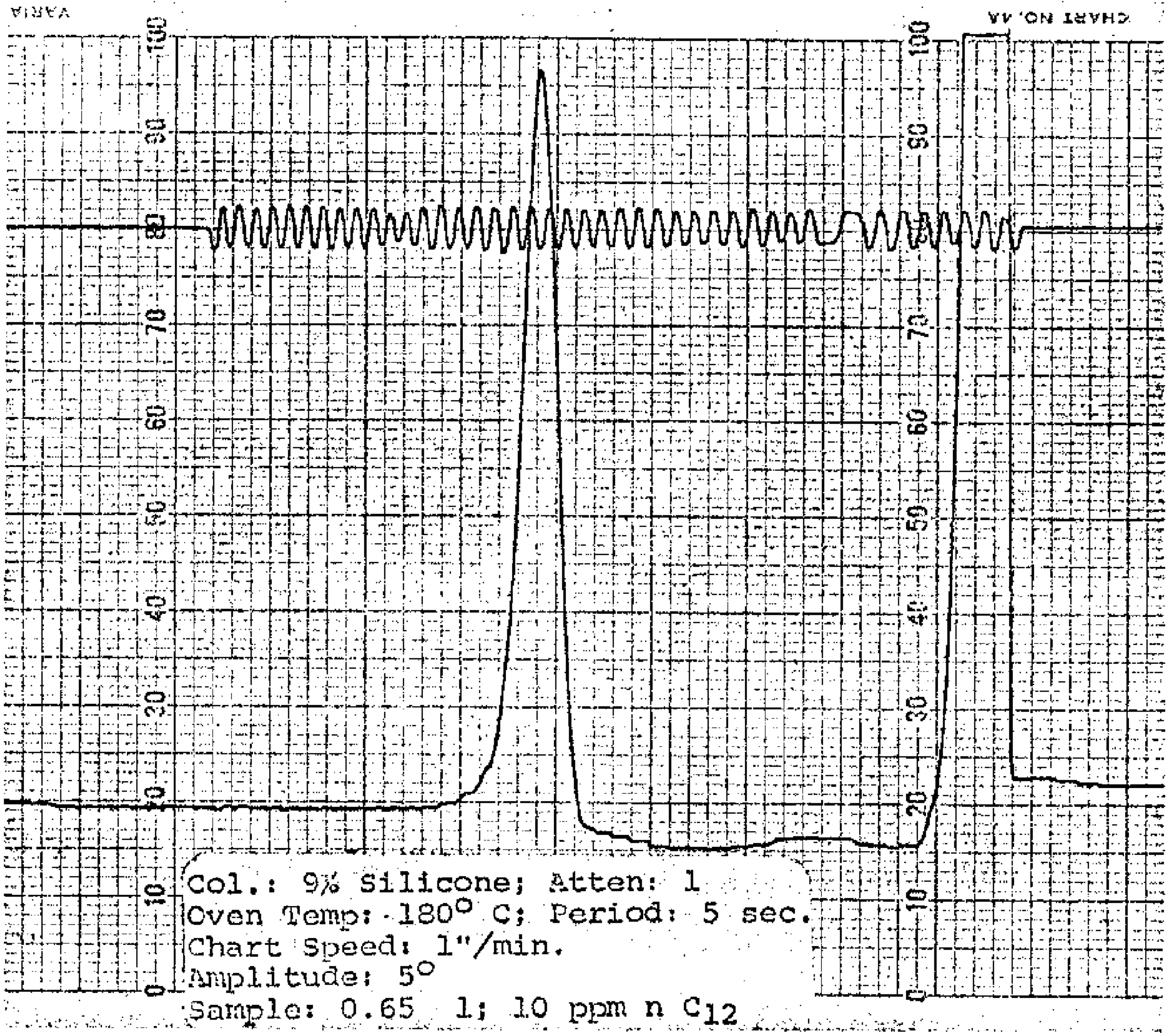
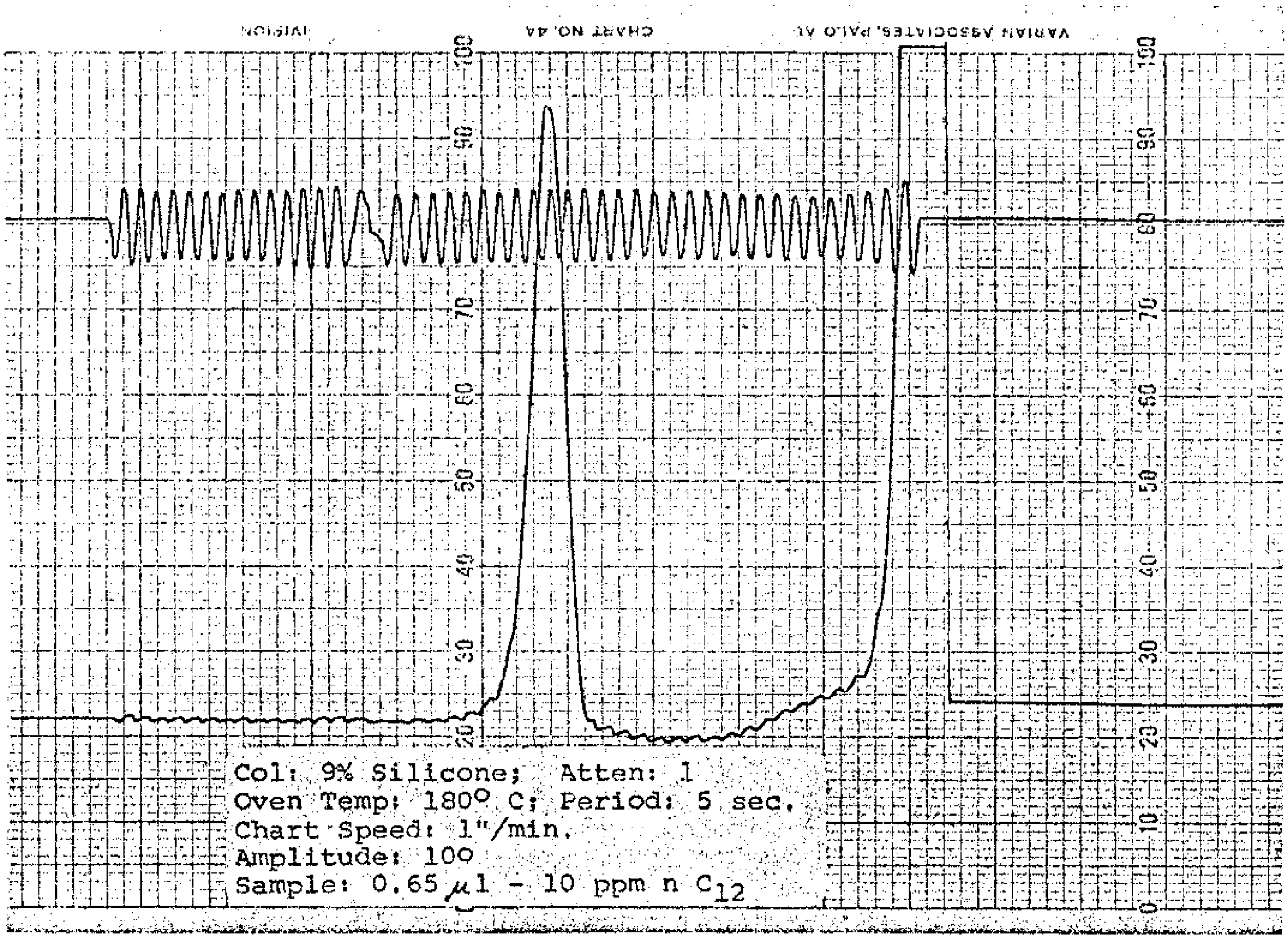


