

## FOREWORD

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This report covers work conducted from April 1960 to March 1961.

# *Contrails*

A gas chromatograph operable at temperatures up to 1000°C is described. Featuring either isothermal or linear programmed temperature operation, the unit utilizes a novel integrated column and hydrogen flame ionization detector for sensitivity and stability. The stainless steel column is heated by passing high currents (up to 120 amperes) directly through the metal. Other wrapped heater columns may also be used.

Design considerations, descriptive information and performance data for the instrument are presented. Organic analysis present no problem, and the detection of organo-metallic compounds appear straight forward. Application to inorganic chloride salts has given anomalous results. The data indicate that reaction of the sample is the primary cause of this behavior, and that proper choice of column materials and sampling techniques will be required for these analyses.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

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# *Contrails*

## I. Introduction

# Contrails

The short history of gas chromatography has been marked by two major trends. One of these has been toward operation at increasingly higher temperatures; the other toward the attainment of higher sensitivity. Early units were generally limited to operation below 150°C and were considered highly sensitive if concentrations on the order of 0.1% could be determined. Improvements in instrument and detector design has increased the upper temperature limits to about 500°C, and analyses in terms of parts per billion are now possible. It is reasonable to assume that as the state of the art continues to improve the application of gas chromatography at still higher temperatures will become both practical and useful. There are many potential uses for an instrument capable of operation at very high temperatures. Some of these are listed in Table 1. As can be seen, they encompass both organic and inorganic analyses, as well as some applications which are not strictly analytical in nature.

A mandatory first step toward the realization of these applications is the development of the necessary instrumentation, and a study of the factors affecting practical operation at these higher temperatures. This report discusses the design and performance of a gas chromatograph operable to 1000°C, using either programmed temperature or isothermal techniques.

## II. Discussion

### A. Basic Considerations

There are many factors to be considered in the design of a gas chromatograph for very high temperature operation. One of the most important of these is the type of detector system to be used. The most common type of detector in use today depends upon changes in thermal conductivity for signal generation. These katharometer detectors are of moderately high sensitivity but have several disadvantages in the higher temperature ranges.

Thermistor elements can be used up to about 300°C, but are most useful with respect to their high sensitivity below 200°C. At higher temperatures their sensitivity falls off and their performance becomes unstable because of degradation of the thermistor coating and other factors.

Filament elements have been used successfully to 500°C, and provide better sensitivity and stability than thermistors at high temperatures. Even though filaments could undoubtedly be used above 500°C, they, like all katharometer detectors, are very sensitive to environmental temperature changes, which become more difficult to control at high temperatures.

Recently, several types of ionization detectors have been developed which can provide up to 10,000 times the sensitivity of katharometers. Most of these utilize a radioactive material as a source of ionizing energy, and are limited to temperatures below about 300°C. The flame

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ionization detector uses a hydrogen flame as an energy source, and hence should be relatively unlimited as far as temperature is concerned. It has the further advantages of high sensitivity, wide dynamic range and simplicity of construction. Since it is relatively insensitive to ambient temperature changes, control of detector temperature becomes less critical. The one major drawback of flame ionization detection is its inability to detect all materials. It is normally considered to be a "carbon-counting" device and hence suitable primarily for organic analyses. However, some early experiments showed that at least some inorganic materials do give a signal. This fact, together with the obvious advantage of its insensitivity to temperature, led us to choose the flame ionization system for this development.

Also of prime consideration is the method of heating the chromatographic column and associated parts. Exclusive of programming and control considerations, there are three general techniques for heating columns, namely:

1. The use of a circulating air oven.
2. Wrapping insulated heater wire directly on the column.
3. Self heating by passing high currents directly through the metal of the column.

The pertinent characteristics of these three methods with respect to gas chromatography are given in Table 2. For our development we chose the self heating technique for the following reasons:

1. Higher attainable temperatures
2. Simplicity of construction
3. Rapid response
4. Least wattage required
5. Temperature cycling and column length are not as critical when using flame ionization and programmed temperature operation.

#### B. Description of the Instrument

A schematic of the instrument is given in Fig. 1. The column, sample injection system and detector are housed in an insulated cabinet. The column is heated by making it the resistive load across the secondary of a step down transformer, the primary of which is powered through a high capacity variable transformer. Temperatures are controlled by means of a conventional thermocouple controller. Column temperature programming is provided by a motorized gear train which drives the set-point of the controller upscale at a linear, preset rate. Ions formed in or passing through the flame are collected on a platinum electrode, and the resulting signal is amplified and recorded by conventional means.

Construction of the injection system, column and detector deserve special mention since it is rather a novel approach and a considerable departure from conventional systems. Usually, both the injection port and detector are contained in relatively massive blocks of metal which are heated independently of the column. When using the self heating technique, these metal blocks, or any other point where the cross-sectional area of the heated zone is increased, would be cooler than



the rest of the system, and sample condensation could occur. Also, in programmed temperature work, the detector block would have to be maintained continually at or above the highest column temperature. This would cause obvious complications with materials of construction at 1000°C.

Our approach to these problems has been to integrate the injection system, column and detector into a single length of 1/4" tubing. Thus the cross-sectional area of the zone to be heated is maintained constant. By attaching the terminal electrode to the end of the column, beyond the jet, maintenance of column temperature through the jet area is ensured. The first three inches of the column itself serves as the injection port. Extra heat is supplied to this zone by a specially constructed heater which slips over the column and the injection port fitting. Carrier gas and hydrogen are introduced counter-currently at the ends of the column through support blocks. The gases mix and pass out through the jet, which is a piece of capillary tubing silver soldered through the column wall. The length of column between the jet and the hydrogen inlet is packed with "Chromosorb" to prevent excess diffusion of column effluent at the jet, and thus ensure smooth, sharp peaks.

One possible objection to this approach is the somewhat increased difficulty of column fabrication. Actually, however, the columns are quite easy to prepare. A special high-melting silver solder is used to weld the jet into the column wall.

The detector cell housing is constructed in three pieces, and is designed to surround the column and jet closely without touching. The necessary air for combustion and flushing of the cell enters through a baffle plate in the bottom of the housing. The collector electrode enters and the gases are vented through a slot in the housing wall.

For proper operation of the column heating system, it is necessary to match the power input to column temperature. Too high a power setting will cause temperature overshoot, while too low a setting will cause the temperature to lag the controller. In order to provide proper matching over a programmed temperature range, the variable transformer feeding the step-down transformer is mechanically coupled to the same gear train which drives the controller. Thus the voltage on the transformer primary is continuously raised as the column temperature increases.

Approximately 120 amperes of current are required to heat a 4 ft. stainless steel column to 1000°C. At high temperatures, the large cyclic variation in current coincident with the on-off action of the controller resulted in severe fluctuations in column temperature. Variations of as much as 40-50°C were observed. By modifying the control action via the circuit shown in Fig. 2, this cycling was drastically reduced. The common terminals of a DPDT relay are connected directly to 115v. AC. The coil of the relay is actuated by the controller. The NO and NC contacts connect to special taps on the transformer winding. With this set-up, the power output varies ---- not between on and off, but between two voltage values differing by an amount proportional to the spacing of the transformer taps. In practice, the transformer is adjusted so that the "on" position provides

slightly more power than is necessary to maintain the set temperature, and the "off" position slightly less. Experimentation showed the optimum variation in current to be approximately 8-10 amperes. With this "high-low" control system, measurement of single point column temperature showed variations of only  $\pm 2^{\circ}\text{C}$ . at  $950^{\circ}\text{C}$ , over the measured time interval of 10 minutes.

