

## **Analysis of Gases in Metals**

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## FOREWORD

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ABSTRACT

This investigation has been undertaken to determine the feasibility of using gas chromatographic techniques in the determination of nitrogen in metals. The resolution of extracted nitrogen, hydrogen, oxygen and carbon monoxide by a molecular sieve 5A chromatographic column is demonstrated. The chromatographic sensitivity is shown to be adequate for part per million determinations.

An apparatus which combines gas extraction from metallic samples, gas transfer, and chromatographic analysis is described and recommendations presented for further improvement in system operation.

The application of the basic principle for the determination of nitrogen in magnesium and ingot iron with the developed apparatus has been investigated. To date these determinations gave largely negative results; reasons for the failures are attributed to apparatus shortcomings and corrective measures are proposed.

Extension of the analytical method to inert-gas fusion extraction is discussed.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

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## I. INTRODUCTION

In recent years an ever increasing emphasis has been placed on the determination of gases in metals. This interest has arisen through discovery of the effects of the interstitial gaseous elements on the physical and mechanical properties of metals and alloys. Methods of analysis which are both rapid and accurate have been developed for the determination of oxygen and hydrogen in a variety of metal systems over wide ranges of concentration. However, existing methods for the determination of nitrogen are either insufficiently sensitive or are not amenable to the more refractory metals of current and future interest.

The present methods for the determination of nitrogen are of two general types: a) digestion-distillation, followed by titration of ammonia or colorimetry, and b) the vacuum fusion method. The limitations of the ammonia procedures are their lack of sensitivity and precision and the difficulties encountered in finding suitable acid combinations for rapid digestion of the metals and complete conversion of nitrogen to ammonia. In the vacuum fusion method, metal samples are fused in the presence of graphite and usually a molten-metal flux of iron (1), tin (2) or platinum (3) at temperatures up to 2200°C. The liberated gases are determined by pressure-volume measurements combined with chemical transformations and separations. Conventional vacuum fusion is generally useful for determining oxygen and hydrogen in the same specimen and with some metals, notably steels, also nitrogen. Even where complete extraction of nitrogen is obtained, the accuracy of vacuum fusion determinations is limited by the circumstance that nitrogen is determined as a residuum, and all systematic errors accumulate in the nitrogen result.

Conventional vacuum fusion is rapidly being supplanted by two separate techniques which permit greater flexibility and simplicity of method and equipment. Hydrogen is readily determined in most metals by hot extraction under vacuum (4). Since only hydrogen is extracted under the conditions used, manometric measurement is unambiguous, and solid samples are disposed of individually. The requirements of the vacuum apparatus are not rigorous. The by-product determination of hydrogen by the vacuum fusion method is really a function of its hot extractability.

Oxygen is accessible to the inert-gas fusion technique which modifies vacuum fusion by replacing an extensive vacuum apparatus with a simple closed system employing a sweeping inert gas (5). The extracted oxygen (as carbon monoxide) is converted to carbon dioxide and determined conductometrically or volumetrically as in carbon determination procedures. The available apparatus

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## *Conclusions*

requires little skilled maintenance and suffers very little from down time. The flexibility of these two methods for oxygen and hydrogen make them very suitable for general laboratory use where the number and types of samples for analysis may undergo wide variation; conventional vacuum fusion is most efficient when operating on a routine schedule with a uniform type of sample.

It would be desirable if a method for nitrogen were available which could utilize a separate instrument or apparatus system approaching the simplicity, speed, and flexibility to that of the inert-gas fusion method for oxygen. Furthermore, it would be of interest to establish the reasons for and to devise means to overcome the inability of conventional vacuum fusion to provide quantitative nitrogen results on refractory metals. The present investigation was undertaken to study gas chromatography and a vacuum fusion-type apparatus as a basis for an analytical method and as a means of defining the limiting parameters of vacuum fusion determinations of nitrogen. Such an approach also offers the possibility of accomplishing the determination of all three gases simultaneously.



## II. BASIS FOR THE INVESTIGATION

In the development of a method for the determination of nitrogen which can supplant existing methods, two separate steps in the process must be considered:

1. The complete extraction of all nitrogen from the sample and conversion of it to a single chemical entity.
2. The quantitative measurement of the nitrogen in its final chemical form.

The possible means of accomplishing these two steps are discussed separately.

### A. The Extraction of Nitrogen from Metals

Nitrogen is present in metallic materials principally as the nitride of one or more of the constituents. In many metals, nitrogen is also held in atomic form in solid solution in the interstices of the metal lattice. Although no separate phase exists under these conditions, the bonding forces holding the nitrogen in the lattice undoubtedly are directed metal-nitrogen bonds of a type not too different from those present in the metal nitride itself. Upon release from the metal at elevated temperature, the nitrogen present in solid solution recombines to form molecular nitrogen. Traces of other nitrogen compounds such as azides, nitrates, nitrites, amides, hydrazides, etc., may also be present, but the amounts of any of these would be exceedingly small and would arise from operations not normal to the production or fabrication of most metals. For the present consideration only nitride and soluble nitrogen need be taken into account.

The removal of nitrogen from a metallic lattice requires that the metal structure be destroyed or that the nitrogen be extracted from the lattice by thermal means alone. Destruction of the metal structure may be accomplished either by acid dissolution or by melting the solid into a mobile, structureless liquid. Acid dissolution liberates uncombined nitrogen, in which case either nitrogen-nitrogen or nitrogen-hydrogen combination occurs to produce molecular nitrogen or ammonia, respectively. An uncertainty exists as to whether all uncombined nitrogen is converted to ammonia (or ammonium salts) in the digestion reaction. Thermal liberation of nitrogen leads only to molecular nitrogen, whether nitride or uncombined nitrogen is the source. If the temperature is sufficiently high to insure decomposition, and if suitable fluxes or cooperating chemical reactions such as carbide formation are provided, all nitrogen should be released in a single chemical form. This reasoning suggests that vacuum fusion is inherently a suitable method for the determination of nitrogen, if the conditions

are sufficiently drastic to cause decomposition of the more refractory nitride compositions. The nitrides of aluminum, beryllium, titanium, zirconium, niobium, vanadium, tantalum, and the rare earths melt in the range 2000-3000°C, and it may be expected that temperatures close to or above 3000°C will be required to liberate nitrogen from these substances (1).

The attainment of a working temperature of 3000°C with a suitable container is a difficult problem. Resistance heating appears unattractive because of the bulk of the materials needed to make a crucible for operation at this temperature. An electric arc could generate the desired temperature in the electrode gap. A spectrographic procedure employing this type of extraction has been described by Fassel for the determination of gases in metals (6). An electron bombardment furnace seems attractive as the source of temperature, but the cost of such an apparatus and handling problems are severe drawbacks. Induction heating routinely achieves temperatures in the range of 2200-2500°C, and the use of a more powerful unit with close coupling and careful design to minimize heat losses could provide the temperatures believed necessary. An induction heating unit meeting these requirements is believed to be available in the instrument now used for the inert-gas fusion oxygen apparatus manufactured by the Laboratory Equipment Company, St. Joseph, Michigan--Leco Model 537 Induction Heater (5). The availability of this apparatus has made induction heating the method of choice for producing the temperatures desired, and this decision has determined the furnace configuration to be used in the investigation.

## B. Analysis of the Evolved Nitrogen

With the selection of an extraction method which will lead to the recovery of all of the nitrogen in molecular form, a method of determination can be chosen to operate on a single nitrogen species. Unfortunately, molecular nitrogen does not lend itself to analytical procedures by direct chemical means. To determine nitrogen chemically, it is necessary to convert the gas to an acidic oxide or ammonia or to absorb it with hot calcium and hydrolyze the calcium nitride to ammonia in a subsequent step. These procedures may be possible, but physical methods of determining molecular nitrogen appear to be more attractive.

If the nitrogen were the sole gas evolved, manometric measurement could be used for the determination. Since hydrogen and oxygen (as carbon monoxide) will be liberated also, separation of the gases is required. The separations employed in conventional vacuum fusion analysis leave nitrogen as a residuum, and the determination by manometric measurement is not altogether satisfactory. Emission spectroscopy, mass spectrometry and gas chromatography are capable of analyzing the gas mixtures without preliminary separation by chemical means or by selective liquefaction or freezing. Because of its inherent simplicity and

small cost of instrumentation, gas chromatography would be the preferred method of analysis of gases extracted from a metal.

## C. Feasibility of Gas-Solid Chromatography

Gas chromatography is an analytical method of recent origin, but it is one of rapid development and wide popularity because of its great utility. Essentially the method consists of permitting a carrier gas with entrained vapors to pass over a supported liquid or solid column where a succession of adsorption-desorption processes separate the various constituents of a gas mixture on the basis of their relative adsorbabilities. Detection of individual components exiting from the adsorber is usually accomplished by means of a balanced bridge containing two thermal conductivity cells. Through one cell only pure carrier gas passes on its way to entrain the unknown gas sample. Through the second cell passes the carrier gas containing small amounts of sample constituents which alter the thermal conductivity from that of the pure reference gas. Unbalance in the bridge is reflected in a voltage signal whose amplitude is proportional to the amount of the unknown constituent in the gas. Each constituent in a mixture will, under reproducible conditions of flow and cell operation, create a signal at a characteristic time after insertion into the carrier gas and with a constant sensitivity which may be calibrated for each substance. Detailed descriptions of the basic principles, instrumentation, and applications of both gas-solid and gas-liquid chromatography may be found in standard reference works (7, 8) and a review of recent developments in the field may be found in the 1960 article by Dal Nogare (9).

The applicability of gas-solid chromatography (GSC) to the separation of inert and low molecular weight gases has been established in recent years by a number of investigators. Janak (10) first demonstrated the general feasibility of the separation in 1954. Green, Moberg and Wilson (11) utilized charcoal columns and a programmed temperature rise to achieve separation of the light gases, while Szulczewsky and Higuchi (12) used columns of silica gel for the same purpose. Kyrycos and Boord (13) have shown the molecular-sieve type of column to be most effective for GSC separation of the non-polar gases at room temperature.

The so-called molecular sieves are a recent development which will continue to have a strong impact on future applications of GSC. The molecular sieves are a class of high molecular weight silicates whose structure provides a series of internal pores or channels with dimensions of molecular size. Gas molecules small enough to enter these channels undergo adsorption and chromatographic separation, while larger molecules do not enter the channels at all. Highly polar gases such as carbon dioxide, water and hydrogen sulfide are so strongly adsorbed that they eventually block the adsorption sites and must be removed by displacement under heat and vacuum (14). Molecular sieve 5A (Linde

Air Products) has channel dimensions suitable for the separation of hydrogen, oxygen, nitrogen, carbon monoxide, and the inert gases. Other molecular sieves have pore openings large enough to accommodate molecules of greater size.

There are two techniques of GSC which must be considered for application to the present investigation. These are the elution and displacement methods of operation. The more common procedure is elution, and the carrier gas usually serves as the elutriant. In displacement development, components present in very small amounts are concentrated into a narrow band by pushing them along the adsorbant before the displacing agent, since they must travel the length of the column at the same rate as the displacement component. Displaced substances usually require subsequent separation by elution, and a two column arrangement must be used. The elution method suggests itself for operation in a gases-in-metals analysis with vacuum equipment, while the displacement technique would be useful for inert-gas fusion operations where a large volume of carrier gas would be employed.

#### D. Potential Utility of the Proposed Method

The selection of vacuum extraction and gas chromatographic determination of nitrogen in metals is not a limiting decision. The happenstance that the method which has initial appeal closely resembles conventional vacuum fusion in the extraction procedure permits a development effort along a line which is in part proven and familiar at least insofar as the behavior of oxygen and hydrogen are concerned. Successful recovery of nitrogen at higher temperatures than those used in conventional vacuum fusion analysis, or the development of a suitable flux or bath system for nitrogen recovery, will permit increased utilization of existing apparatus and procedures. Furthermore, if the chromatographic method of determination proves to be adequate, it will be possible to modify existing vacuum fusion apparatus so as to employ this means of analysis of extracted gases.