FIGURE 16: DETECTOR RESPONSE TO ROLLING MOTION AT DIFFERENT FREQUENCIES



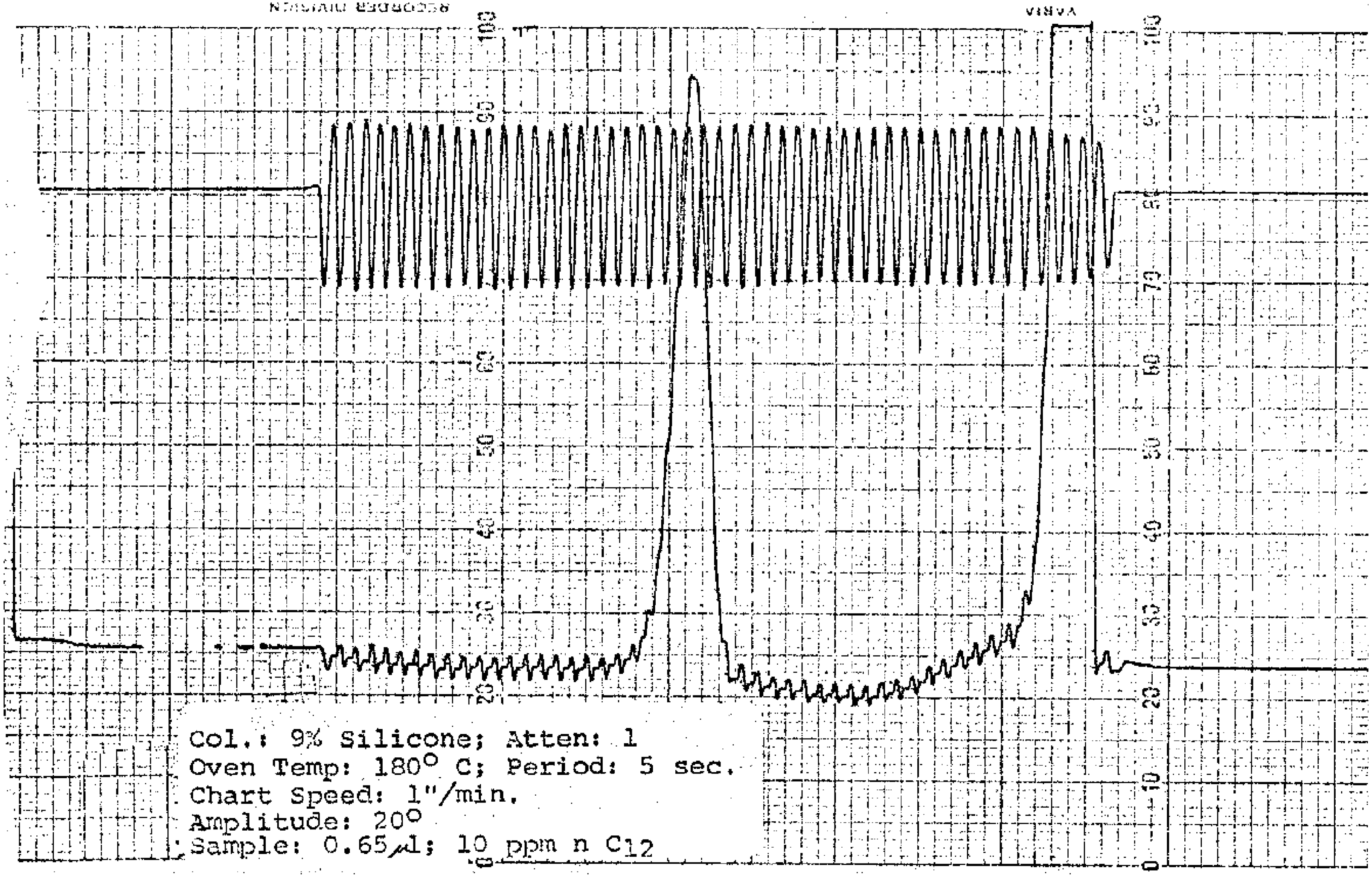
Col.: 9% Silicone; Atten: 1
Oven Temp: 180° C; Period: 5 sec.
Chart Speed: 1"/min.
Amplitude: 5°
Sample: 0.65 1; 10 ppm n C_{12}

FIGURE 17: DETECTOR RESPONSE TO TEN ppm OF DODECANE WHILE SUBJECTED TO A FIVE DEGREE ROLL.



Col: 9% Silicone; Atten: 1
Oven Temp: 180° C; Period: 5 sec.
Chart Speed: 1"/min.
Amplitude: 10°
Sample: 0.65 μl - 10 ppm n C_{12}

FIGURE 18: DETECTOR RESPONSE TO TEN ppm OF DODECANE WHILE SUBJECTED TO A TEN DEGREE ROLL



Col.: 9% Silicone; Atten: 1
Oven Temp: 180° C; Period: 5 sec.
Chart Speed: 1"/min.
Amplitude: 20°
Sample: 0.65 μl; 10 ppm n C_{12}

FIGURE 19: DETECTOR RESPONSE TO TEN ppm OF DODECANE WHILE SUBJECTED TO A TWENTY DEGREE ROLL.

peak is distorted along the side as well as at its base and maximum.

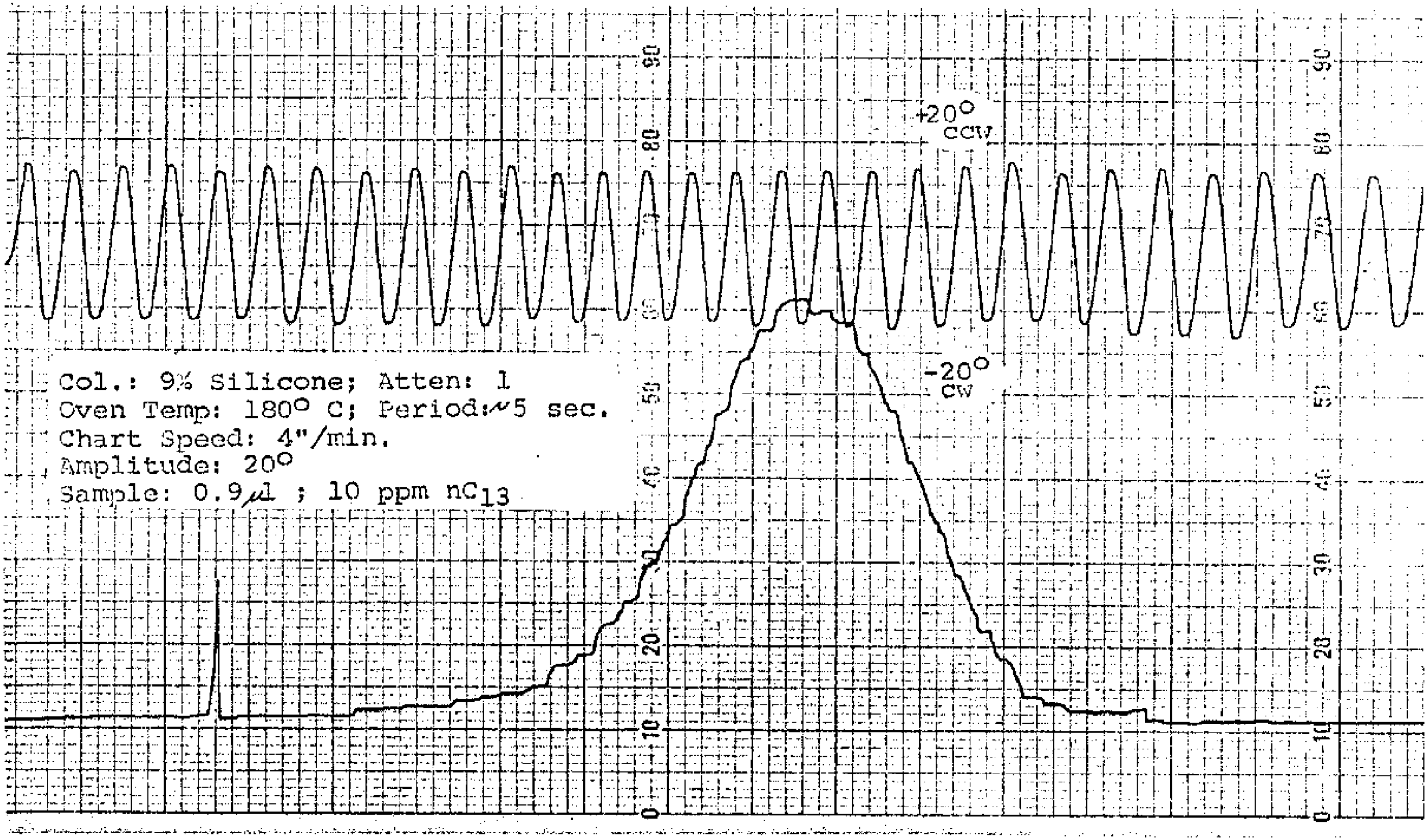
In Figure 20, 0.9 microliters of ten parts per million or 16.5×10^{-6} milligrams of tridecane were injected. Here the peak has been extended using a chart speed of four inches per minute to illustrate the side lobes. In Figure 21, 0.7 microliters of one-hundred parts per million tridecane were injected. This also illustrates "side spikes" which are shown at "A". These were quite prevalent during large oscillations and it is suggested that these are "fines" or pieces of the stationary phase of the column that are dislodged by the acceleration loads.