The instrument itself consists of three major components, as shown in Fig. 3. The large cabinet houses a lmv recorder and all the controls necessary for operation of the unit.

The electrometer for measuring ion currents is housed in a separate box mounted behind the front panel. The separate housing provides electrical shielding and also makes it easy to remove the entire electrometer for maintenance. The electrometer circuit is given in Fig. 4. It is a line operated 4-tube unit having completely balanced circuitry using nearly 100% feed-back for stability. The input voltage is developed across five precision resistors ranging from  $10^6$  to  $10^{10}$  ohms. The input can thus be attenuated in decades by means of a range switch. The output can be further attenuated in steps of 2 from 1 to 1024, giving a total attenuation factor of over 10,000,000. By combining input and output attenuations, ion currents from  $2 \times 10^{-12}$  to  $2 \times 10^{-5}$  amperes may be recorded as full scale deflections on the recorder. Coarse and fine zero controls are provided. The noise of the electrometer is approximately  $8 \times 10^{-14}$  amperes, and the drift is less than  $10^{-13}$  amperes per hour after warmup. The time constant on all ranges is less than 1 second.

The temperature controller is a Barber-Colman "Capacitrol" unit actuated by a Chromel Alumel thermocouple attached to the chromatographic column. The main power variac controls the power input to the column. Both the temperature controller and the variac are coupled to the programmer by chain drives through a push-button clutch assembly. The clutch allows independent setting of column temperature and power level, and is necessary to provide for proper functioning of the heater system at both high and low programming rates and for isothermal operation. The programmer is a motor driven gear train which provides nine heating rates from  $5.8^{\circ}\text{C}/\text{min}$ . to  $84^{\circ}\text{C}/\text{min}$ . A limit switch prevents overheating of the column. Injection port heat is provided by the small variac and switches are provided for remote ignition of the flame. The meter indicates the injection port temperature, or, by means of the selector switch, the temperature inside the detector housing.

The oven unit contains the injection system, column and detector. Rotameters and valves are provided for all gas streams. Liquid samples are injected through a silicone rubber septum, using a long needle so that injection is made directly into the heated zone. Water cooling prevents degradation of the septum. An accessory fitting is used for the introduction of solid samples.

The middle cabinet houses two General Electric 1.5KVA transformers and a 0-150 ampere meter. The windings of the transformers are connected in such a way as to provide a step down ratio of 7.5:1. For those cases where a metal column having the proper electrical resistivity

cannot be used, columns with wrapped heaters can be connected directly to the variac output through a selector switch which by-passes the step down transformers.

Fig. 5 is a photograph of the oven interior, showing the placement of the injection port heater, column and detector cell. The cabinet is insulated with fibrous potassium titanate faced with stainless steel, which acts as both a support and a reflector to prevent excessive heat loss. The column is U-shaped and is supported at one end only to allow for expansion on heating. Although a 4 ft. stainless steel column will elongate by approximately  $3/4$ " at  $1000^{\circ}\text{C}$ , the location of the jet near one end restricts its movement, and no difficulty in maintaining detector alignment has been experienced.

The collector electrode enters through slots in the oven wall and the side of the detector housing. It is a loop of flattened 18 ga. platinum wire, and is held in a metal arm extending from a "Teflon" pivot block attached to the outside wall. The pivot block allows the electrode to be swung up out of the way for easy disassembly of the cell. The external mounting of the insulator was found necessary to avoid electrical leakage caused by the breakdown of insulation at high temperatures. In Fig. 6 the detector cell has been disassembled to show the relationship between the column, jet, igniter wire and temperature measuring thermocouple. This type of cell construction offers several advantages. First, it is easily dismantled for cleaning and other maintenance. (Incidentally, some cleaning will be necessary. Substrate bleeding will cause the detector components to become coated with combustion products. Also, incomplete combustion of certain large organic samples will cause soot deposits which lead to electrical leakage if not removed). Second, the collector electrode can be adjusted and aligned before the cell housing is put in place. Third, the use of only one insulated electrode makes the cell geometry less critical than it is with the more usual two-electrode configurations. There is also less chance that portions of the cell other than the collector electrode will act as collection sites, resulting in loss of signal.

### C. Performance

Operation of the instrument has been generally satisfactory. After extended operation at high temperatures, oxidation of the stainless steel parts inside the oven housing markedly affects their appearance but does not seem to cause adverse effects as far as operability is concerned. Maintaining an inert gas blanket inside the oven would be helpful in minimizing this oxidation.

At fast programming rates the column temperature lags the controller at very high temperatures because of the rapid heat loss at these temperatures. Wrapping a layer of "Fiberfrax" ceramic fiber loosely around the column reduces the heat loss and causes minimum lag. Normally, the settings on the main power variac are approximately proportional to column temperature; that is, a setting of 50 would provide about  $500^{\circ}\text{C}$ . For fast programming rates the power should be increased slightly, and for slow rates or isothermal operation the

setting should be reduced. The exact settings will be determined by the column resistance and rate of heat loss.

With the integrated column and jet system used, the temperature of the jet increases with column temperature. Although the flame detector is quite insensitive to ambient temperature changes, some change in baseline is observed. This shift is gradual up to a column temperature of about 900°C, when the background current begins to rise quite sharply, possibly due to thermionic emission of the jet. At a column temperature of 950°C., this background amounts to approximately  $6 \times 10^{-9}$  amperes. Based on a 10 $\mu$ l sample, this is equivalent to a component concentration of 400 ppm.

Under isothermal conditions, the temperature of the injection zone may be maintained constant at any temperature above the column temperature. For programmed runs, however, the temperature of the injection zone will increase, since it receives heat from two sources. Ordinarily this presents no difficulty, but at very high column temperatures the injection port heat should be turned off or reduced to prevent melting of the Swagelok nuts used for mounting the column.

#### D. Organic Analyses

Organic analyses have presented no problem. Operation with these materials is essentially similar to that of any flame ionization system.

The chromatogram shown in Fig. 7 is a low temperature run of a hydrocarbon mixture using a silicone gum rubber column. It is shown here for two reasons. First, it illustrates the excellent peak shapes obtained with the counter-current flow of carrier gas and hydrogen. Second, it points up one of the major difficulties encountered with conventional liquid phases at high temperatures; namely, the drift in baseline with increasing temperature caused by substrate bleeding. Fig. 8 shows the same mixture run at higher temperatures on a solid adsorbent type column. Here the baseline is flat over the entire temperature range, which illustrates a potential advantage of this type of column for hydrocarbon materials at temperatures above 350°C. Similar results have been obtained on silica gel columns and on columns of alumina deactivated with NaOH. The latter technique shows considerable promise, since non-deactivated material is extremely retardant, and decomposition occurs before all the material has eluted.

Sensitivity and noise values are difficult to specify since so much depends on the conditions of the analysis, such as temperature, amount of substrate bleeding, etc. In a specific test at 600°C, the injection of 0.1 $\mu$ l of cyclohexane afforded a signal of  $3 \times 10^{-8}$  amperes with no discernible noise. This signal represents 1.5 times full scale deflection at 1/10,000 of the maximum sensitivity. Reproducibility for organic materials is on the order of 1-2% relative.

#### E. Organometallic Compounds

A few runs were made on metal benzoylphenyl-hydroxylamines. The chromatograms obtained for the zirconium compound is shown in



Fig. 9. No attempt was made to interpret this chromatogram in detail, but it would appear that we are probably dealing with a case of sample decomposition. There seems to be little doubt that the flame detector is applicable to the detection of organometallic compounds, although the sensitivity will probably be less than with organic materials.