With the availability of several techniques of gas chromatography, it should be possible to modify an extraction procedure so as to operate an inert-gas fusion method solely for nitrogen. The last process would then accomplish the desired result of providing a simple apparatus and method for the last gas of the hydrogen-oxygen-nitrogen triad. An eventual possibility is an inert-gas fusion method applicable to the simultaneous determination of all three gases.

#### E. Specific Problems Investigated

An overall method has been described for the determination of nitrogen in metals. The method involves apparatus and an approach which requires study of

# Contrails

several portions of the system separately. The specific problems resulting from this necessary fragmentation of the investigation are the following:

1. The quantitative extraction of nitrogen from the metals.

This is the major question of the total investigation. In terms of the system proposed, it relates to the construction and operation of the fusion portion of the apparatus, the temperature of operation, the choice of vacuum or inert-gas operation, and the nature of the bath or flux to be employed. Being the ultimate limitation on the proposed method, completeness of extraction will be the last question to be resolved.

2. Transfer of the liberated gases.

The gases liberated by the extraction unit must be transferred by means of an intermediate handling system into the chromatograph. For vacuum operation the transfer must be made with pumps and a collecting reservoir so that a known fraction of the total gas volume is ultimately introduced into the GSC column. For inert-gas fusion, a transfer system would be supplanted by a preliminary gas adsorber and displacement system.

3. Chromatographic determination of nitrogen and other gases.

The chromatographic portion of the proposed apparatus may be constructed and its performance evaluated separately to determine the GSC conditions needed to resolve hydrogen, oxygen, nitrogen and carbon monoxide. Calibration of chromatograph response for each gas may be accomplished external to the full apparatus. Modifications of conventional equipment are required to permit introduction of gas into an evacuated sample loop. These, too, may be evaluated separately from the completed unit.

4. Preparation of samples of known nitrogen content.

In the absence of standard samples, materials of approximately known nitrogen content must be prepared in a Sievert's-type apparatus. Uncertainties in the gas content of metal starting materials limit the degree to which the nitrogen content of specimens will be known. The problem of inhomogeneity may be avoided by preparing individual samples which will be used in toto rather than subdivided.

The development of a sample preparation system has proceeded concurrently with the study of the chromatography, but the remainder of the investigation has been performed generally in inverse order to the listing of the foregoing problems.

## III. SYSTEM DEVELOPMENT

### A. Sample Preparation Apparatus

An apparatus has been constructed for the preparation of individual samples of known added amounts of nitrogen, oxygen, or hydrogen. A diagram of the unit is shown in Figure 1 and a photograph in Figure 2. The apparatus description may be followed readily from the drawing. The apparatus consists of four sections:

#### 1. Purifying system for nitrogen, oxygen and hydrogen.

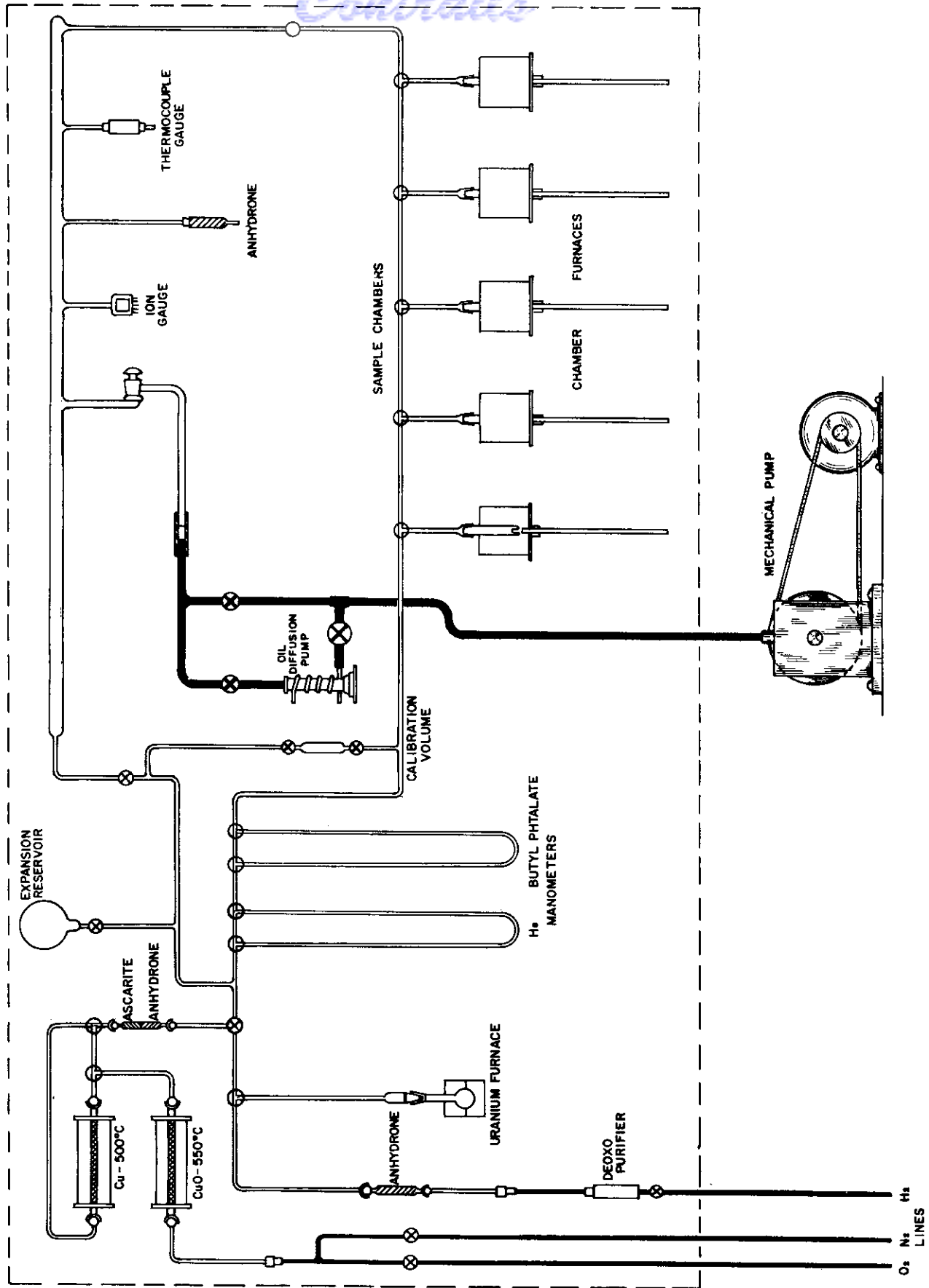
Three separate supply lines from cylinders to the apparatus are each valved on the rack at the far left. The nitrogen and oxygen lines converge above the valves and pass through a CuO (black wire) furnace for removal of hydrocarbons. A stopcock arrangement permits diverting the nitrogen stream through a Cu-turnings furnace to remove oxygen. Exit gases pass through an Ascarite-Anhydrone trap to eliminate carbon dioxide and water, and they then enter the manometer unit.

Hydrogen is purified in a separate stream through a Deoxo catalytic unit to remove oxygen by conversion to water. The water is absorbed in an Anhydrone trap. A uranium furnace absorbs hydrogen and nitrogen at about 200°C in a batch operation. Heating to a higher temperature releases the hydrogen first to a reservoir and then to the manometer unit. The uranium nitride does not decompose at the temperature employed.

#### 2. Manometer unit for measurement of system pressure.

Both mercury and butyl phthalate manometers have been incorporated in the system for measurement of pressure in the sample units and in the purification trains. The mercury manometer also serves to monitor early stages of system evacuation, when the pressure is too high for thermocouple or ion gage measurement. The butyl phthalate manometer provides approximately 10 times the pressure sensitivity of the mercury manometer, and it is used exclusively to measure the change in system pressure on gas absorption.

A calibrated volume has been incorporated in the manometer unit to permit calibration of the volumes of the various sections of the apparatus.



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Figure 1. Sample Preparation System

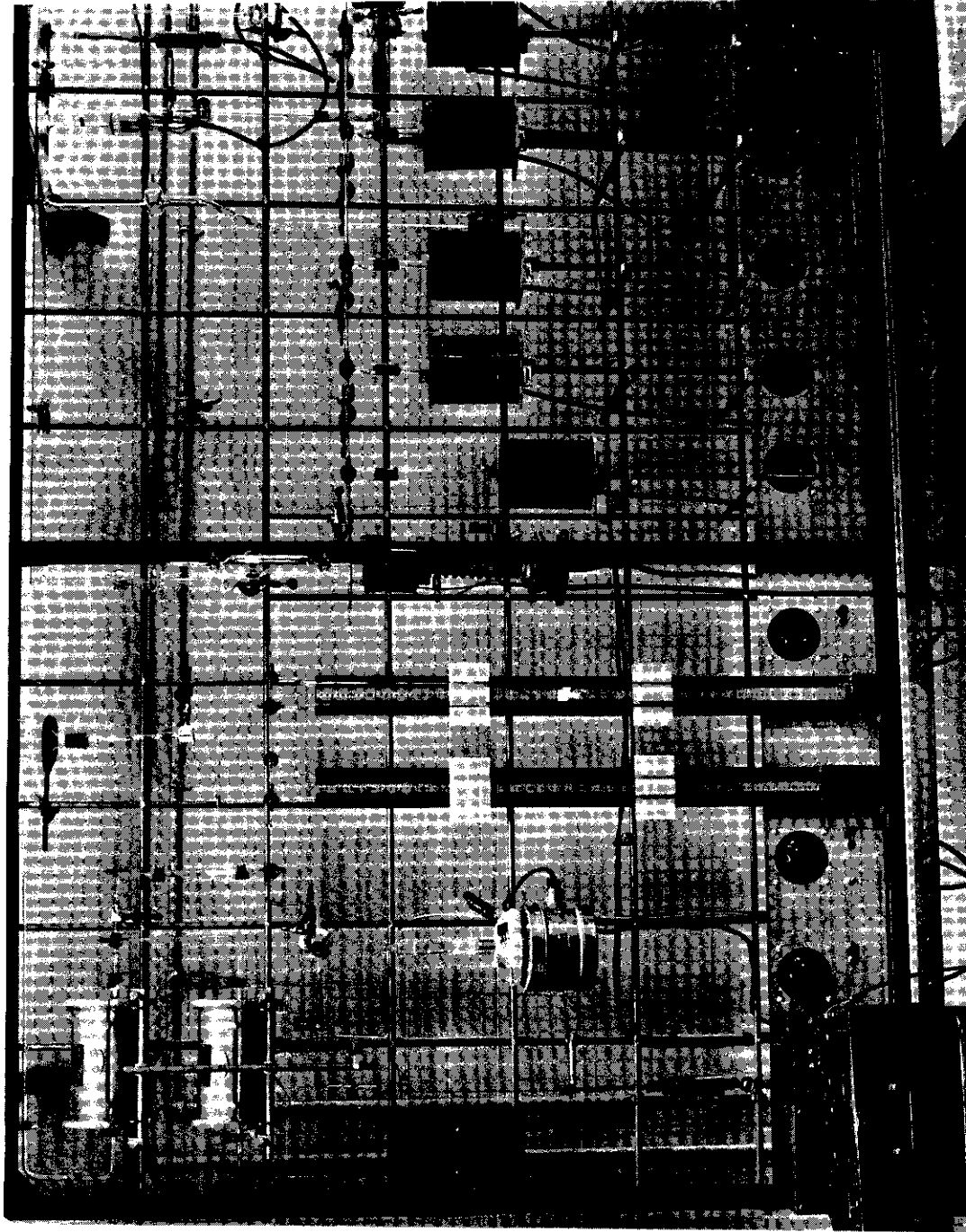


Figure 2. Sample Preparation System



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## 3. Sample preparation chambers.