The final series of tests performed in the rolling mode were to obtain isothermal chromatograms of a sample containing straight chained hydrocarbons. Individual chromatograms were produced for stationary (control), 5, 10, and 20 degree roll and stationary at 20 degrees in a clockwise and counterclockwise orientation. Examples are shown in Figures 22 and 23. These tests were performed with an attenuation of one thousand and no appreciable variation in peak areas or retention times was noted.

b) Pitch

To test the detector's response to pitching motions, the same fixture (shown in photographic plate 9) or for roll response was used. The same series of tests performed for roll were performed for pitch. Typical detector response to a constant signal is shown in Figures 24 and 25.

A similar situation is evident from these responses as was observed in roll. At low pitch angles the symmetry of the ion collector



Col.: 9% Silicone; Atten: 1
Oven Temp: 180° C; Period: ~5 sec.
Chart Speed: 4"/min.
Amplitude: 20°
Sample: 0.9 μl ; 10 ppm nC_{13}

FIGURE 20: DETECTOR RESPONSE TO NINE-TENTHS MICROLITER OF TEN ppm TRIDECANE WHILE SUBJECTED TO A FIVE SECOND TWENTY DEGREE ROLL.

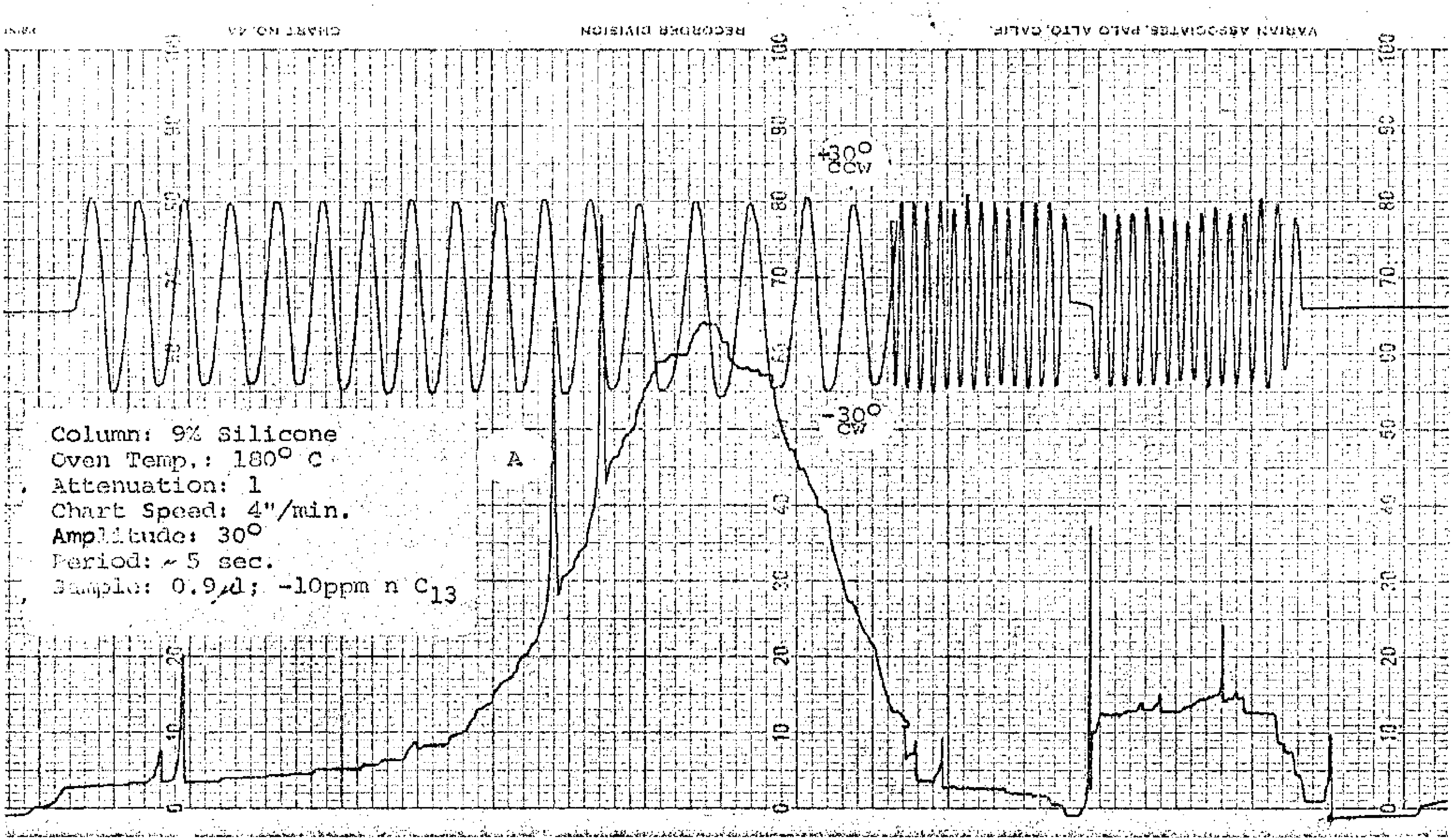
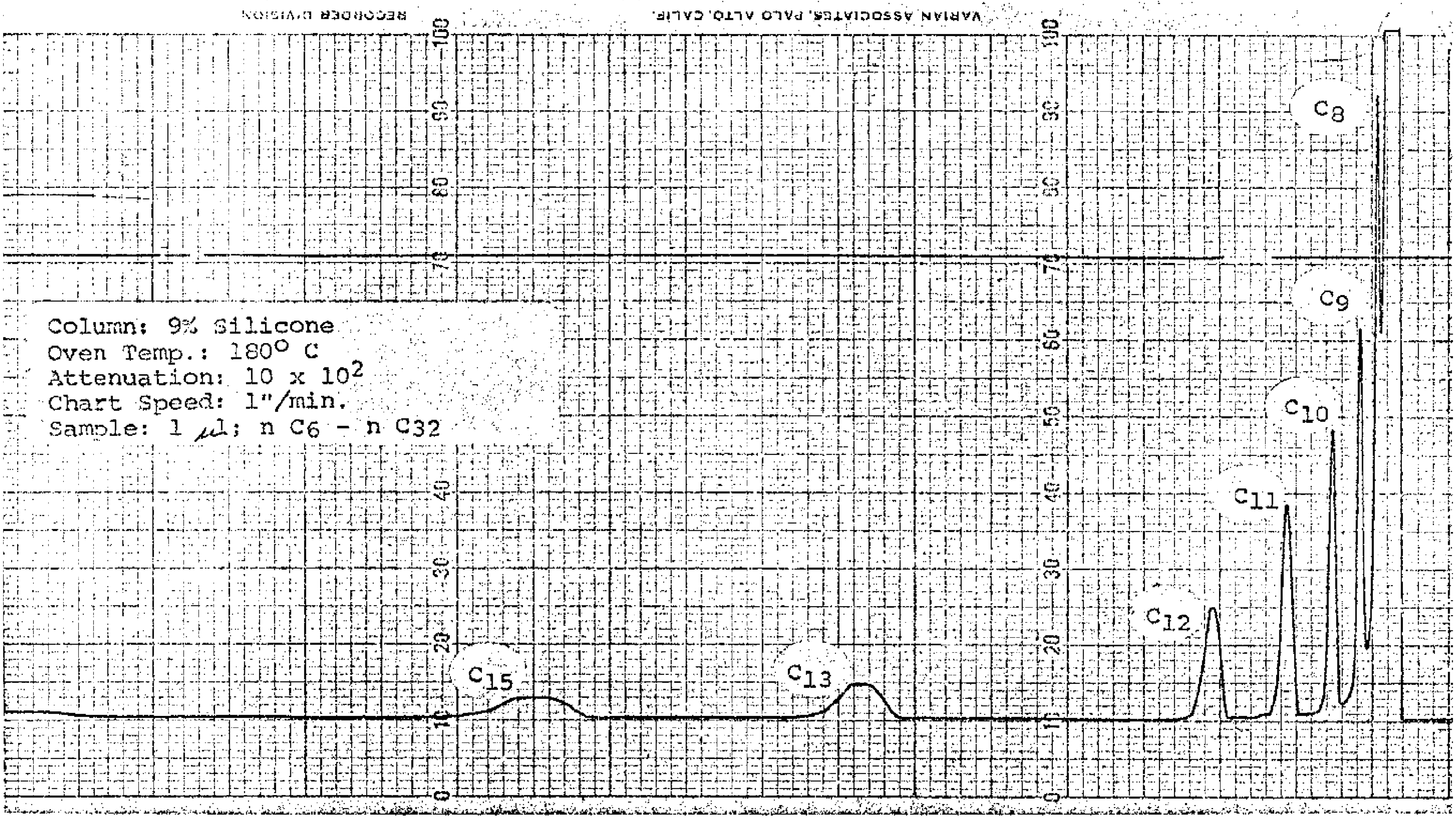


FIGURE 21: DETECTOR RESPONSE TO SEVEN-TENTHS MICROLITER OF 100 ppm TRIDECANE WHILE SUBJECTED TO A FIVE SECOND THIRTY DEGREE ROLL.