#### F. Inorganic Compounds

The situation with respect to the detection of inorganic materials is not nearly as clear cut, and a good deal of anomalous behavior has been observed. Some early experiments were run to determine whether or not the flame detector could detect these compounds. In these tests, a clean platinum wire was moistened with the test substance and then held directly in the flame. The results of these tests showed that compounds containing  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{NO}_2^-$  or  $\text{Cl}^-$  ions did give signals. It is significant that the platinum wire alone or moistened with water afforded no signal.

With this background, it was felt that inorganic salts might be detected, since they are ionic in nature and hence might not depend solely upon the energy imparted by the flame for ion formation. The chloride salts in particular looked promising, since 28 elements form chlorides boiling below  $1000^\circ\text{C}$ .

Following this premise, peaks have been obtained for the injection of the chlorides of stannic and stannous tin, ferric iron, zinc and cadmium. Both sensitivity and reproducibility are greatly reduced from that obtained with organic materials. Although we have obtained reproducibility values on repetitive samples of  $\pm 3\%$  relative, we have also observed results differing by 50% or more, and this unpredictable behavior makes the assignment of more exact values impossible. The peak heights from  $\text{SnCl}_4$  samples were found to increase linearly with collector voltage up to at least 1000v. (Attempts to operate at 1800v. were unsuccessful due to electrical leakage which "swamped" the electrometer circuit.) This behavior is quite different from the results with organic materials, where saturation currents (constant signal with increasing voltage) are obtained at voltages as low as 50v. It was also observed that the signal increased with increasing jet to collector distance, up to separations of at least  $1/2"$ .

Attempts to separate inorganic chlorides have generally been unsuccessful. Figure 10 is a chromatogram of a mixture of stannic and ferric chlorides run on a column consisting of 50%  $\text{CdCl}_2$  on "Chromosorb". Here the sample was injected as a solid at a column temperature intermediate between the boiling points of the two materials. After the first peak had been obtained, the temperature was increased rapidly, affording a second smaller peak eluting at a temperature approximately equal to the boiling point of ferric chloride.

Although we have not been successful in obtaining analytical data from these chloride salts, it appears that the major problem lies in the reactivity of the samples rather than an inherent fault of the detection system. Several pieces of evidence point to this conclusion, as listed below.

1. The peaks obtained for the chloride salts tested have essentially the same shape and do not follow the expected variation in elution time with temperature. For example, stannic chloride (BP 1190°C.) does not give an appreciable peak at column temperatures much below 200-250°C, whereas CdCl<sub>2</sub> (BP 972°C.) gives a peak at only 660° column temperature. The elution times of these peaks are approximately the same at the column temperature employed.

2. After a column has been used for a while, a solid deposit is observed in the injection zone, possibly indicating the formation of the oxide or some other non-volatile material.

3. In the SnCl<sub>4</sub>-FeCl<sub>3</sub> mixture shown, the second peak is very much smaller than the first, even though approximately equal amounts of the components were injected. At slow heating rates, the second peak is not seen, which may indicate that complete reaction is occurring before the component can elute from the column.

4. Essentially similar results were obtained on several different column combinations. These included stainless steel, glass and Inconel columns. Packings used were "Chromosorb", 50% CdCl<sub>2</sub> on Chromosorb, micro-glass beads and alumina.

5. Large signals were observed for aqueous solutions of SnCl<sub>4</sub> when the sample was placed on the outside of the hot column and allowed to vaporize in the detector housing. Under identical detector conditions, the same samples injected onto the column gave no signal.

6. In one case, a column which afforded reasonably consistent results for SnCl<sub>4</sub> injections later failed to give any peaks at all. Examination of the column showed that the "Chromosorb" packing had changed from pink to light gray in color, and contained magnetic flakes whose shape indicated that they came from the inner walls of the column. The fact that only that portion of the packing traversed by the sample changed color, while that beyond the jet remained pink, rules out the possibility that overheating or some other environmental factor was responsible for the change.

We are not able at this time to explain the anomalous behavior we have observed. We are, however, quite certain that the peaks resulting from the injection of the chlorides used are due to the passage of an inorganic material through the flame. The possibility of peaks arising from degradation of the silicone rubber septum was prevented by water cooling the septum, and by making a background run prior to the sample run under the same operating conditions.

It was felt that some of the peaks might be caused by the sudden increase in column pressure due to the rapid vaporization of the sample. This was checked by rapidly injecting 10cc of air. Although a deflection of the baseline did occur, it was immediate rather than equal to the elution times of the sample peaks, and was negative rather than positive in direction. A more positive proof that the peaks are caused by sample component rather than an upset in operating conditions is evidenced by the appearance of flame coloration coincident with elution of the peak.

It is obvious from the above that much remains to be understood about the determination of inorganic chlorides by this technique. The proper choice of column materials and the development of suitable sample handling techniques will be of prime importance for these analyses.

### III. Recommendations for Future Work

We hope to be able to continue this study, with the primary emphasis placed on the application of the instrument to various types of analysis. This work should include as a minimum the following points.

1. Find explanations for the anomalous behavior observed in the detection of inorganic chlorides. This will involve a study of operation parameters and possibly identification of the components giving rise to peak formation.
2. In conjunction with the above, determine the applicability to other inorganic analyses, e.g., metals.
3. Determine the limitations of high temperature chromatography as applied to organic materials. The major problem appears to be sample degradation. Special techniques in column preparation may be required to extend the method to very high molecular weight or polymeric materials.
4. Investigate the use of certain substrates of potential high temperature use, such as adsorption type packings with and without controlled deactivation, salt eutectics and possibly metals.
5. At least a preliminary investigation should be made of other detector systems of possible value at very high temperatures in order to extend the applicability of the instrument to additional materials.
6. To improve operability of the instrument as use indicates necessary.

TABLE 1

Potential Applications of Ultra High Temperature  
Gas Chromatography

Catalyst Studies  
Analysis of Metal Impurities  
Inorganic Reaction Mechanisms  
Thermal Stability Studies  
Evaluation of Adsorbents  
Determination of Organics in Soils  
Destructive Distillation of Coal  
Kinetic Studies  
Oil Content of Shales  
Small Lot Purification of Metals



TABLE 2

CHARACTERISTICS OF COLUMN HEATING METHODS

<u>Characteristic</u>	<u>Wrapped Heater</u>	<u>Selfheating</u>	<u>Air Oven</u>
Upper Temperature Limit	B	A	C
Temperature Cycling	B	C	A
Temperature Uniformity	C	B	A
Cold Connections	C	B	A
Restrictions On Column Lengths and Materials	B	C	A
Ease of Making Columns	C	B	A
Speed of Response	B	A	C
Speed of Column Replacement	B	A	C

"A" is considered most desirable.