Five quartz chambers, shown in Figure 3, have been assembled and enclosed with movable furnaces. Individual specimens are introduced into these chambers for gas loading. The chambers are sealed with Apiezon W wax for gas-tight connection to 3-way, T-shaped stopcocks which permit isolation of each chamber or connection separately to the manometer unit.

Chamber furnaces are wound with 20 ga. nichrome V wire on alundum cores. Fibrefrax insulation between the core and the container's metal walls, floor and lid prevents drastic heat loss to the atmosphere. Test temperatures of 1025°C have been obtained with an electrical input of 400 watts. The furnaces are mounted with spring clamps to slide on 1/2-inch stainless steel rods. Thermocouples are fastened to the rods and rise one inch above the rod ends into wells in the hot zone of each quartz chamber. The furnaces are raised to a height such that the upper three inches of the chambers are outside of the furnace. The samples rest at the top of the thermocouple well, one inch from the bottom of the chamber, in the hottest zone of the furnace. The temperature at the wax-sealed joint is maintained below the softening point of the wax by air streams from small blowers installed at each end of the row of furnaces.

## 4. Vacuum unit.

The vacuum unit consists of a Welch Model 1405 mechanical pump backing up a Consolidated MCF-60 oil diffusion pump. The other units are connected to the vacuum line through a glass manifold and 3/4-inch glass and vacuum tubing. Stopcocks isolate the vacuum line and manifold from the other units, and 3/4-inch vacuum valves isolate the oil diffusion pump from the mechanical pump. An air-bleed line is on the manifold, and an Anhydrone trap ensures only dry air being admitted to the system.

A National Research Corporation ion gauge and thermocouple vacuum gauge on the manifold permit measurement of high vacuum in the system. A National Research Corporation Model 710 Meter is used with the above gauges.

All furnaces are separately switched and are controlled individually by Variacs. All thermocouples have been brought to a central station for easy reading with a Rubicon potentiometer. A telephone jack is used to switch from point to point. A central power station has been provided for the apparatus, and all electrical circuits have been drawn from this circuit breaker panel.

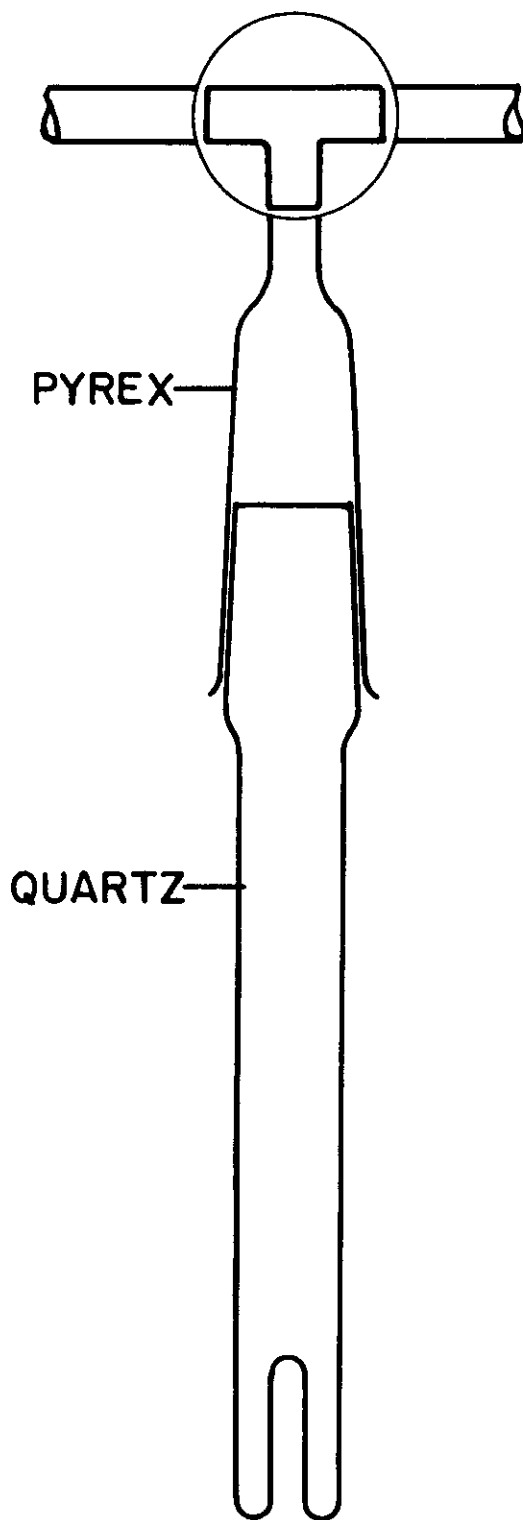


Figure 3. Quartz Sample Chamber

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Calibration of the sample preparation apparatus has been accomplished by expansion of air from the calibration volume into the butyl phthalate manometer and the sample chambers. Repeated measurements were made until a satisfactory degree of precision was obtained. All expanded volumes have been corrected for displacement of the liquid level in the 3 mm. bore of the butyl phthalate manometer. This volume correction is termed  $V_c$  and is equal to 0.00706 ml./mm displacement from the zero differential level.

The final volume calibrations are shown in Table I. Standard deviations for additive volumes have been obtained from

$$\left( \sum_{i=1}^n \sigma_i^2 \right)^{\frac{1}{2}}$$

TABLE I

Calibration of Furnace Volumes

<u>Furnace</u>	<u>Chamber Volume (Ml.)</u>	<u>Expanded Volume (Ml.)</u>
1	27.83 ± .13	45.81 + $V_c$ ± .19
2	26.77 ± .05	47.81 + $V_c$ ± .15
3	28.34 ± .07	52.81 + $V_c$ ± .17
4	29.29 ± .01	58.04 + $V_c$ ± .18
5	27.87 ± .05	60.05 + $V_c$ ± .19

Testing of the apparatus under vacuum has shown that a system pressure of 1 micron or less may be held in the manifold, sample chambers, and butyl phthalate manometer for at least one week at 600°C furnace temperatures. The gas purifying section of the system does not hold a good vacuum for long periods, but this portion of the system is isolated except when purified gas is being introduced into the manifold for delivery to the furnace chambers at 10 to 50 mm. Hg.

## B. Chromatographic System

The design and construction of the present chromatographic unit has been based on the desire to provide a relatively simple system from commercially available apparatus or components. The provision of adequate gas flow rate and column temperature control is most important, and the Beckman GC-1 apparatus was selected as the least expensive model meeting this requirement. The GC-1 is normally supplied with a vacuum-tight slide valve which introduces two sample loops alternately into the carrier gas stream. The Beckman instrument employs

# Contrails

a standard thermal conductivity detector cell whose output is a voltage signal which operates a 0 to 1 millivolt Brown recorder. This basic system was considered ideal for preliminary evaluation of the proposed method, though it was recognized that eventually the apparatus would have to be cannibalized to obtain a more efficient packaging and possibly to substitute components better suited to a finished instrument.

The GC-1 was modified immediately to permit operation in conjunction with a vacuum system. These modifications may be understood by referring to Figure 4, which is a schematic flow diagram of the GC-1 as purchased. The slide valve has a total of six openings. Two of these are on the back face of the valve for slide connection to the sample loops. The other four, running clockwise from the lower right, are the sampling-valve inlet line, the chromatographic column line, the sample loop exhaust line and the carrier gas inlet line. Points of modification are shown in Figure 4 by broken lines. The sampling valve was disconnected from its inlet line and removed. A capillary tube connection was attached instead and brought straight out through the side of the instrument cabinet to connect the chromatograph to the rest of the apparatus by the shortest possible gas path. Both sample loop evacuation and sample introduction were accomplished through this line. The exhaust line was cut off close to the slide valve and sealed with a tapered brass plug. The seal was made vacuum tight and the void between the plug and the face of the slide valve was filled with Apiezon putty Q. By this means the sample loop was sealed off at the slide valve, and an essentially zero volume of lost sample space was assured. The standard 1 ml. sample loops were replaced by 10 ml. Beckman loops so that a large fraction of the gas was transferred to the chromatograph.

The volumes of the sample loops and connecting tubing and the sensitivity of the chromatograph to various gases were calibrated by an external system similar to that shown in Figure 5. Expansion of pure gases from the standard volume provided data for calculating the volume of the sample loops. With known volumes of gas at various pressures, the number of micrograms of gas introduced into the chromatograph could be calculated from the Perfect Gas Laws. Calibration data for  $N_2$ ,  $H_2$ ,  $O_2$ , and  $CO$  are shown in Figures 6 through 9 as plots of peak area versus both gas pressure and micrograms of gas. For these data the original 1 ml. sample loops were used. Composite curves are presented in Figure 10 for calibrations using peak height as the variable, but the sensitivity and linearity are not as good as they are when peak area is used for calibration.