Column: 9% Silicone
Oven Temp.: 180° C
Attenuation: 10 x 10^2
Chart Speed: 1"/min.
Sample: 1 μl; n C_6 - n C_{32}

FIGURE 22: ISOTHERMAL CHROMATOGRAM WITH DETECTOR STATIONARY.

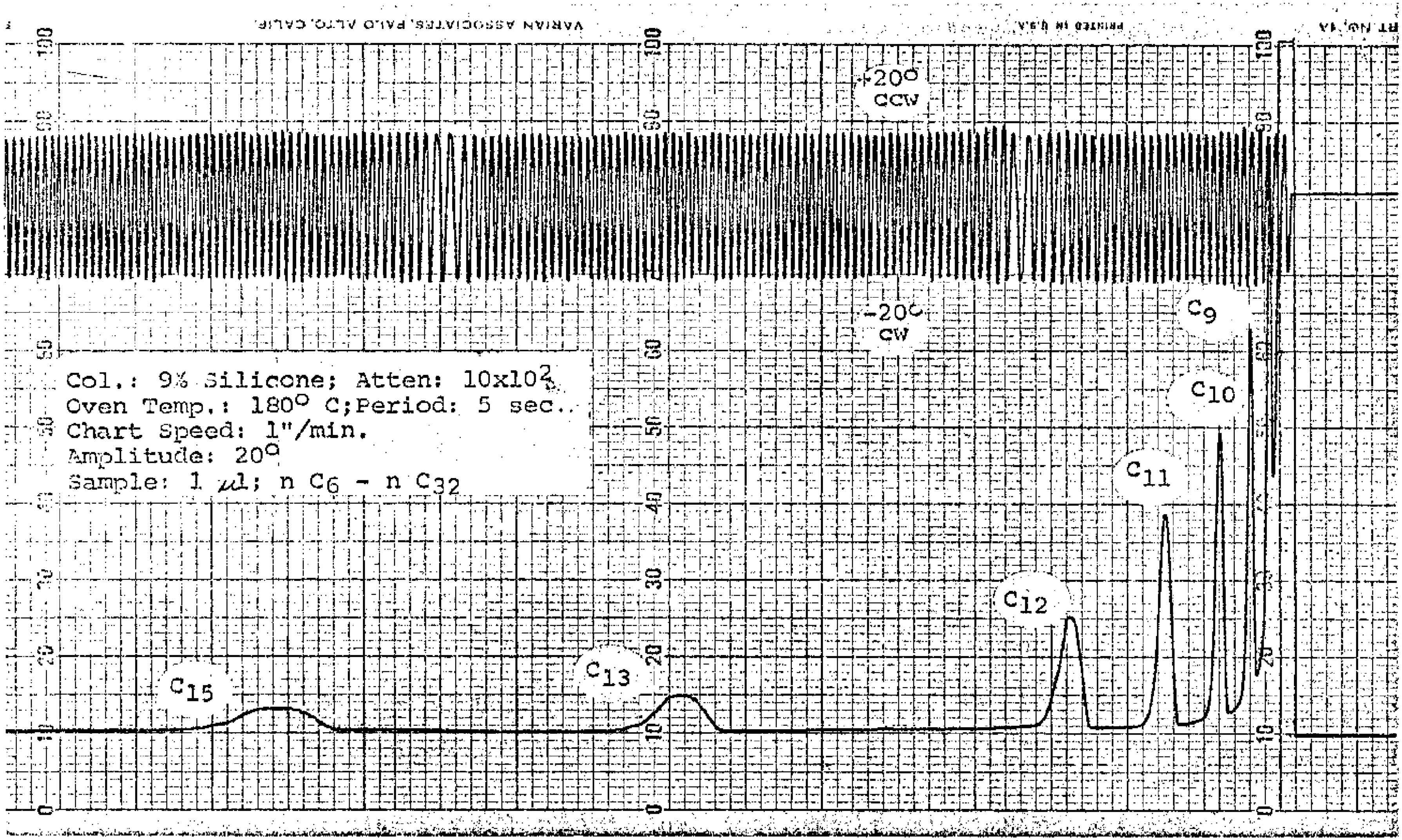


FIGURE 23: ISOTHERMAL CHROMATOGRAM WITH DETECTOR SUBJECTED TO A FIVE SECOND TWENTY DEGREE ROLL.

dominates and the maximum response occurs in the clockwise direction. Also, it can be seen in Figure 24 that the counterclockwise maxima are suppressed by the use of a linear probe. From Figure 7 it can be seen that there is less detector asymmetry in pitch, and this is substantiated by Figure 24. That is, the higher frequency is not visible and is not observed until pitching angles of around ten degrees are reached. This is illustrated in Figure 25.

The results of the injection of known quantities of hydrocarbons were the same as in roll. That is, the motion response appeared to be a problem only at low attenutations. The isothermal chromatograms of the straight chained hydrocarbons tested at the various pitch angles were similar within the limits of the accuracy of injection technique. Examples are shown in Figures 26 and 27.

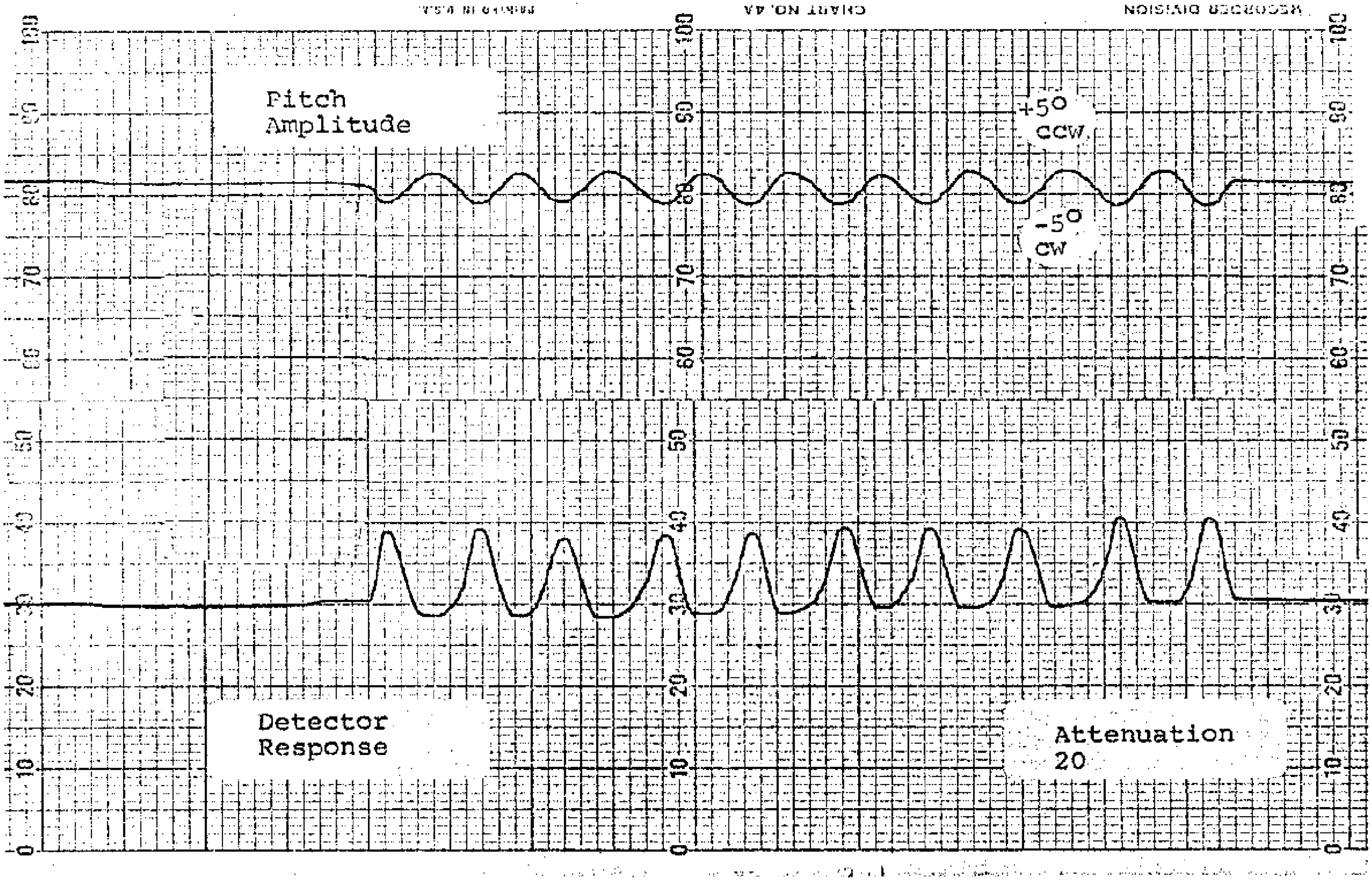


FIGURE 24: DETECTOR RESPONSE TO A CONSTANT DODECANE SIGNAL WHEN SUBJECTED TO A SEVEN SECOND FIVE DEGREE PITCHING.