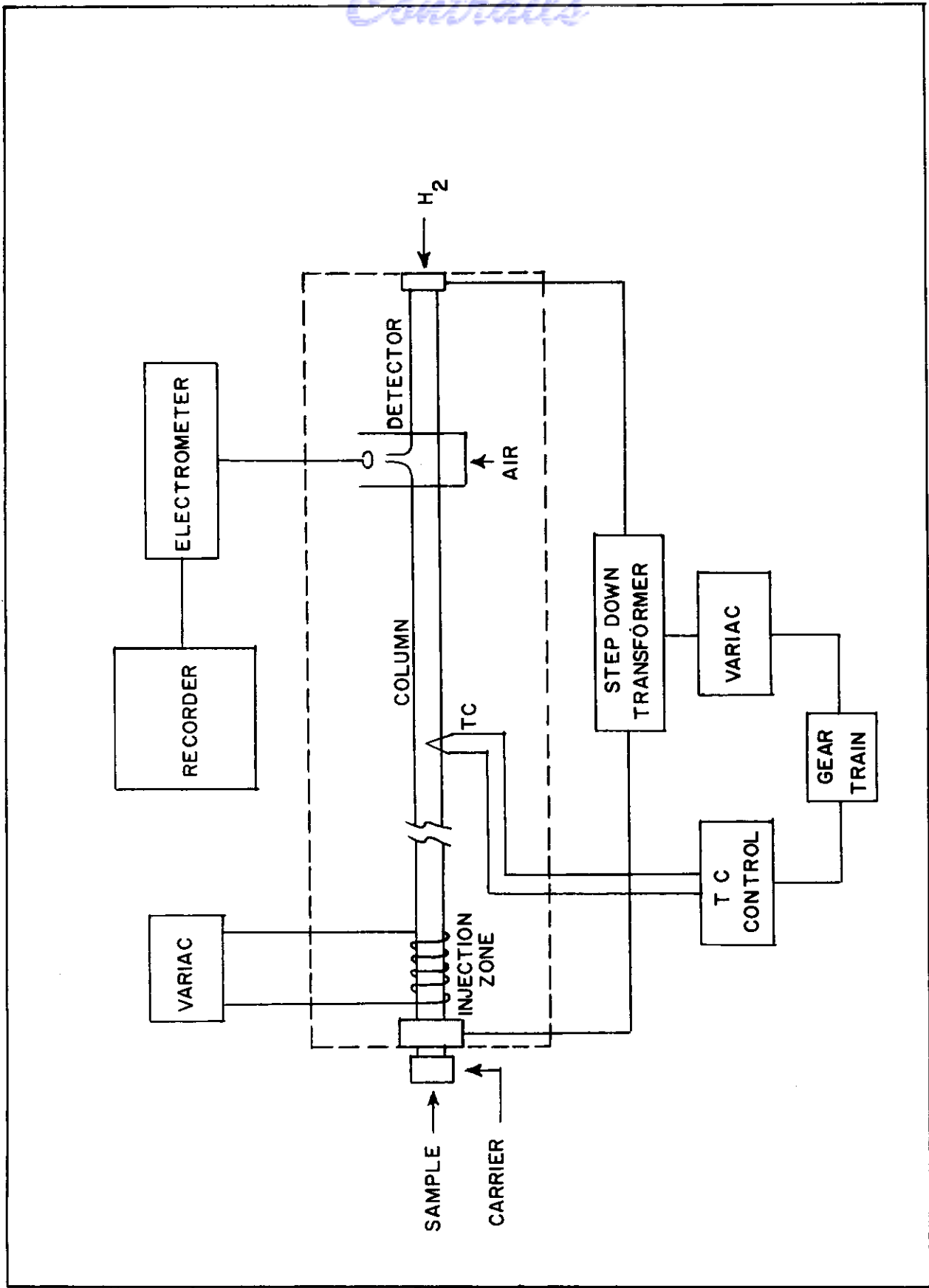


Figure 1 - Schematic of Instrument

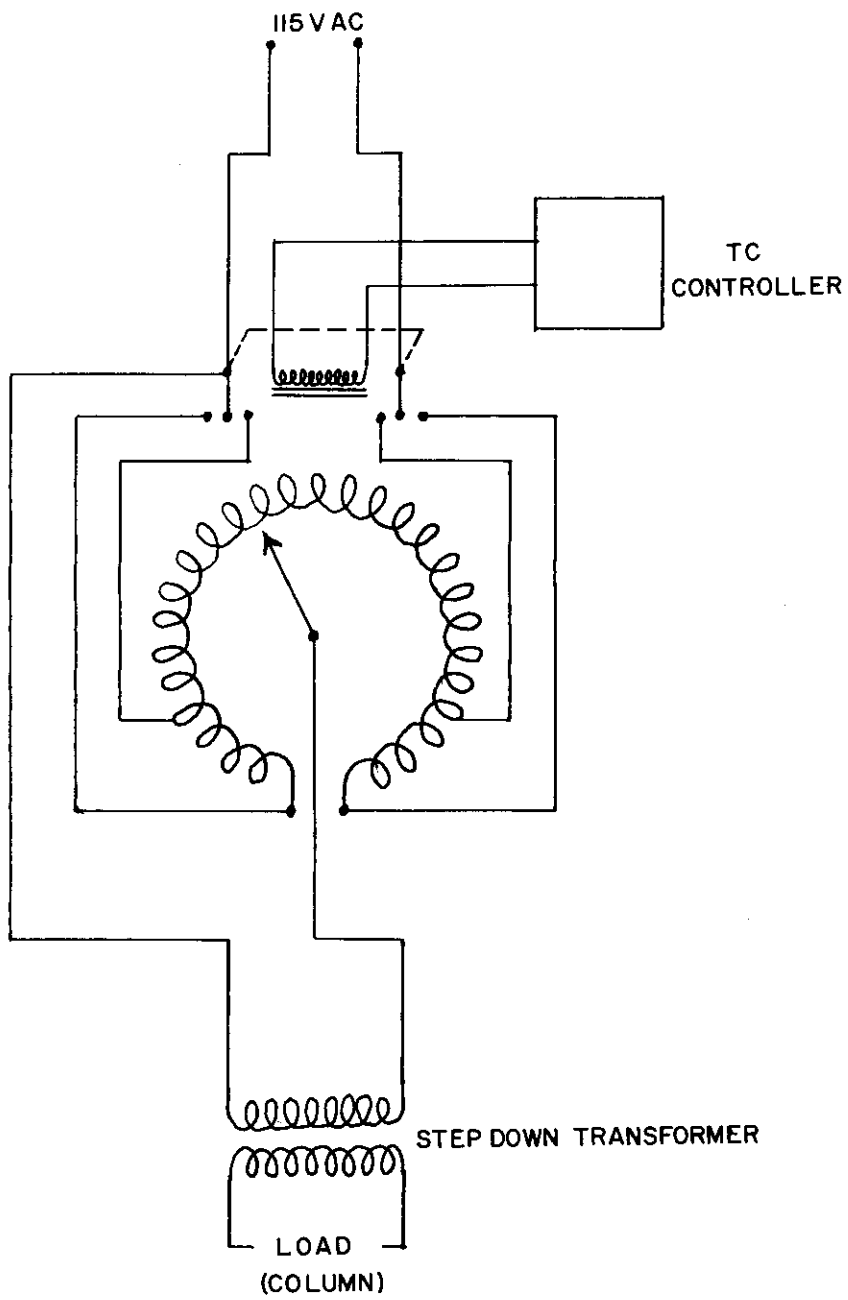


Figure 2 - "High-Low" Heat Control Circuit

*Controls*