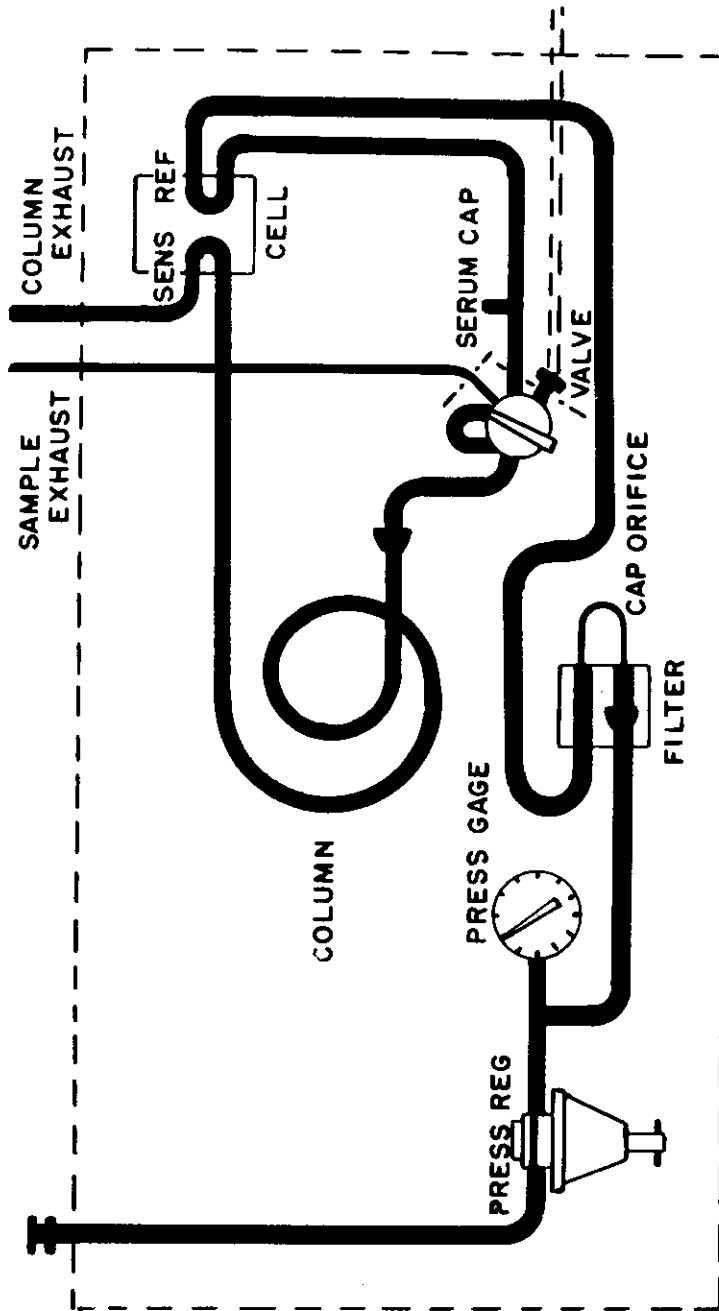


Figure 4. Flow Diagram of GC-1 Chromatograph

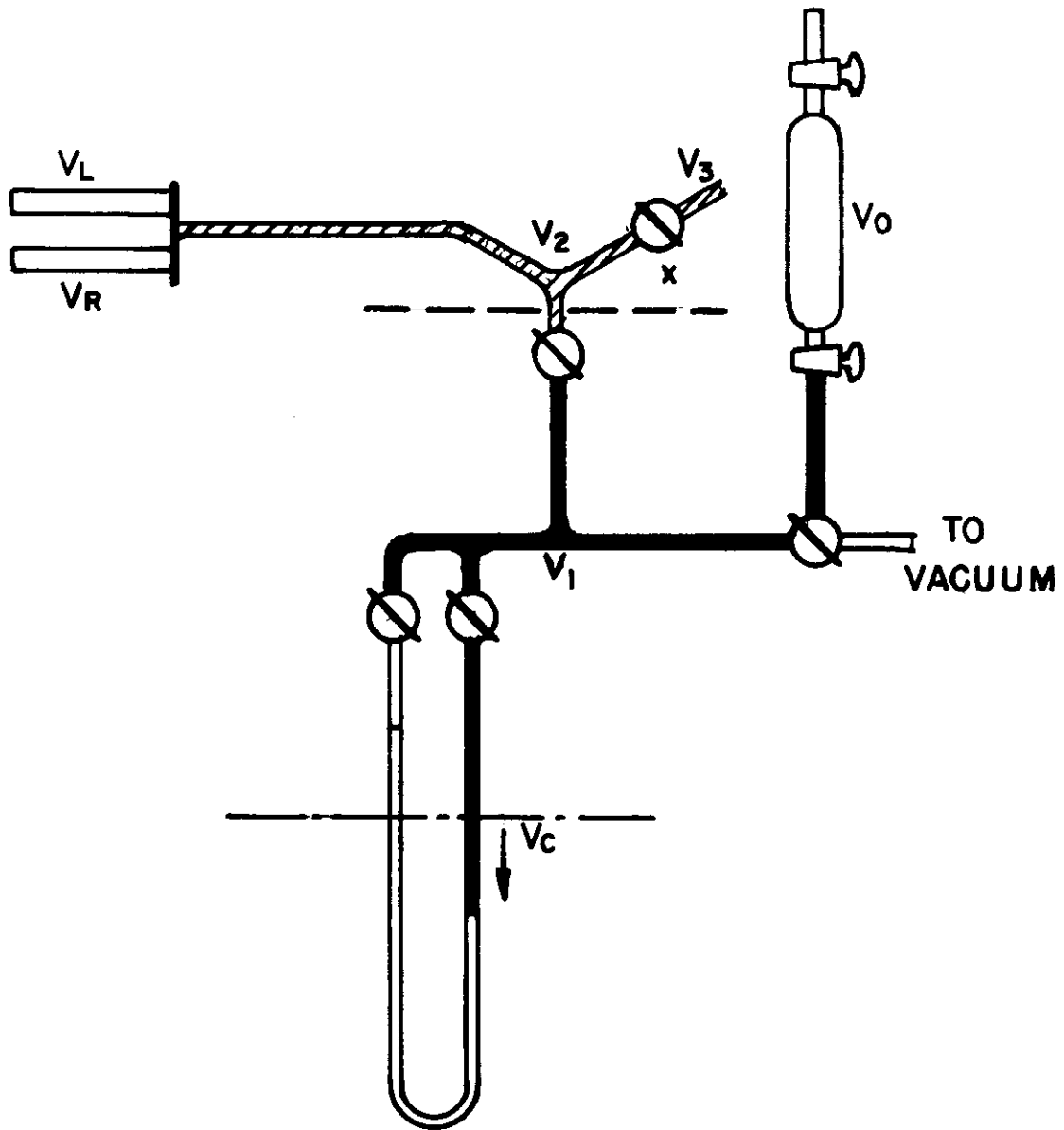


Figure 5. Volume Calibration Arrangement

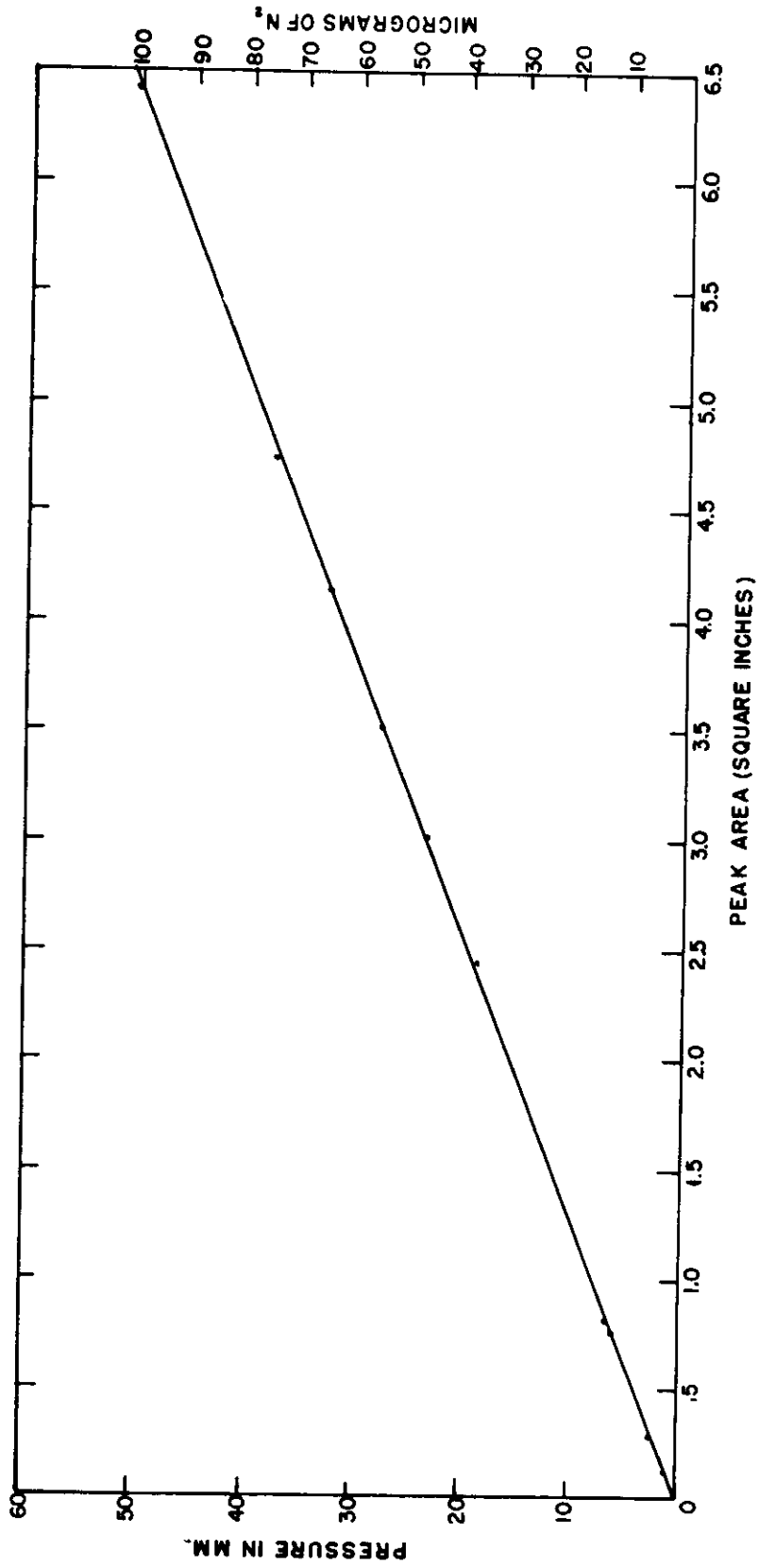


Figure 6. Nitrogen Calibration

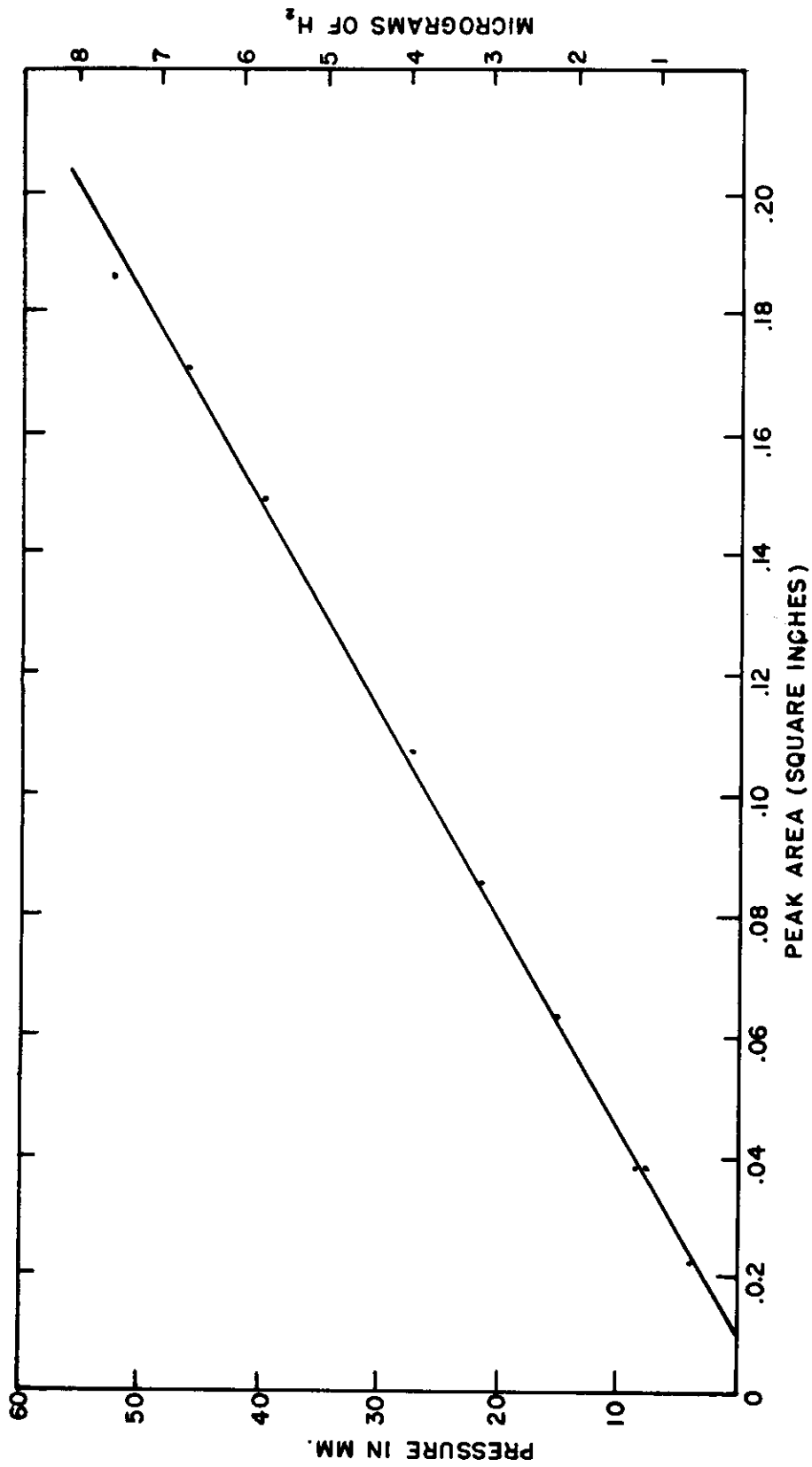


Figure 7. Oxygen Calibration



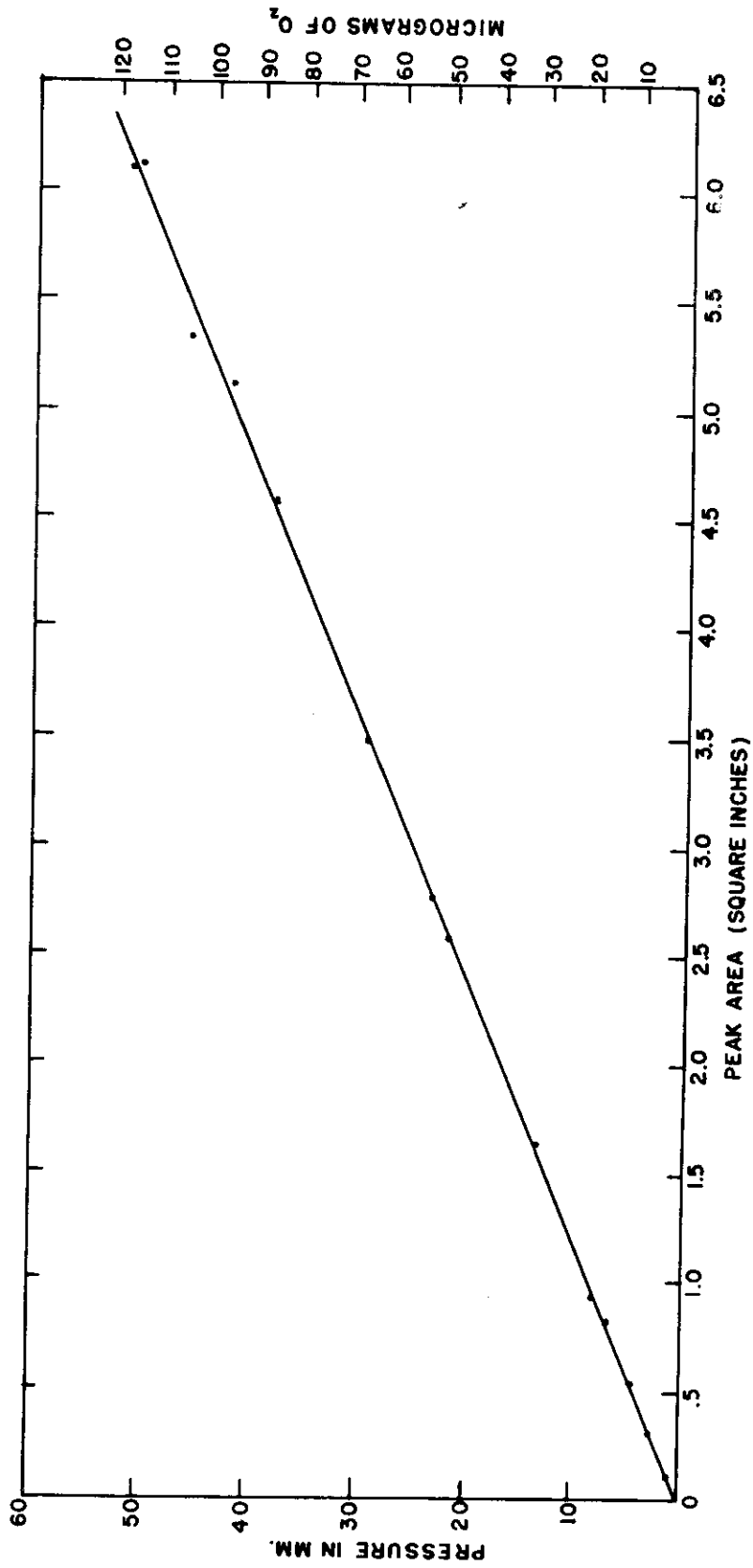


Figure 8. Hydrogen Calibration

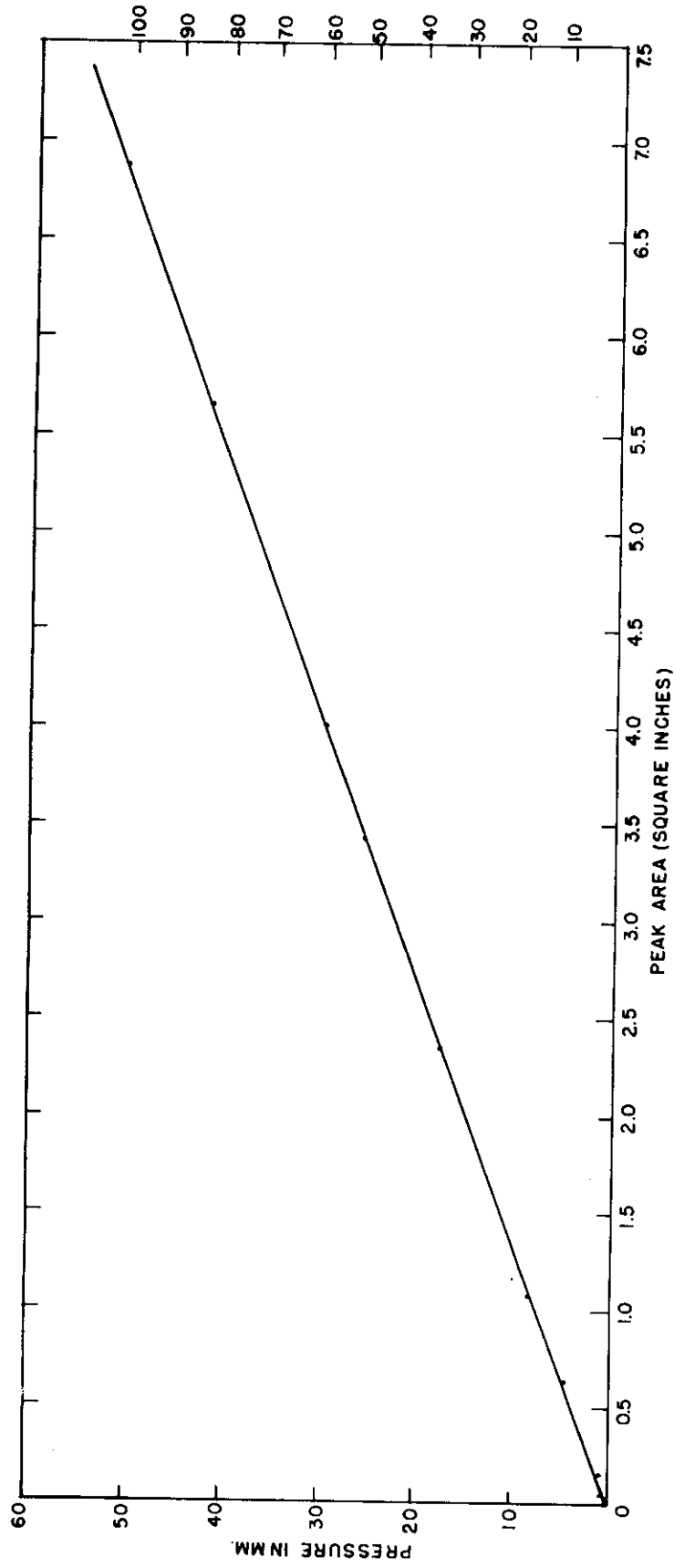