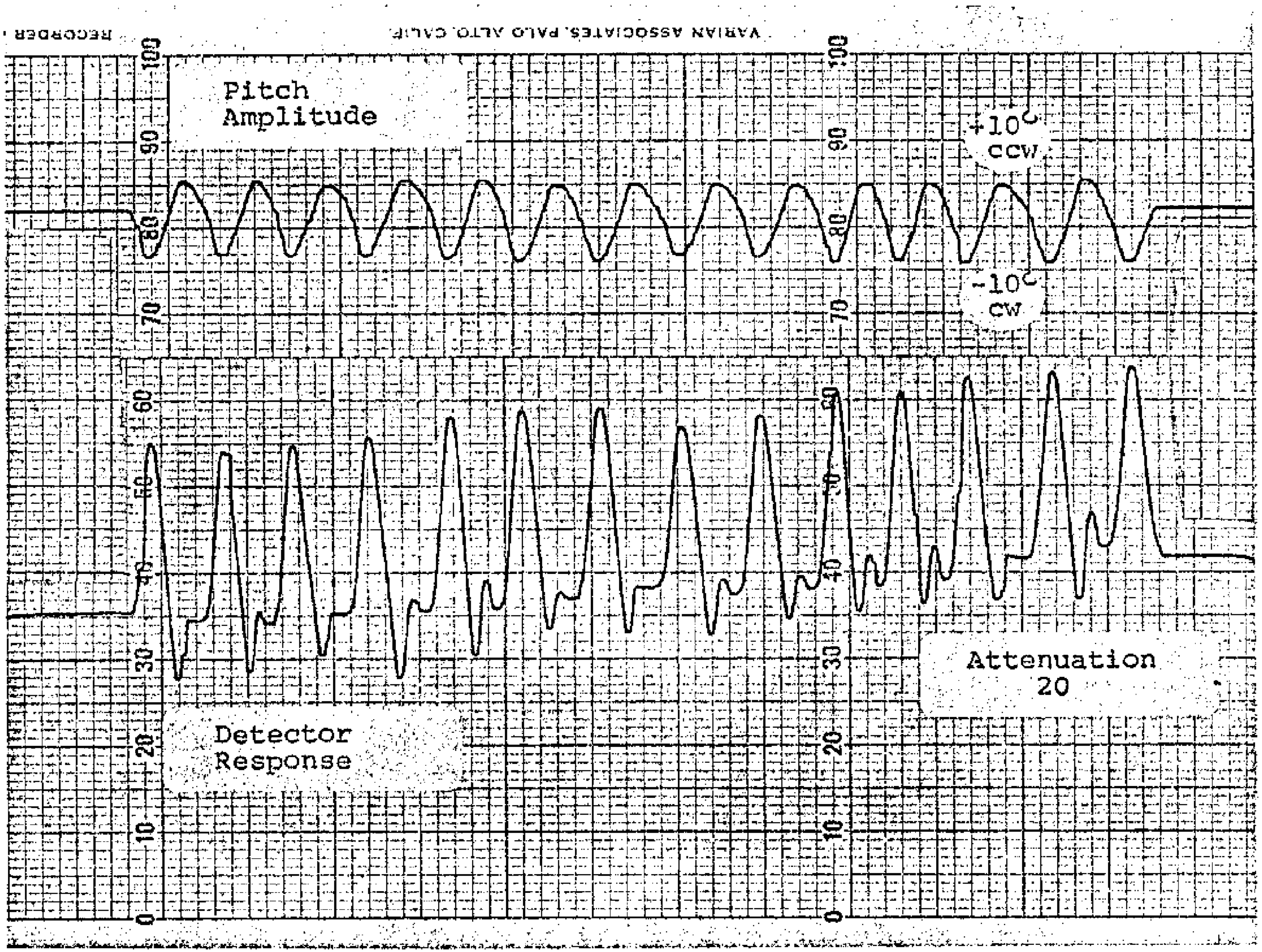
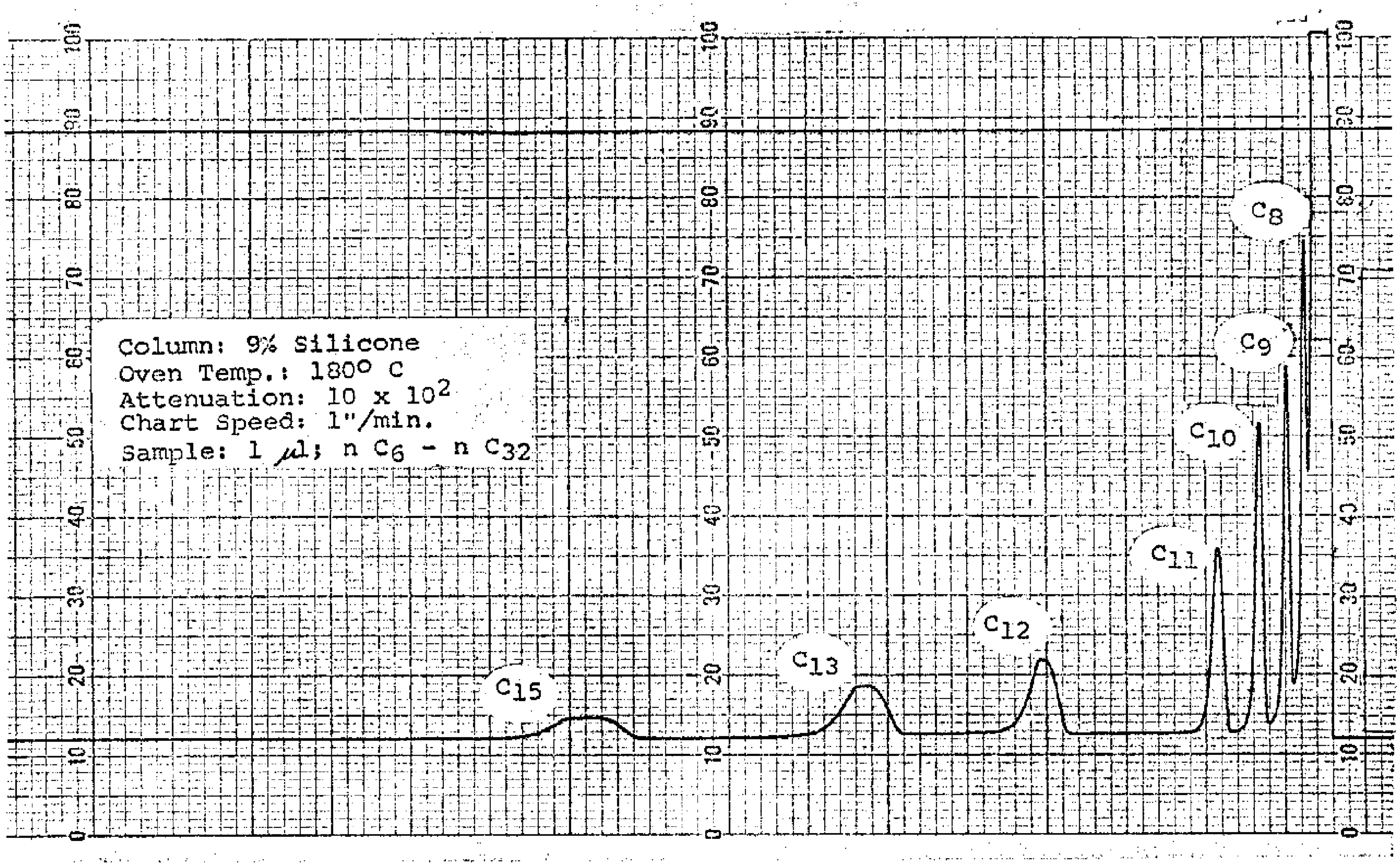
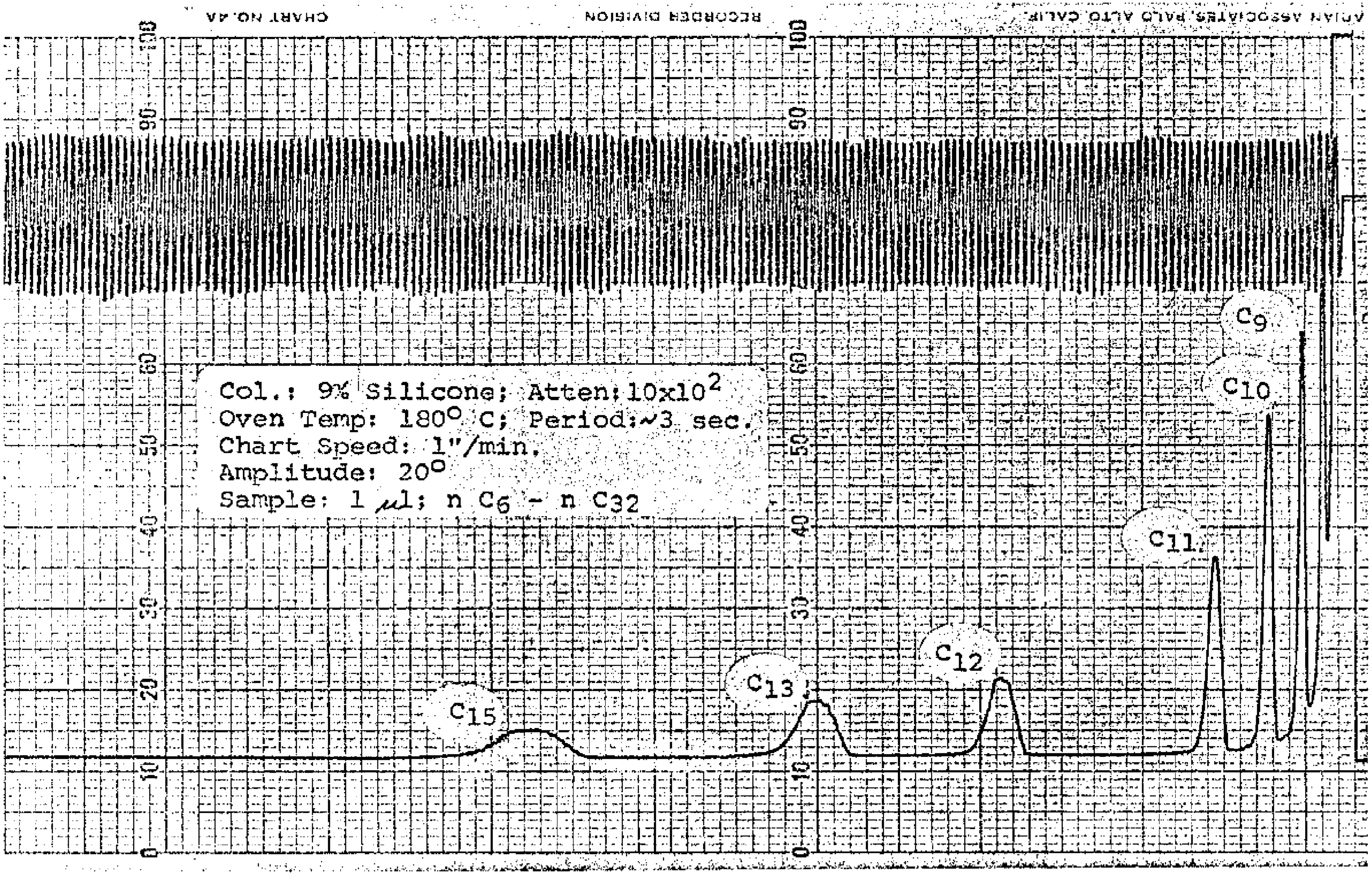