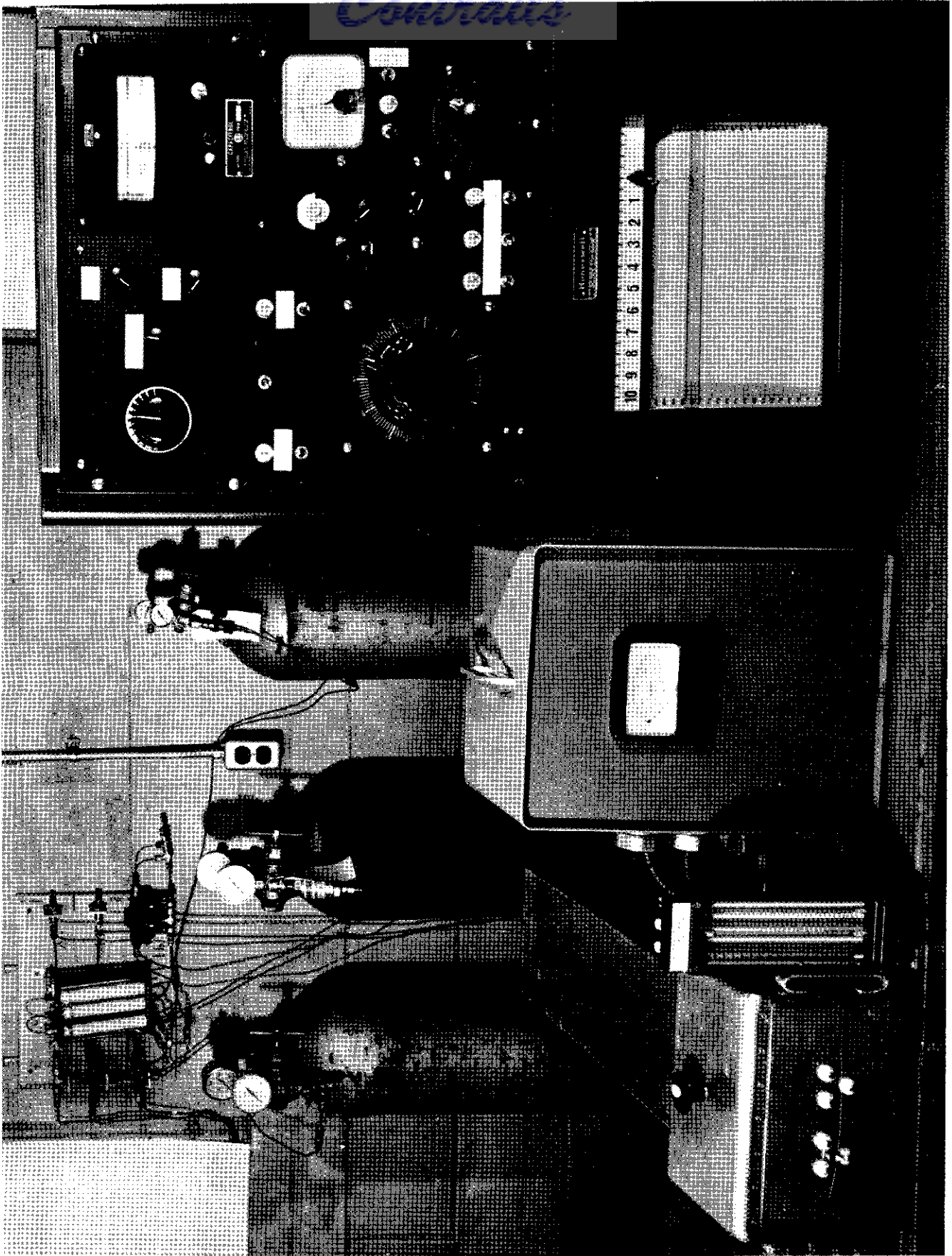


Figure 3 - Overall View of Instrument

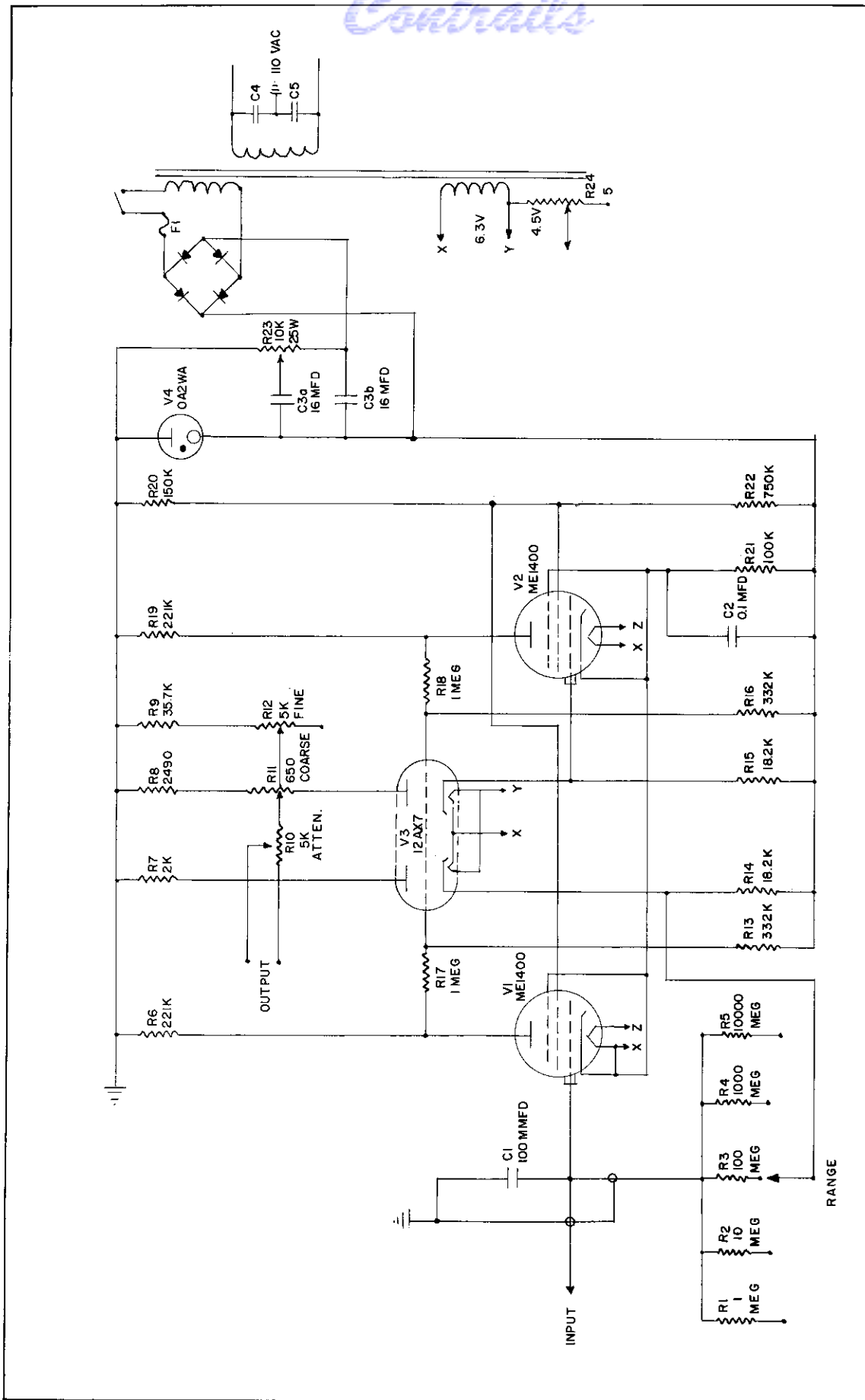


Figure 4 - Electrometer Circuit