Figure 9. Carbon Monoxide Calibration

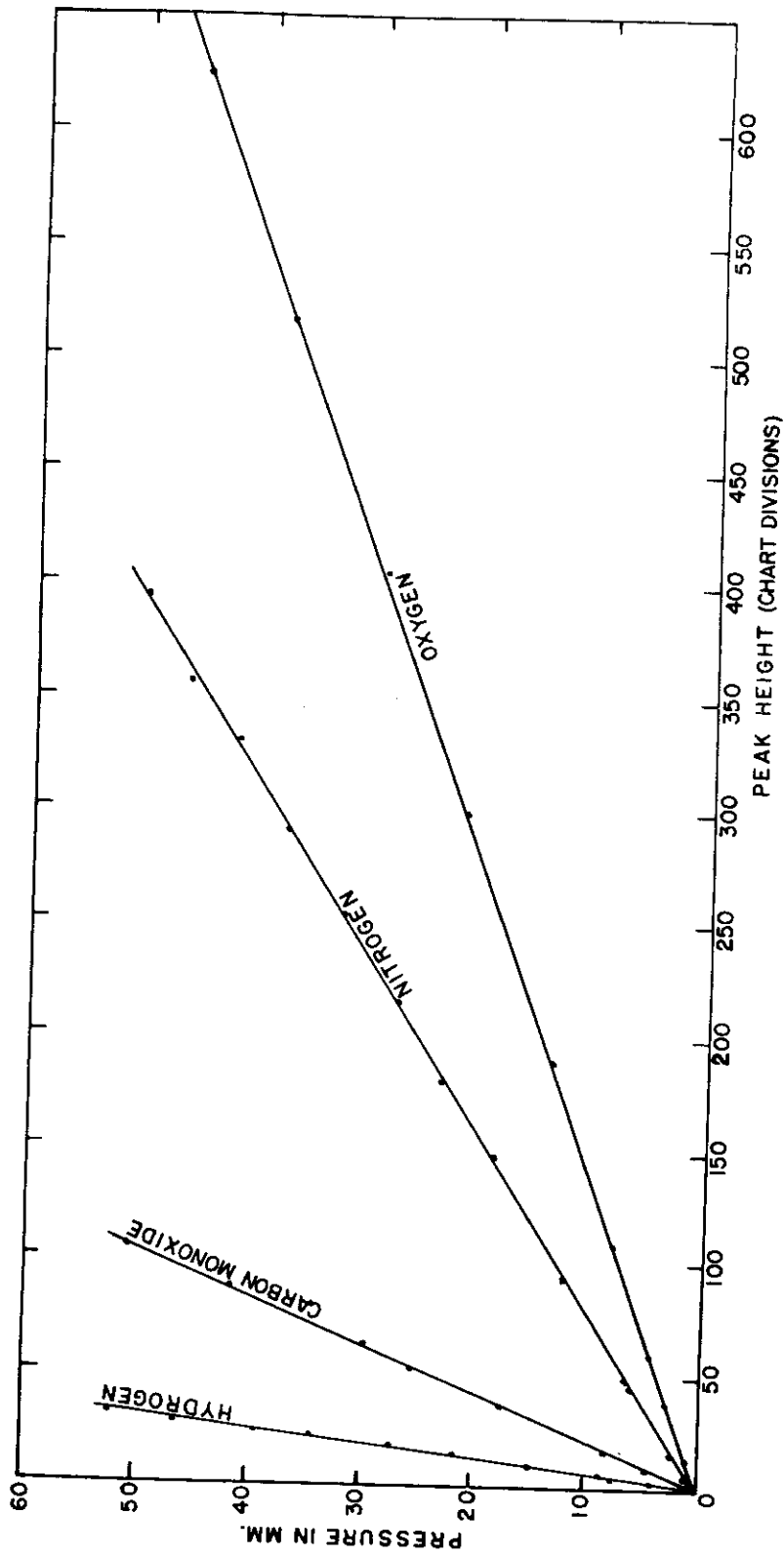


Figure 10. Peak Height Calibrations

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Operating conditions for the chromatographic determination of nitrogen and the other gases were selected after a few preliminary trials as follows:

Carrier Gas ----- He  
Pressure ----- 20 psig.  
Temperature ----- 40°C  
Filament Current ----- 350 mamp.