FIGURE 25: DETECTOR RESPONSE TO A CONSTANT DODECANE SIGNAL WHEN SUBJECTED TO SEVEN SECOND TEN DEGREE PITCHING.



Column: 9% Silicone
Oven Temp.: 180° C
Attenuation: 10 x 10^2
Chart Speed: 1"/min.
Sample: 1 μl; n C_6 - n C_{32}

FIGURE 26: ISOTHERMAL CHROMATOGRAM WITH DETECTOR STATIONARY AT A TWENTY DEGREE POSITIVE PITCH.



Col.: 9% Silicone; Atten: 10×10^2
Oven Temp: 180° C; Period: ~3 sec.
Chart Speed: 1"/min.
Amplitude: 20°
Sample: 1 µl; n C_6 - n C_{32}

FIGURE 27: ISOTHERMAL CHROMATOGRAM WITH DETECTOR SUBJECTED TO THREE SECOND TWENTY DEGREE PITCHING.

IV. RESULTS AND INTERPRETATION

A) Sensitivity Calculation

The behavior of solutes in a continuously flowing system such as column chromatography can be most accurately represented by a Poisson distribution (13). As the number of re-equilibrations becomes large the distribution can be treated a Gaussian without any loss in accuracy.

The method that was to determine the area of the peaks was first described by Cremer and Muller (13). The area is obtained by multiplying the height of the peak by its width at half height. This method is reported to give an area somewhat less than the actual area, but gives reasonably good results with narrow chromatographic peaks.

Following the procedure described above, the base of the peak to be used in computing the average value for the peak will be taken as twice the width at half height. This is very close to the 4σ value for a Gaussian distribution.

For the peak shown in Figure 28 the maximum value is approximately six millivolts. With an attenuation of 20 this represents 120 millivolts output. The width at half height is approximately 1.7 divisions. For a chart speed of two inches per minute each division represents three seconds. Thus taking the base of the pulse as twice the width at half height, it is about five seconds. Replace the triangular pulse by an equivalent square pulse whose height is the average of the triangular pulse and whose duration is equal to the base of the triangle. With the assumptions stated above, the average

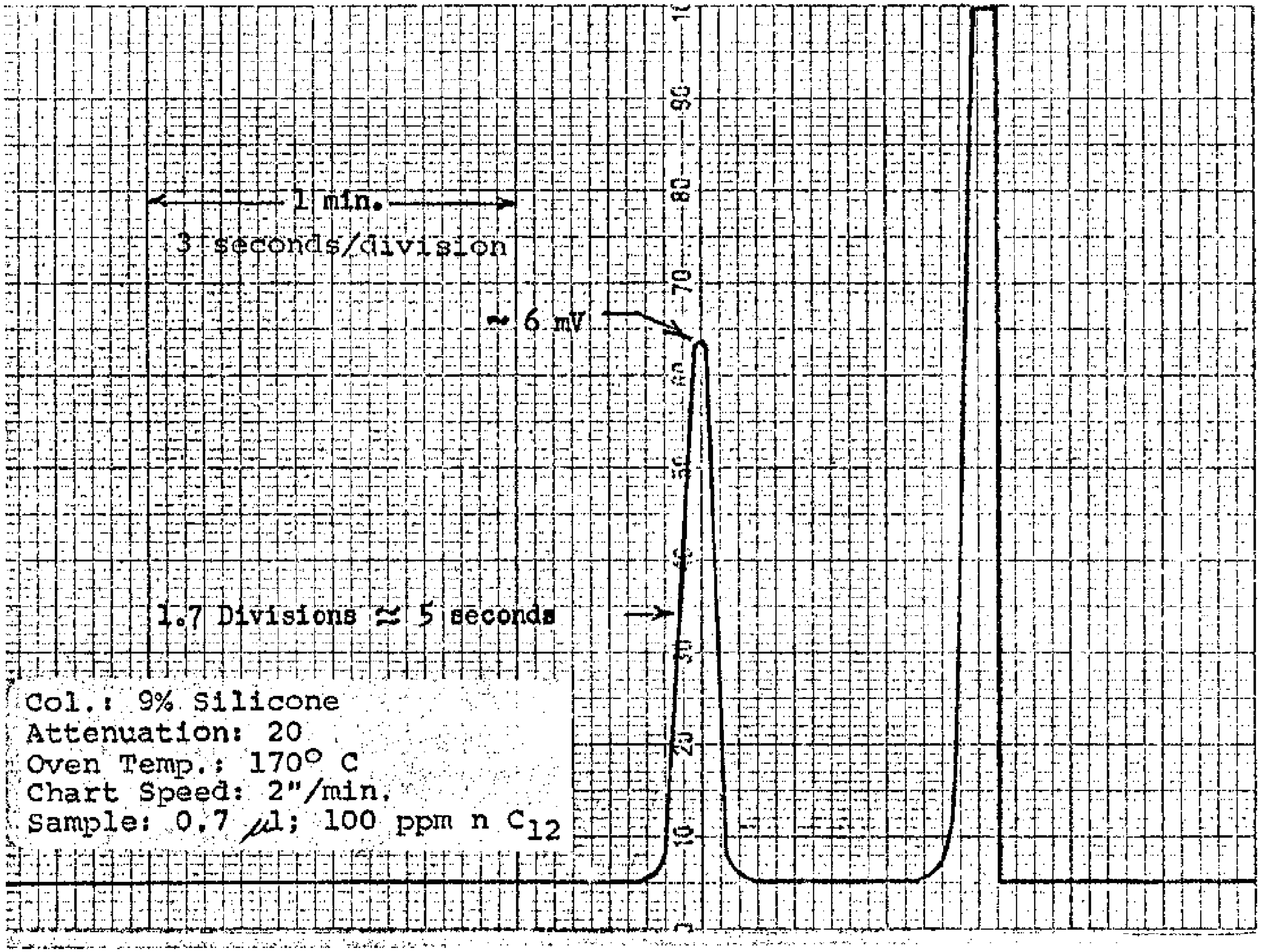


FIGURE 28: DETECTOR RESPONSE TO 0.7 µl OF ONE HUNDRED ppm OF DODECANE WHILE STATIONARY

of the triangular pulse is then just half of the peak value and the duration is twice the width at half height.