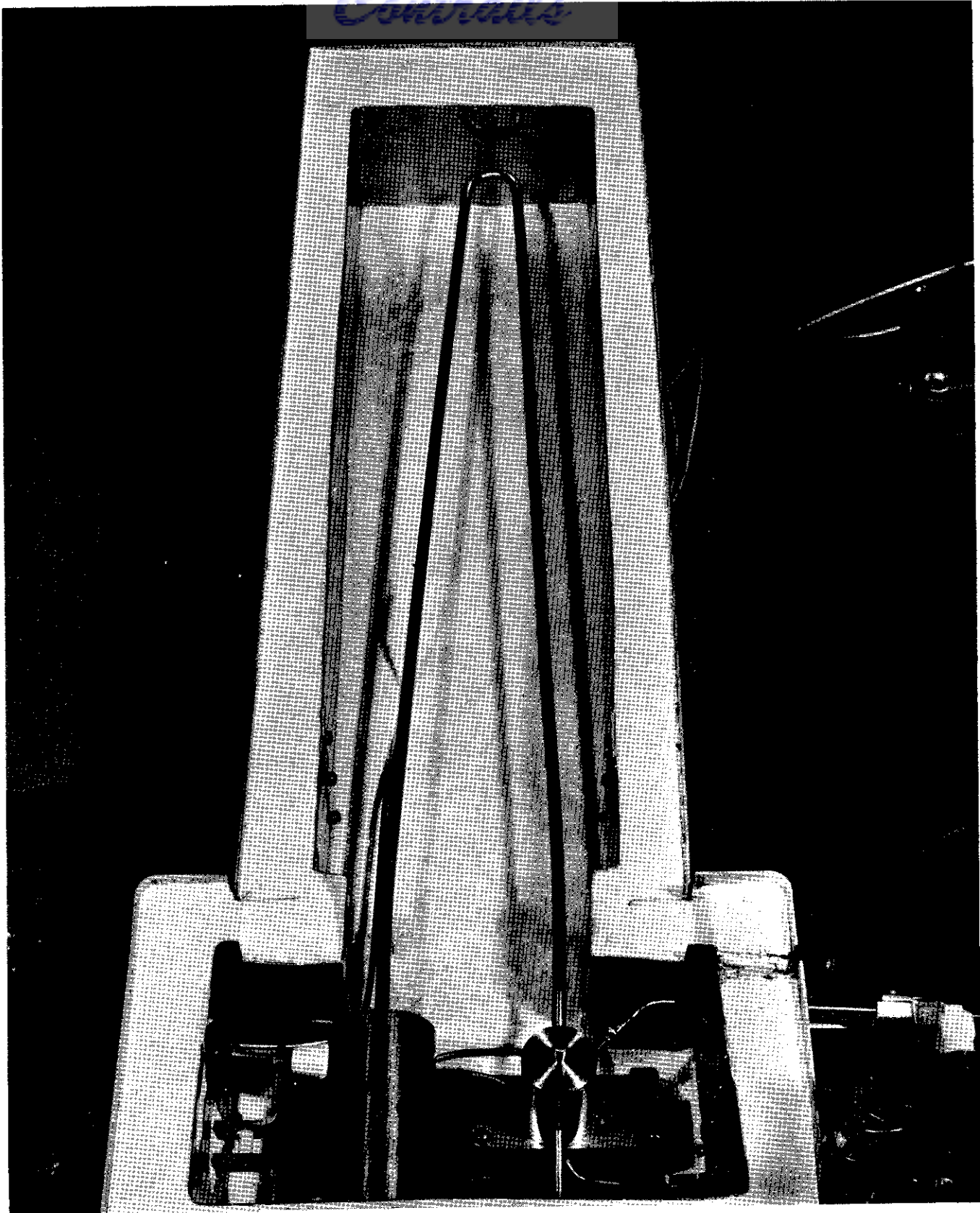


Figure 5 - Interior of Oven Unit

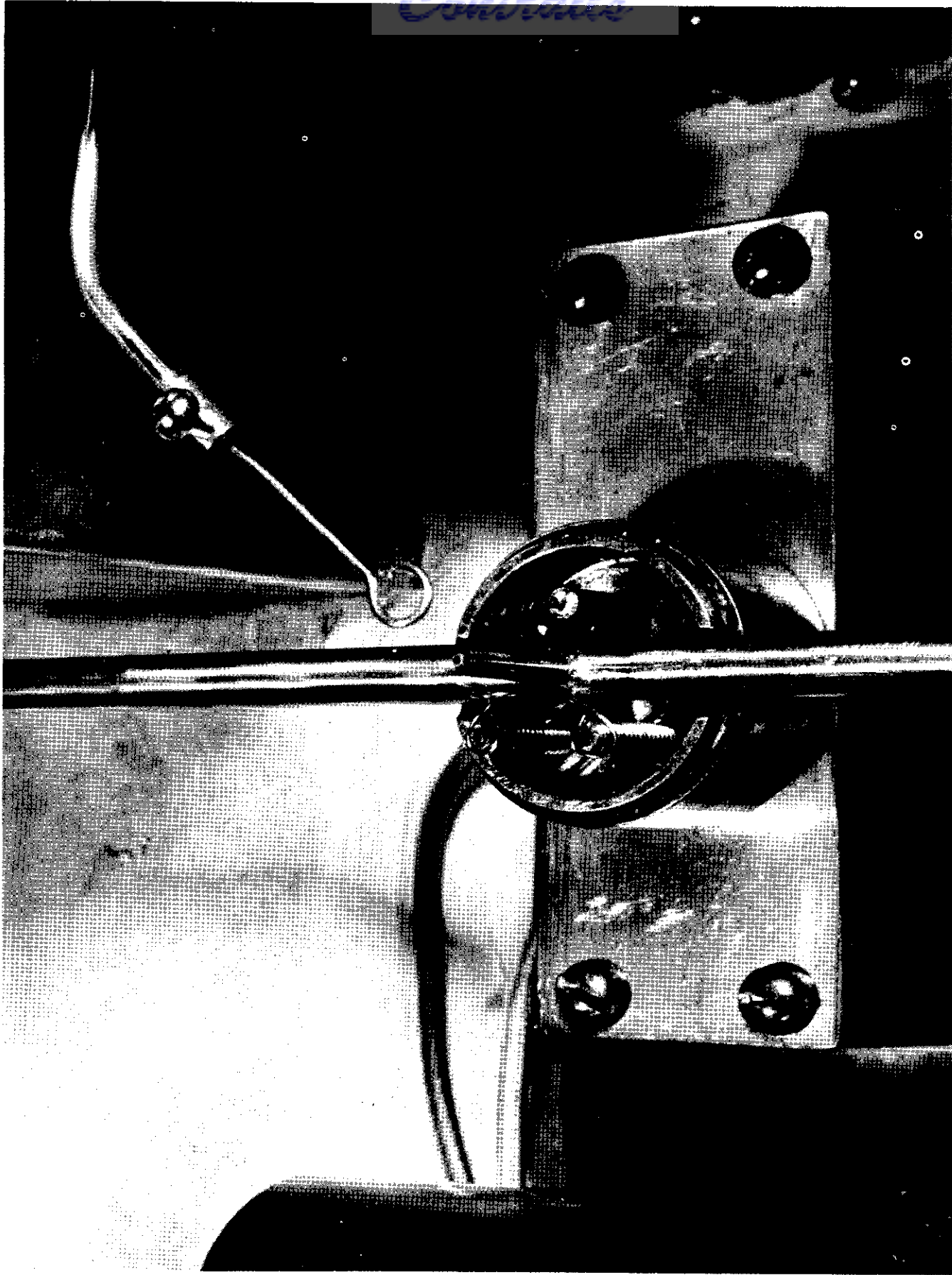


Figure 6 - Close-up of Detector

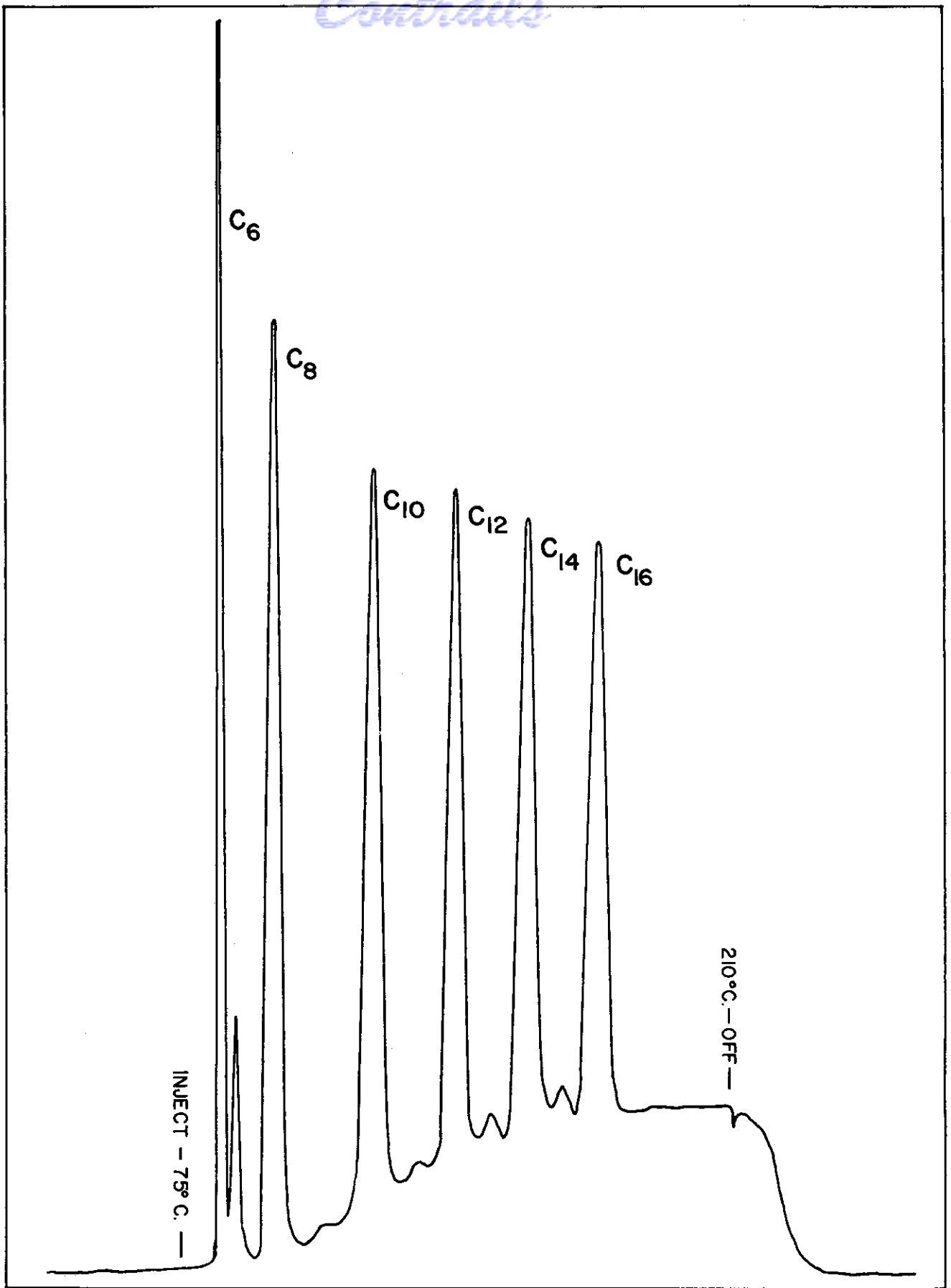