The conditions selected resolved the gases into peaks at the following intervals after turning the sample loop into the carrier gas stream:

hydrogen ----- 1 minute  
oxygen ----- 2 minutes  
nitrogen ----- 4 minutes  
methane ----- 6 minutes  
carbon monoxide ----- 14 minutes

A typical chromatogram containing these gases is shown in Figure 11.

The relatively high filament current was chosen to obtain the highest sensitivity compatible with reasonable filament life. Higher sensitivities could be obtained if a different detector were employed, but other system limitations eliminate the need for greater sensitivity in the present work.

The introduction of the sample into the carrier stream as essentially 10 ml. of vacuum creates a strong negative pulse in the output of the detector. This may be seen in Figure 11. At the flow rate determined by a pressure of 20 psig., this pulse returns to a normal base line immediately prior to the hydrogen peak. Higher carrier gas pressures result in an overlap of the negative pulse and the hydrogen peak, although the other peaks are still resolved and a shorter analysis period is achieved. Lower pressures draw out the peaks, and the appearance of CO is delayed to still later times. This increases analysis time unduly.

Calibrations for the several gases of concern are presented in Table II. All of these are linear functions of the amount of gas present, but the hydrogen data produce a straight line which does not go through the origin. The linearity of the oxygen and nitrogen calibrations was checked at high concentrations by

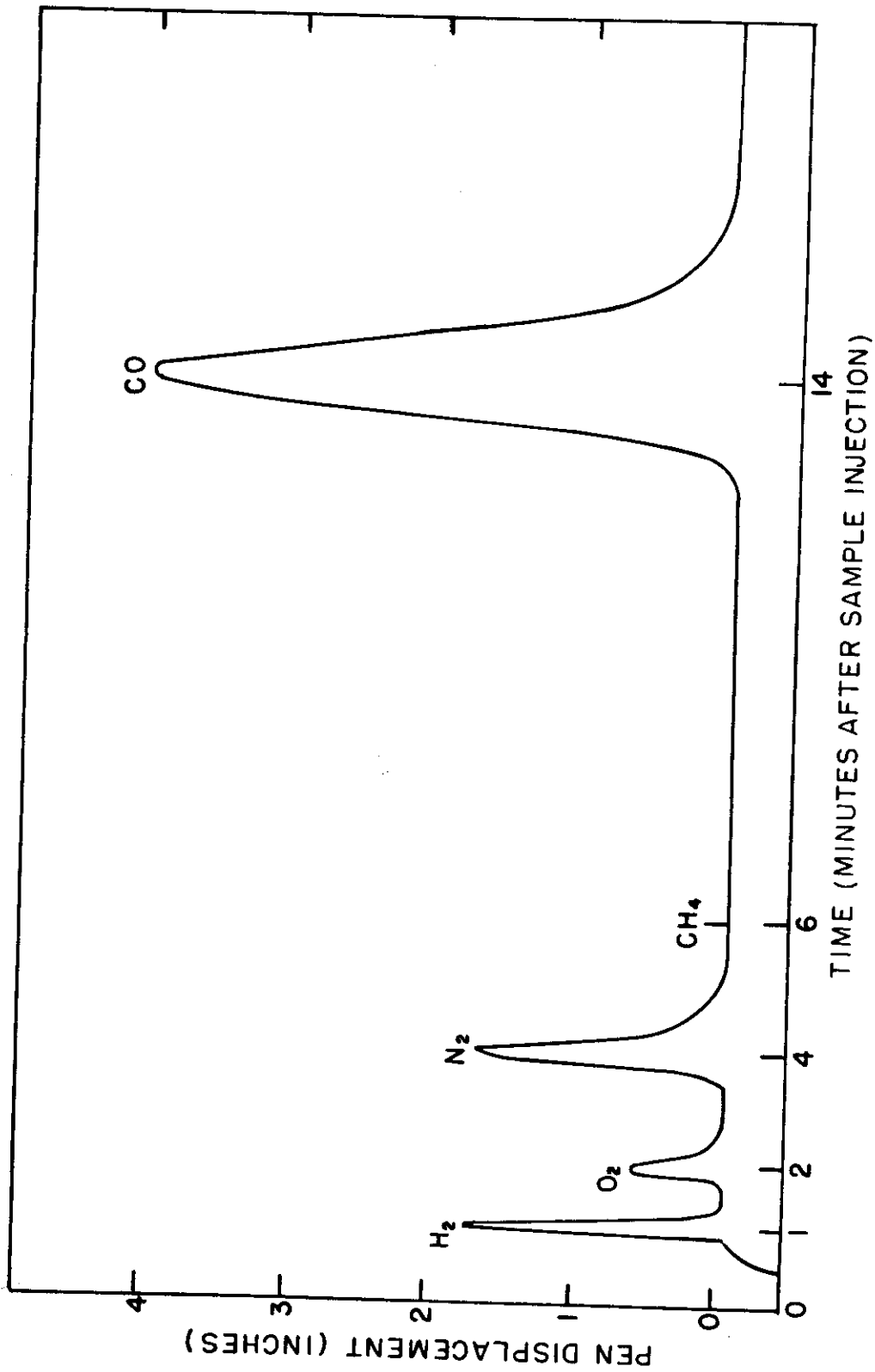


Figure 11. Typical Chromatogram for 30 Minute Furnace Blank at 1900°C,  
Recorded at Maximum Sensitivity

means of dry air at various pressures. From the results shown in Figure 12, the linearity of calibration is assumed to hold up to one atmosphere.

TABLE II

Calibration of GC-1 Sensitivity

<u>Gas</u>	<u>gamma/in.<sup>2</sup> of Peak Area</u>
H <sub>2</sub>	41.36 (less 0.01 in. <sup>2</sup> )
O <sub>2</sub>	15.92
N <sub>2</sub>	13.29
CO	14.93
CO as O <sub>2</sub>	8.52

C. Intermediate Gas-Handling System

Preliminary operation of the chromatograph demonstrated the feasibility of introducing a gas sample to an evacuated sample loop. This permitted the selection of a gas-handling system which would unite vacuum operation of a furnace with gas transfer to the chromatograph.

The gas-handling system must provide evacuation of the furnace and its transfer lines, of the chromatograph and its transfer line, and of the device on the furnace assembly for addition of samples. It must also permit rapid transfer of evolved gases from the reaction furnace into a collecting unit from which these gases may be transferred as a total sample into the chromatograph.

The system finally evolved is shown schematically in Figure 13 along with the furnace and sample loader. Gases are removed from the furnace by a 2-stage Delmar mercury diffusion pump. On system pump-down, the large manifold stopcock is opened, and gases are exhausted through the Welch 1405 mechanical pump. The oil diffusion pump shown in the figure was found to be unnecessary, and it was eliminated from the apparatus. Pressures of about 1 micron were obtainable with this system. On the furnace side of the mercury diffusion pump, the pressures are estimated at about 0.1 micron.

For the collection of evolved gases, the large stopcock was closed, and a Delmar-Urry automatic Toepler pump was used to transfer gases through a Y-stopcock into a mercury-well collection volume of about 200 ml. capacity.