For the illustrated case in Figure 28 the equivalent square pulse has a magnitude of 60 millivolts and a duration of 10 seconds.

As noted on Figure 28, 0.7 microliters of 100 parts per million dodecane in carbon disulfide was injected or 0.7×10^{-4} microliters of dodecane. This is equivalent to 0.7×10^{-4} milligrams of dodecane.

Now assuming that this resulted in an average signal of 60 millivolts for 10 seconds the mass flow rate is then 7.0×10^{-6} milligrams per second. For the Carle electrometer used in this study the specifications indicate 10^{-6} microamperes per millivolt. Thus the 60 millivolt signal is equivalent to 60×10^{-6} microamperes.

Finally because the sensitivity of flame ionization detectors is usually given in microamperes output per milligram per second of mass entering the detector, the 60×10^{-6} microampere is divided by 7.0×10^{-6} milligrams per second and a sensitivity of approximately 8.6 microamperes per milligram per second or microcoulombs per milligram was determined. A value of 8.6 microcoulombs per milligram has been used in calculations throughout this report. This value seems reasonable since Condon, et al, obtained sensitivity of 30 microcoulombs per milligram for the particular detector they were using (17).

B) Limits of Detection Due to Motion Sensitivity

It is accepted practice to use twice the peak-to-peak noise level for establishing limits of detection (13). A similar approach will be used to obtain a figure for the minimum detectable sample size per unit time for the motions and ranges studied. The limit of detection for a particular motion and acceleration is defined as:

$$Q_{min} = \frac{2R}{S}$$

where "Q" is the minimum mass flow rate (mg/sec) detectable for a particular motion and acceleration and "R" is the peak-to-peak response induced by the motion (μA). The sensitivity "S" will be taken 8.6 coulombs per milligram. The minimum detectable sample concentration entering the detector in mg/ml or parts per million can be obtained by dividing the limit of detection by the carrier gas flow rate in milliliters per second. Using this expression and Figure 16, the following table relating roll to limits of detections was achieved. These values will apply to a range of periods from about 6 to 20 seconds.

TABLE 1. LIMITS OF DETECTION FOR ROLL

Degrees	Peak-to-peak (mV)	2(peak-to-peak) (mV)	Q_o(mg/sec)
5	4	8	0.93×10^{-6}
10	10	20	2.3×10^{-6}
15	18	36	4.2×10^{-6}
20	25	50	5.8×10^{-6}
25	50	100	11.6×10^{-6}
30	94	188	21.8×10^{-6}

With respect to the limits of detection for heave the unit was oscillated in the vertical direction with a period of approximately two seconds. A maximum acceleration of 0.6 of gravity was achieved and then the forcing of the system was stopped, and it was allowed to damp. The result was a continuous decrease in acceleration accompanied by a decrease in flame response. A plot of peak-to-peak response versus vertical acceleration is shown in Figure 29. Using the expression for the limits of detection given above and Figure 29, the following limits of detection for vertical accelerations were obtained.

TABLE 2. LIMITS OF DETECTION FOR HEAVE

Acceleration (g's)	(mV) Peak-to-peak	(mV) 2(Peak-to-peak)	Q_o (mg/sec)
0.1	6	12	1.4×10^{-6}
0.2	18	36	4.2×10^{-6}
0.3	35	70	8.2×10^{-6}
0.4	55	110	12.8×10^{-6}
0.5	75	150	17.5×10^{-6}
0.6	94	188	21.8×10^{-6}

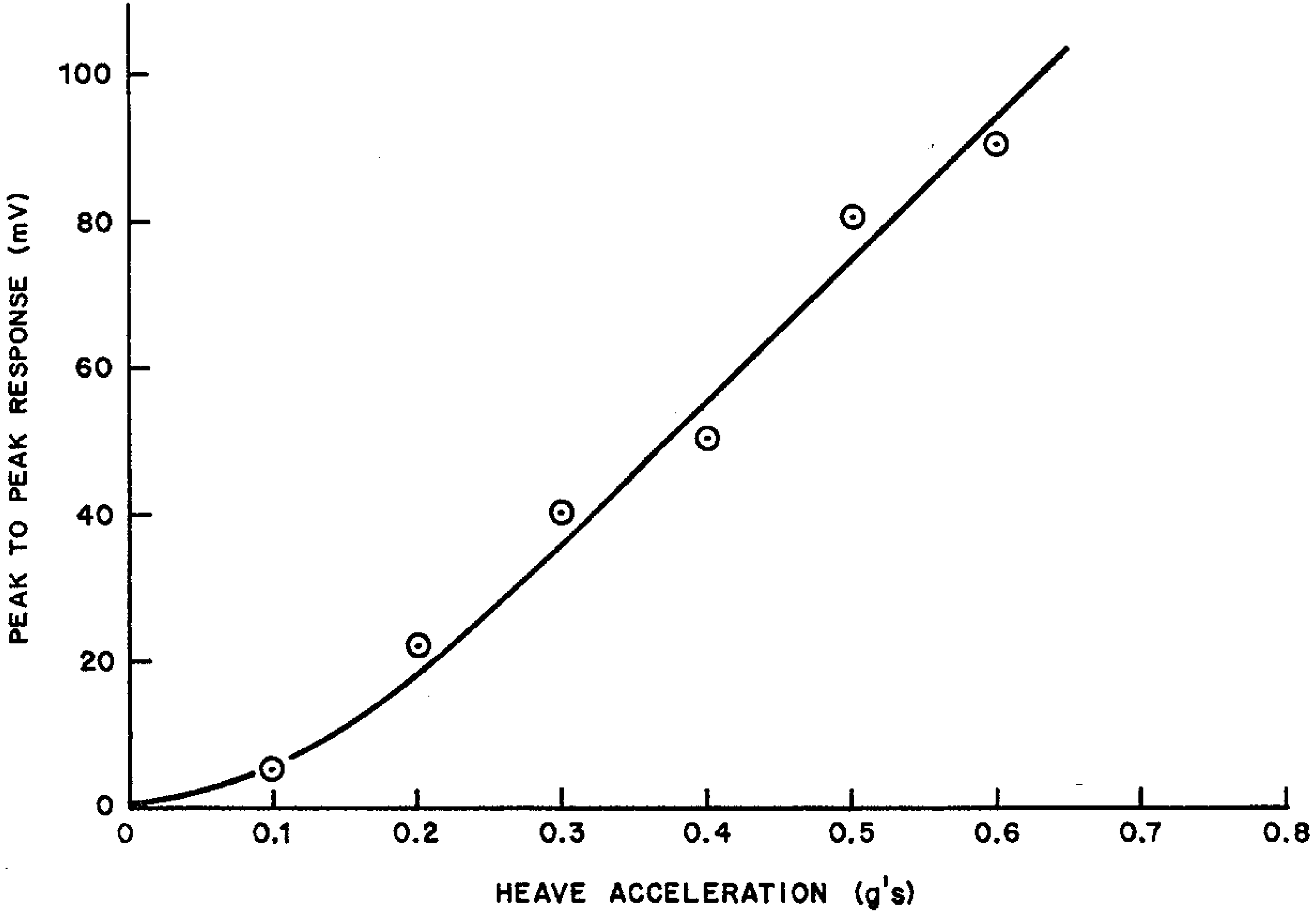


FIGURE 29: DETECTOR RESPONSE TO HEAVE ACCELERATION

The peak-to-peak response of the detector receiving a constant mass flow rate of hydrocarbons as a function of pitch angle is shown in Figure 30. The pitch period was varied from 3 to 8 seconds and no appreciable change in response was noted. Using this figure and expression on page 78, the limits of detection for various pitch angles were determined and are given in the following table.