Figure 7 - Chromatogram of Hydrocarbon Mixture on Silicone Rubber



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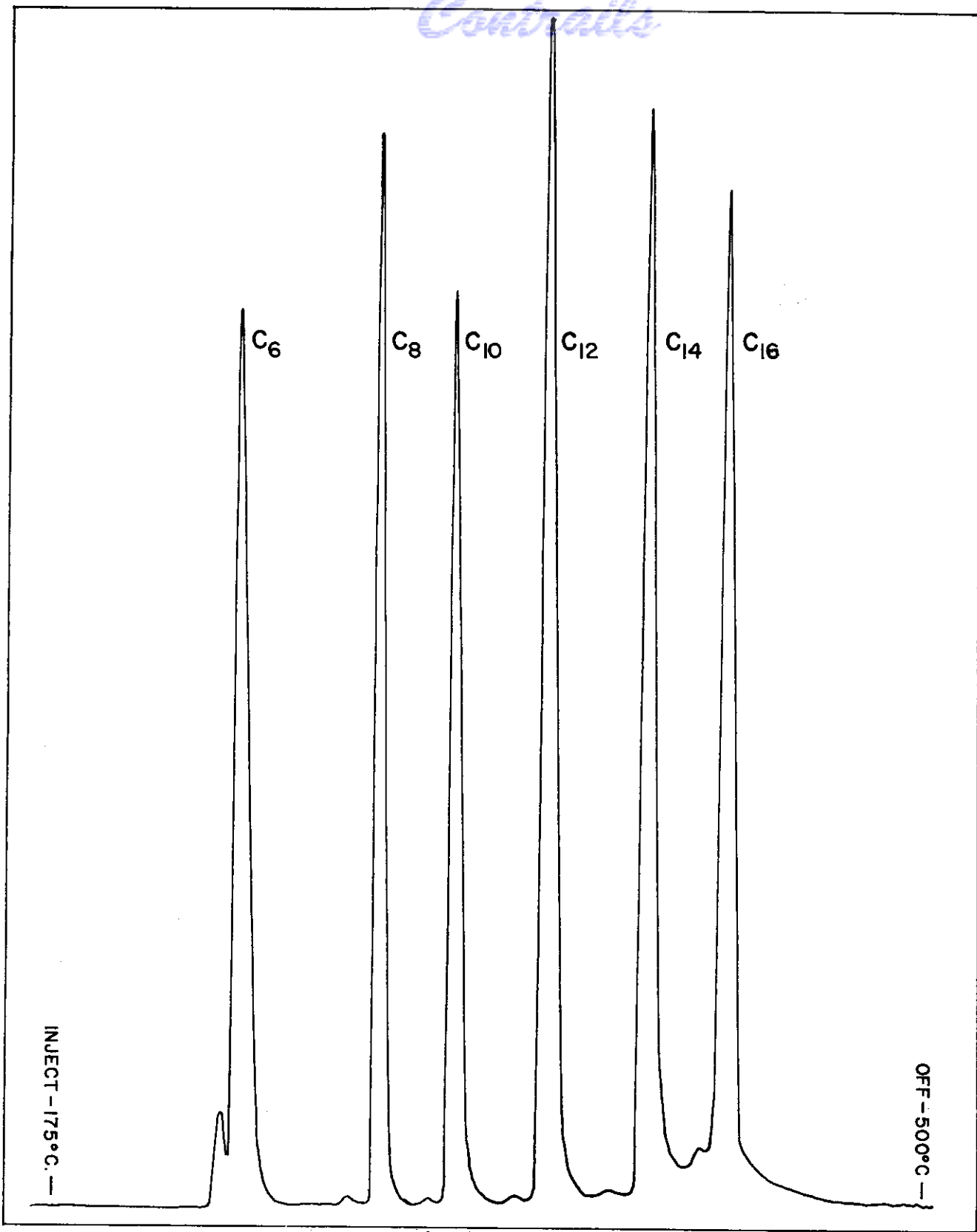