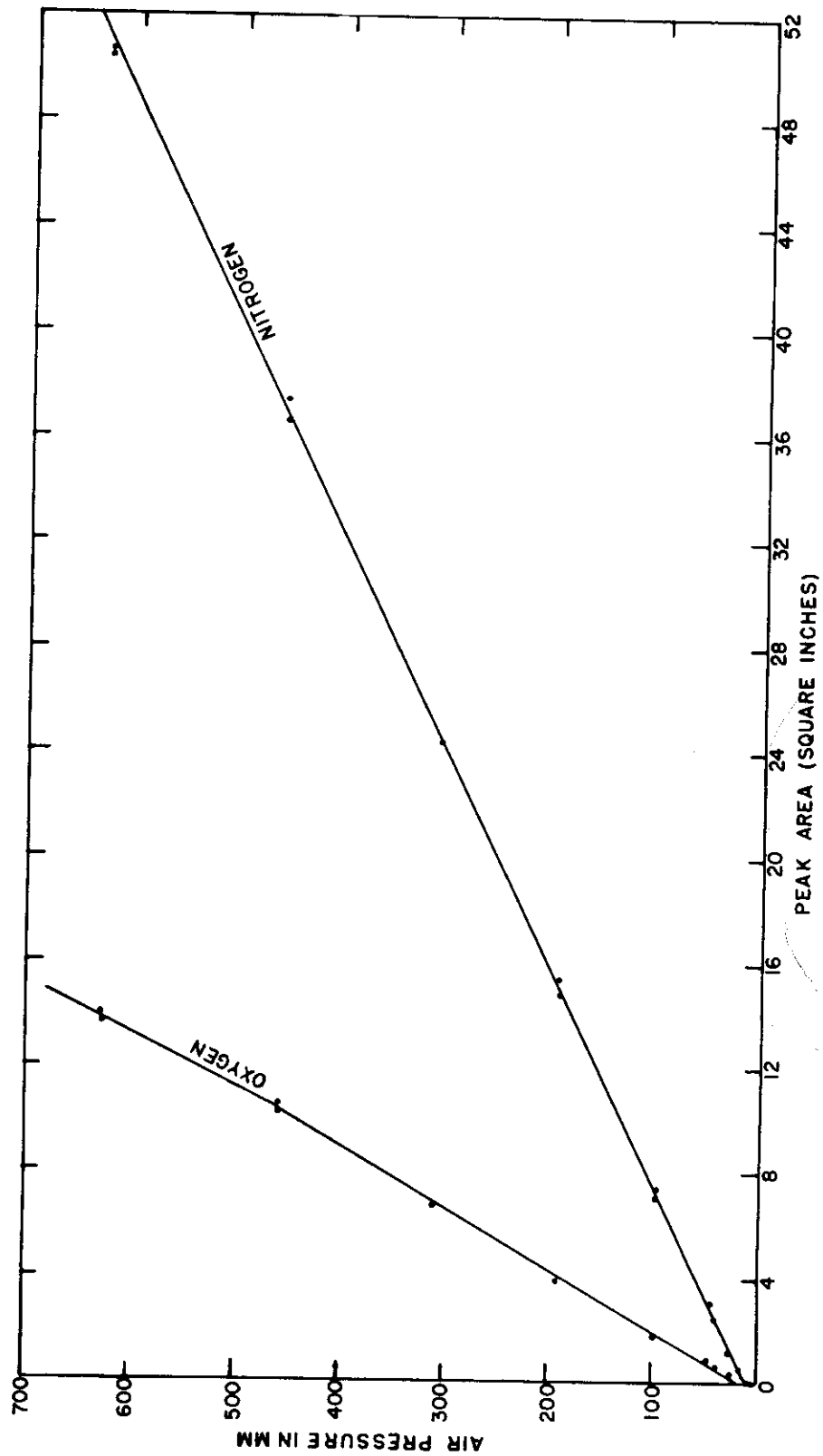


Figure 12. Calibration With Air

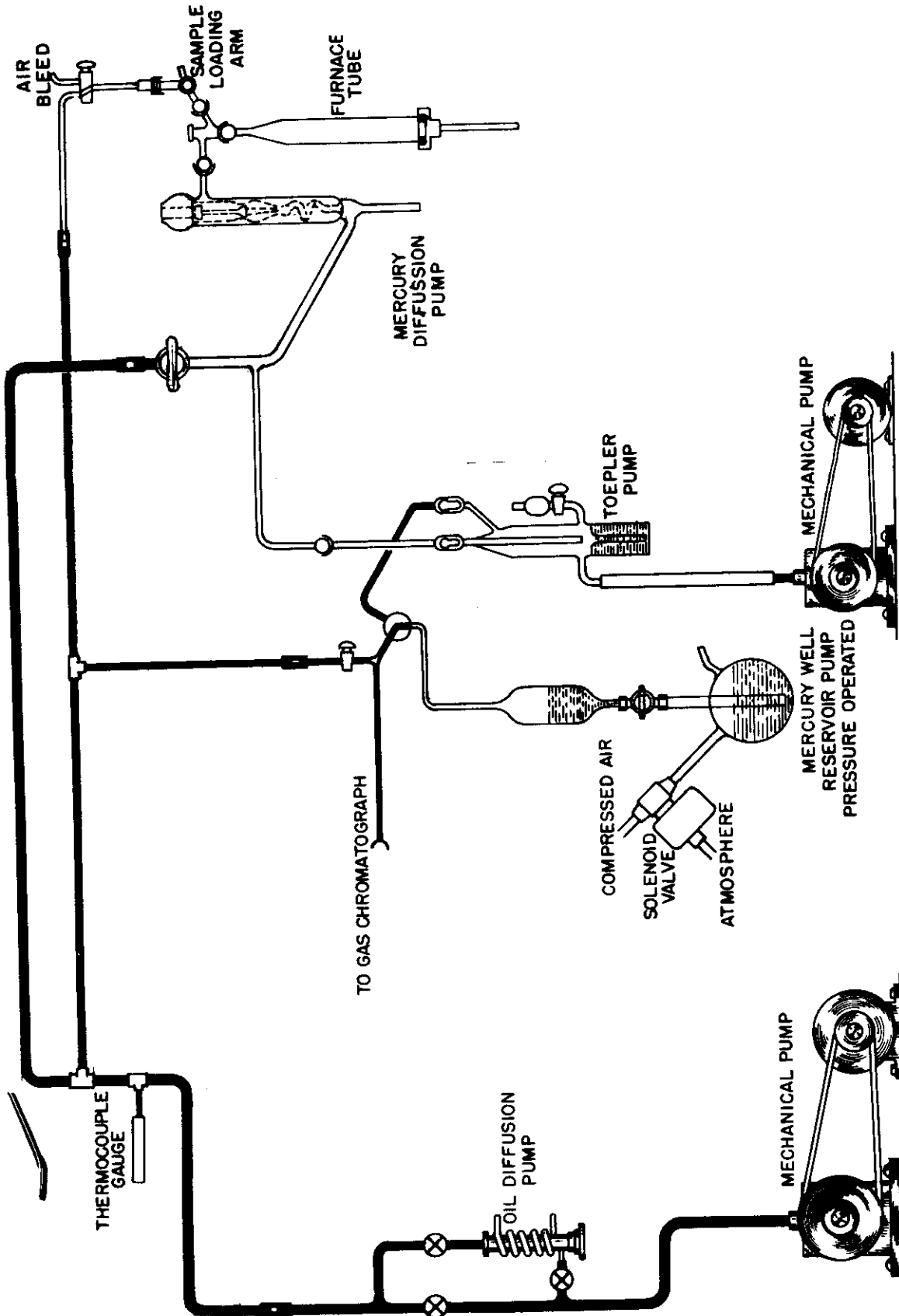


Figure 13. Intermediate Gas-Handling System



# Contrails

The Toepler pump operated on a 30 second cycle, driven alternately by a Welch 1400 mechanical vacuum pump and by an atmospheric bleed. Transfer of gases into the chromatograph loop was achieved by rotating the Y-stopcock and raising the mercury level in the collection volume to the stopcock. Proper manipulation of several stopcocks permits evacuation of the mercury well, the chromatograph loop, and the exit side of the Toepler pump through the small manifold line shown over the mercury well. The main chamber of the Toepler pump is evacuated through the large stopcock on the input side and the main manifold.

Two methods of transferring gas samples from the mercury well to the chromatograph were tried. Initially the mercury was raised and lowered manually with a large reservoir connected by Tygon and heavy rubber tubing. This system proved to be inadequate when the collection volume was evacuated. The replacement device consisted of a pressure-driven mercury reservoir working on about 10 psig. of compressed air to raise the mercury to the Y-stopcock. When the reservoir was opened to atmosphere, the mercury fell to a level below the collection volume in the mercury well. A stainless steel needle valve was placed in the heavy-walled glass line between the lower mercury reservoir and the sample collection volume. Normal atmospheric pressure maintained the mercury level above the height of the valve. The needle valve controlled the rate of mercury rise and fall and gave fine control for adjusting the final position of the mercury in the Y-stopcock. The final sample volume was divided between the sample loop of the chromatograph, the transfer line, and some small part of the collection volume.

When the apparatus was operated on a sample, the gas pumped into the collection well by the Toepler was raised into the chromatograph loop, and the Y-stopcock was then turned so that the collection volume was again connected to the Toepler. A second expansion and transfer cycle was then performed to reduce the fraction of the total gas left in the Toepler exit line to a negligible amount.

The transfer system was operated by a solenoid valve actuated by a toggle switch. In the normally closed position, atmosphere was connected to the mercury reservoir. Closing of the circuit connected the reservoir to the compressed air line. This method of transferring gas has been borrowed from the Titanium Metals Corporation of America laboratory at Henderson, Nevada, where a similar device is used to drive a McLeod gauge in an oxygen-determining apparatus.

The fraction of sample reaching the chromatographic detector was determined by calibration of the volumes of the various sections of the transfer system.

# Contrails

The method of calibration is seen from Figure 5, (page 16). The calibration apparatus (a standard volume gas collection bottle and a butyl phthalate-filled differential manometer) is attached where copper tubing from the vacuum manifold connects to the chromatograph line at the stopcock. The pertinent volumes indicated in the figure are:

- $V_0$  , the volume of the gas bottle.
- $V_1$  , the expansion volume outside the stopcock.
- $V_2$  , the dead volume between the Y-stopcock, the chromatograph slide valve, and the manifold stopcock.
- $V_3$  , the dead volume between the Toepler exit valve and the Y-stopcock.
- $V_L$  , the volume of the sample loop with the slide valve indicator to the left.
- $V_R$  , the volume of the sample loop with the slide valve indicator to the right.
- $V_C$  , the volume of the manometer tubing created by displacement of the manometer liquid.

By expansion of gas from known pressure in  $V_0$ ,  $V_1$  has been determined. Expansion of  $V_0$  into  $V_1 + V_2$  gives the sum of these volumes;  $V_2$  is obtained by difference.  $V_L$ ,  $V_R$  and  $V_3$  are obtained similarly. Expansions are done in replicate until an average figure is obtained with the desired precision.

The most recent calibrations are summarized in Table III.

TABLE III

Calibration of Transfer System Volumes

$$V_2 = 2.71 \pm 0.175 \text{ ml.}$$

$$V_3 = 8.98 \pm 0.15 \text{ ml.}$$

$$V_L = 10.13 \pm 0.02 \text{ ml.}$$

$$V_R = 10.13 \pm 0.17 \text{ ml.}$$

# Contrails

The fraction of sample transferred from the collection volume into the chromatograph column is equal to

$$\frac{10.13}{10.13 + 2.71} \times 100 = 78.9\%$$

If the reservoir volume (not actually measured) is assumed conservatively to be 150 ml., the fraction of sample not transferred by the Toepler pump into the reservoir for each transfer cycle is as follows:

<u>No. Transfers</u>	<u>Percent Lost</u>
1	6
2	0.36
3	0.02

Two transfers with the reservoir will leave essentially none of the gas between the Toepler pump exit and the reservoir. The overall sample recovery in the chromatograph will be 78.6 percent of the gas collected by the automatic Toepler pump.

## D. Sample Extraction System

The reaction furnace and associated components have undergone several changes from the initial concept of what this portion of the total apparatus should be. These alterations all have been made in the attempt to make commercially available inert-gas fusion equipment perform under vacuum. Complete success has not yet been achieved, but the remaining improvements required should not be difficult to accomplish.

The starting point for the construction of the extraction apparatus was the acquisition of a Leco Model 537 induction heater and the furnace components of a Leco 534-300 Oxygen Analyzer. The choice of apparatus was based on the claim of the manufacturer of operating temperatures as high as 2700°C (5) and on the advantageous construction features of the furnace system for loading and for addition of samples. A drawing of the original purchase equipment is presented in Figure 14.

The changes introduced immediately were intended to provide vacuum operation of the apparatus, and these were made at the base seal of the furnace and at the sample loading stopcock.

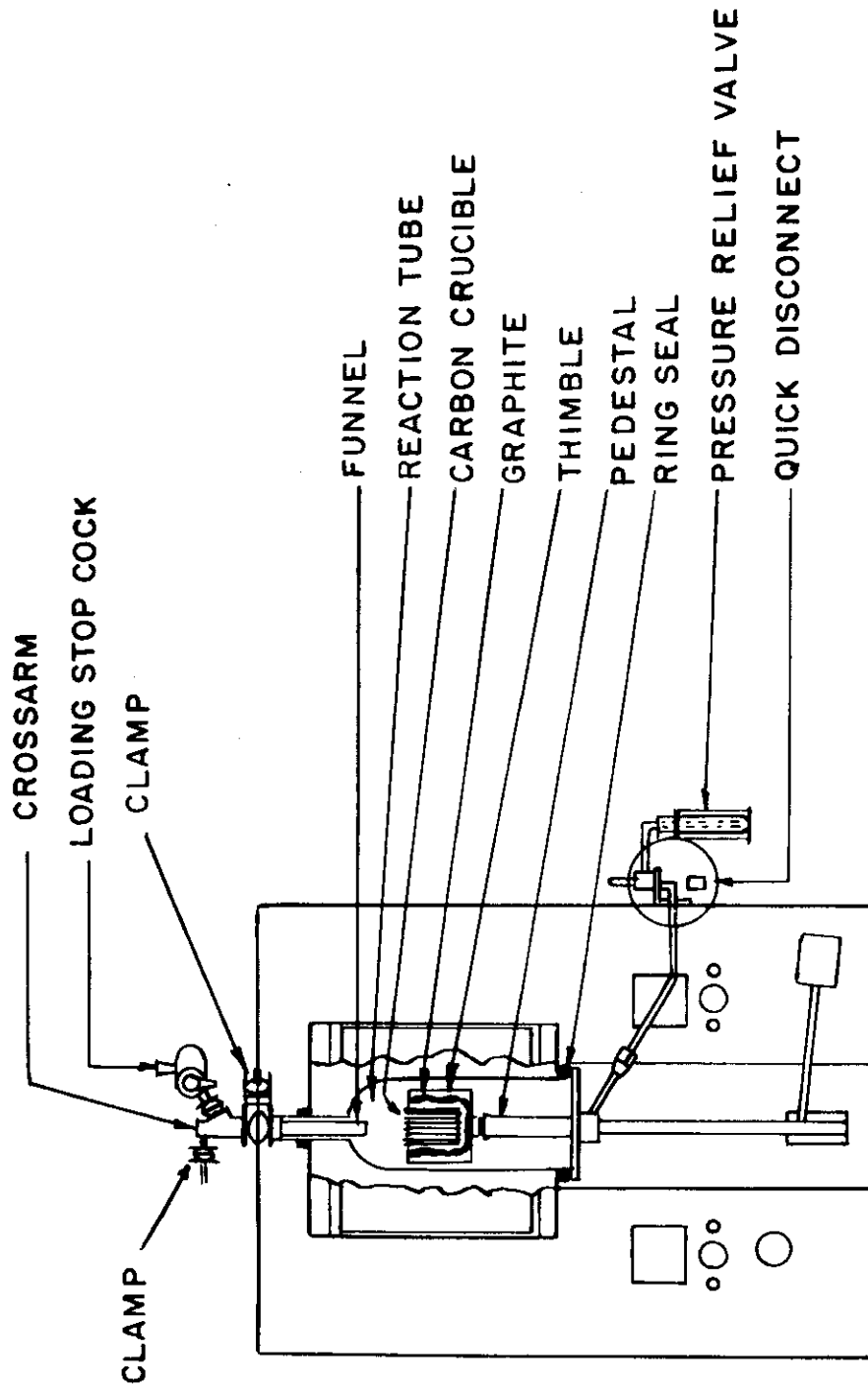


Figure 14. Original Leco Induction Heater and Furnace Assembly

# Contrails

The furnace tube base seal on the original equipment was a simple O-ring designed to hold the system against an internal argon pressure. This O-ring seal would not hold when vacuum was applied to the furnace. Addition of a brass back-up ring inside the O-ring did not suffice. The original base plate and seal were finally abandoned completely and a totally new base constructed. Its design is shown in Figure 15.