TABLE 3. LIMITS OF DETECTION IN PITCH

Pitch Angle	Peak-to-peak (mV)	2(Peak-to-peak)	Q (mg/sec)
2.5	7	14	1.6×10^{-6}
5	20	40	4.7×10^{-6}
7.5	34	68	7.9×10^{-6}
10	50	100	11.6×10^{-6}
12.5	68	136	15.8×10^{-6}
15	87	174	20.2×10^{-6}
17.5	105	210	24.4×10^{-6}
20	125	250	29.1×10^{-6}

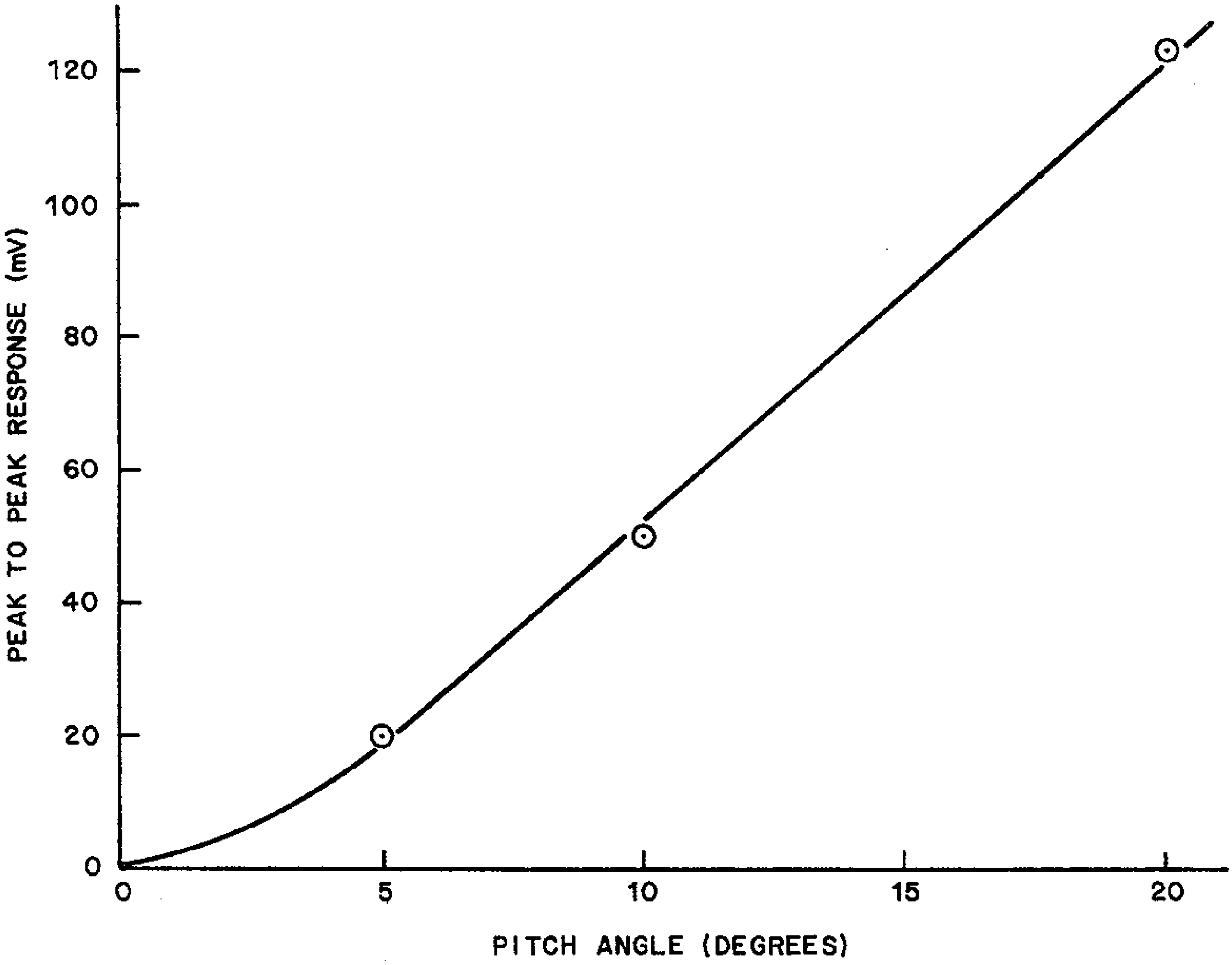


FIGURE 30: DETECTOR RESPONSE TO PITCHING MOTION

V. CONCLUSIONS AND RECOMMENDATIONS

For the range of translational and angular accelerations used in this experiment, it was found that medium resolution gas chromatograms could be produced for the lower boiling point straight chain hydrocarbons without any detectable distortion. In the trace analysis region distortion of the chromatogram was evident.

With respect to the tests that were run with a steady signal, the amplitude of the response was in general proportional to the magnitude of the acceleration and not the frequency. The response in all cases included the same frequency and the excitation acceleration, and in roll and pitch a frequency twice that as the excitation frequency was observed. The translational response was essentially the same form as the acceleration and approximately one hundred and eighty degrees out of phase. The limits of detection were raised as a result of the motion induced flame response.

The following are suggested modifications which might be applied to an already existing flame-ionization-detector to allow it to be used more satisfactorily on a moving platform. The electrometer should be located as close as possible to the detector (assuming that they are not already integral). This will keep the electrometer leads as short as feasible. The leads between the electrometer and the detector cell should be electrically shielded and constrained to eliminate any relative motion. The detector cell should also be secured to prevent it moving with respect to the remaining hardware. Also the collector and probe mounting should be inspected and, if necessary, additional supports provided if there is a possibility of any relative motion.

With respect to detector configuration, a design with the greatest possible symmetry should be sought. That is, a cylindrical collector which is shorter than the one used in this experiment would probably be less sensitive to angular accelerations. Also this would allow the use of a circular probe which would probably also be less sensitive to angular motions. It is difficult to conclude anything with respect to alleviating translational sensitivities from this experiment. In general there is a high probability that these could be reduced by using a dual flame configuration.

In the event that symmetry exists in the detector cell, then it is advisable to align the cell in such a direction as to minimize the response. In the particular detector used in this experiment the response in roll would have probably been reduced or at least the complexity of the response by aligning the ignitor probe with the roll axis.

With respect to the gas system, it is suggested that filters be used on all three gases and that these be located as close as possible to the detector. This together with the shortest possible lines should eliminate any surges in the lines due to acceleration loads.

If the instrument is located in an environment in which it might be subjected to wind gusts, a stack similar to the one used in this experiment could be employed. This will not alleviate any noise induced from pressure fluctuations.

The above hints certainly do not include everything that is required for the successful operation of a gas chromatograph at sea, but includes only those idiosyncracies that become evident in this research.

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BIBLIOGRAPHIC DATA SHEET

1. Report No.

2.

3. Recipient's Accession No.

4. Title and Subtitle

MOTION SENSITIVITY OF FLAME IONIZATION DETECTORS

5. Report Date
July 1972

6.

7. Author(s)
Ronald Carl Gularte

8. Performing Organization Rept. No. WHOI-72-52

9. Performing Organization Name and Address

Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543

10. Project/Task/Work Unit No.

11. Contract/Grant No.
Sea Grant 2-35252

12. Sponsoring Organization Name and Address

NOAA Office of Sea Grant Programs

13. Type of Report & Period Covered
Technical

14.

15. Supplementary Notes

16. Abstracts

A portable gas chromatograph, using a single flame ionization detector, was constructed. The unit was tested for response to surge, sway and heave accelerations up to 0.3g. Also the detector's response was studied for roll and pitch up to 25 degrees with periods ranging from 3 to 20 seconds. The effect on the detector's response of variation in hydrocarbon concentrations in the parts per million range was investigated and response increased with increasing concentration. Samples containing 1, 10, 100, 1000, and 10,000 parts per million dodecane were analyzed, and under the higher accelerations trace distortion was evident for concentrations below 10 parts per million. Stationary isothermal chromatograms of a normal alkane sample (nC_6 - nC_{32}) were compared with those obtained under the various test conditions and no detectable difference in peak area (which represented approximately 1 microgram of the particular hydrocarbon) or retention time was evident. The limits of detection for the Aerograph detector were found to be 21.8×10^{-6} mg/sec (CONT)

17. Key Words and Document Analysis. 17a. Descriptors

1. Gas Chromatography
2. Flame Ionization Detector
3. Detector Motion Sensitivity

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group

18. Availability Statement

19. Security Class (This Report) UNCLASSIFIED

20. Security Class (This Page) UNCLASSIFIED

21. No. of Pages

22. Price

Woods Hole Oceanographic Institution
WHOI-72-52

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By Ronald Carl Gularte. 86 pages, 30 figures and 9 Photographic Plates. July 1972. Grant 2-35252.

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1. Gas Chromatography
2. Flame Ionization Detector
3. Detector Motion Sensitivity

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