Figure 8 - Chromatogram of Hydrocarbon Mixture on Alumina

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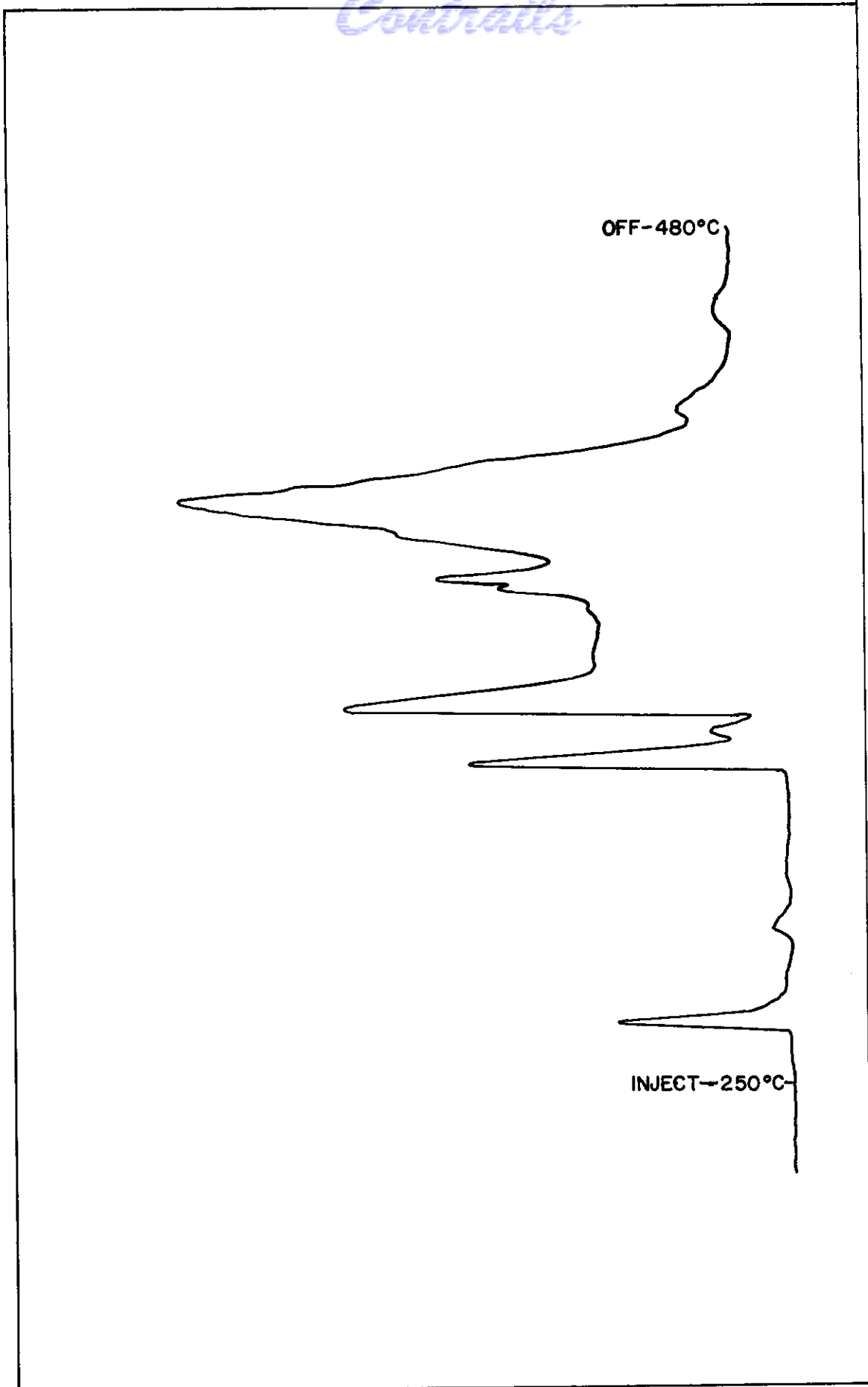


Figure 9 - Chromatogram of Zirconium Benzoylphenyl Hydroxylamine

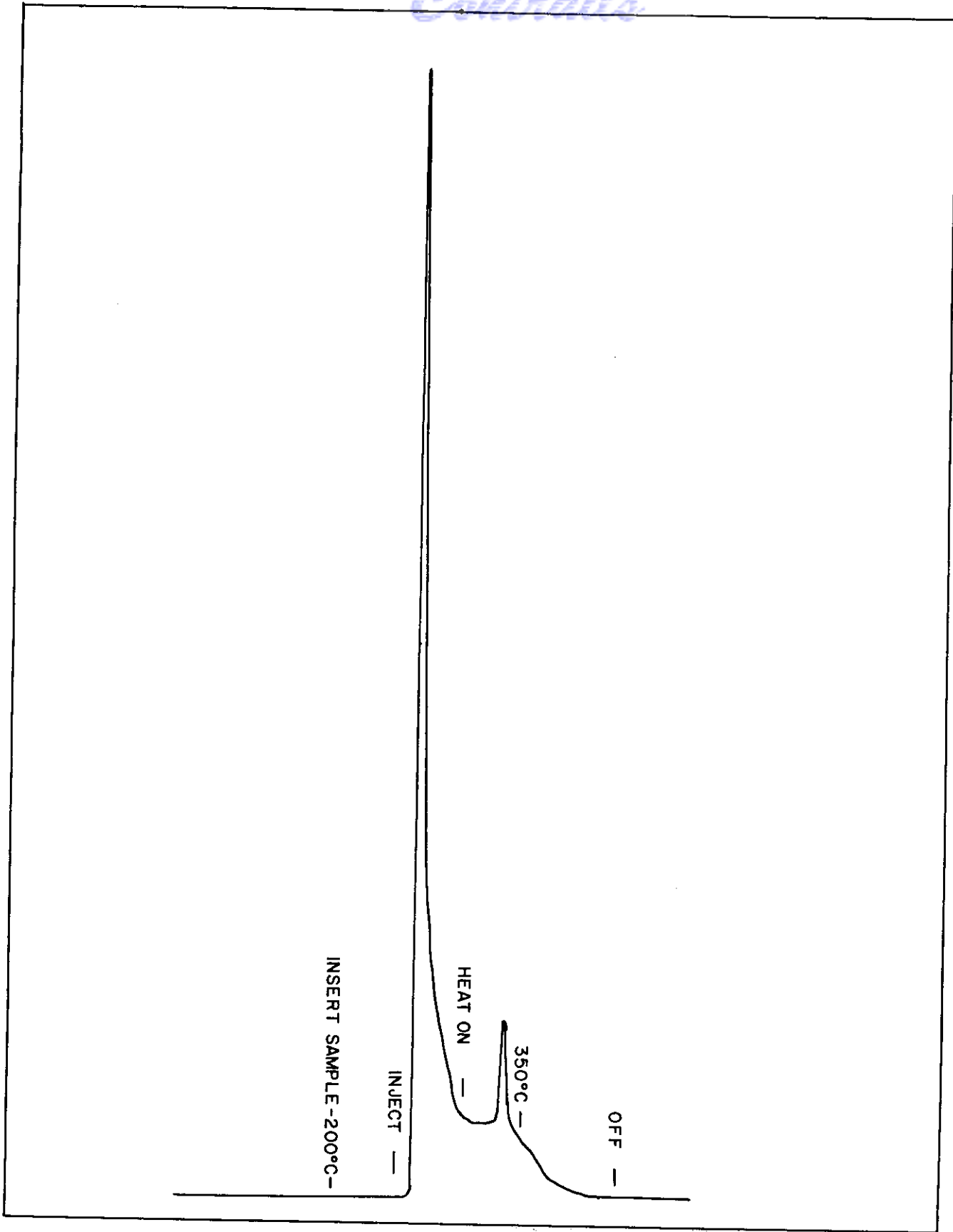


Figure 10 - Chromatogram of  $\text{SnCl}_4\text{-FeCl}_3$

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