The central insert of the metal base was replaced by a new piece from which the argon feed line was omitted. A side support was provided with a groove for a 1-3/4 inch O-ring (actual O-ring I. D. of 1.725 inches). The furnace tube was lapped to an O. D. of 1.750 inches, and the seal was made with Dow-Corning silicone grease to reduce the possibilities of introducing hydrocarbon vapors. The base plate insert was tapped for the central pedestal mount as on the original piece. The new base plate seal tested satisfactorily with a helium leak detector.

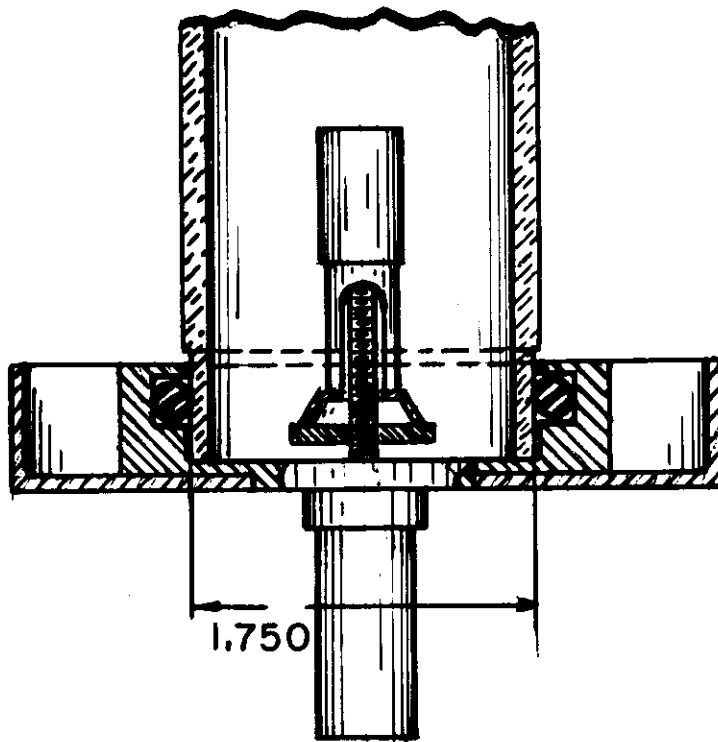
The loading stopcock originally was graphite lubricated, and it had a small hole drilled through the barrel into the loading well to permit argon to flow out of the stopcock while the sample was being added. The graphite was cleaned off and replaced by Apiezon grease T, and the bleeding hole was filled with Apiezon wax W. The modified stopcock was nominally vacuum tight, but continued use showed serious defects in the general construction. If a slight deficiency of grease is applied, serious leakage occurs around the stopcock barrel. Any excess of grease on the barrel leads to a pile-up of grease below the stopcock, and every sample introduced becomes contaminated with hydrocarbon. This is objectionable, but the effects noted are not the major difficulties being encountered.

A brass bonnet with a rubber O-ring seal was fabricated to fit over the sample loading stopcock. The bonnet connects to the vacuum manifold and to an atmospheric bleed through a 3-way stopcock. With this device, a sample may be placed in the stopcock and the stopcock evacuated before the furnace system is exposed to receive the sample.

The remainder of the extraction apparatus is simply that required to connect to the gas-handling system and the various crucible arrangements. These may be described best under considerations of the combined analytical apparatus and operations on particular metallic systems.

## E. Unification of the Apparatus

After the requirements of the individual instrument systems had been determined, the apparatus was assembled into a single piece of equipment. Figure 16 shows the arrangement of the system at the termination of the



ACTUAL I.D. OF "O" RING  $1.725 \pm .010$

Figure 15. Furnace Tube Base Seal

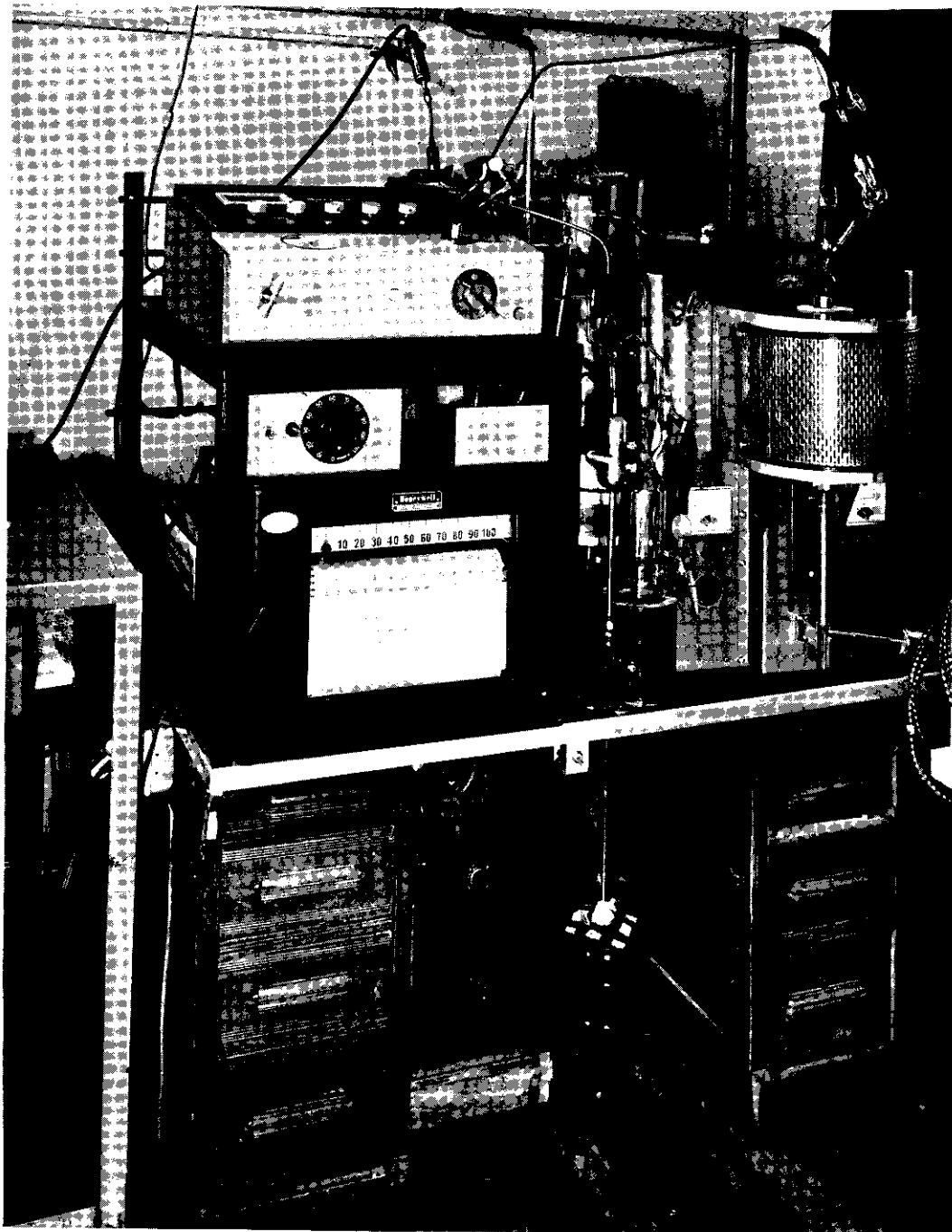


Figure 16. Unified Apparatus

# Contrails

experimental work on this contract, but several changes were incorporated after the apparatus had been assembled and before the picture was taken.

Initially, the manifold line was of 3/8-inch copper tubing for most of its length. The oil diffusion pump was in use, but the mercury diffusion pump was not in the system. The transfer of gases from the sample collection volume into the chromatograph was performed by the manual mercury lift. None of the furnace modifications had been attempted.

The chromatograph, recorder and induction heater were positioned for assembly, and the Toepler pump and collection volume were placed to give the shortest possible connecting lines between units. The vacuum manifolds were constructed to conform to the geometry of the other units.

Attempts to achieve vacuum on the various sections of the apparatus led first to the necessary changes in the furnace base plate. Successful modification of the furnace base permitted evacuation to less than 1 micron with no crucible in the furnace. This indicated adequate capacity in the pump system. When the induction heater was energized with a graphite crucible in the furnace, the furnace went into continuous glow discharge. This demonstrated that pumping speed was inadequate in the furnace zone and that localized pressure build-up was occurring. Installation of the mercury diffusion pump next to the furnace overcame the discharge difficulty, and it also eliminated the need for the oil diffusion pump on the manifold system. At the same time the mercury diffusion pump was installed, larger diameter glass connecting tubing was substituted for smaller lines from the furnace, and the main manifold was reconstructed of 3/4-inch copper tubing throughout. These changes eliminated throttling and provided rapid pumping speed as well as the necessary pumping capacity.

The apparatus as finally evolved permitted effective and reasonably simple vacuum operation and transfer of gases from the furnace into the chromatograph. The remaining limitations of furnace operation and sample analysis conditions became and remain the principal problems of the investigation.



IV. DETERMINATION OF NITROGEN IN METALSA. Magnesium

Magnesium was chosen as a material for investigation primarily because of the ease with which it may be nitrated and later decomposed. It was intended that the feasibility of the method would be established with magnesium as a simple metal and tested for applicability on refractory nitrides of other metals. The base material selected for use was Johnson, Matthey spectrographically standardized magnesium rod containing about 60 ppm. of total metallic impurities. The gas content of the metal was not known, but it was assumed to be as low as that of any material available.

Operation of the apparatus for magnesium was complicated by the high temperature of the crucible obtained with minimum setting of the controller on the induction heater. With the crucible centered in the coil, the minimum temperature obtained was of the order of 1400°C. Magnesium boils at about 1100°C at one atmosphere.

Variations were made in the length of Vycor pedestal used, in the type of crucible packing material (graphite, boron nitride, no packing), and in the use of tin as a low volatility bath. None of these permitted a temperature under 800°C, and the metal contents of the bath were always volatilized and deposited on the glass walls of the apparatus.

When the crucible was set off-center below the coil, the magnesium vapor deposited at the level of the coil produced such a high plate current in the oscillator circuit of the induction heater that the unit overloaded without transferring energy to the crucible.

With the crucible raised above the coils on a long pedestal, no deposition occurred in the furnace zone, but the crossarm and connecting tubing became coated with magnesium, and the crucible emptied itself of metal during the analysis of ten 1/4-gram samples. The resultant chromatograms looked satisfactory, but the data were considered meaningless because of the nitrogen-absorbing properties of the vapor-deposited magnesium.

Nitrogen blanks at the analysis temperature (850°C) before addition of magnesium were consistent at 0.23 to 0.26 in.<sup>2</sup> (integrated area of peak) for 30 minutes of collection. The source of the relatively high blank has been determined subsequent to the attempts to determine nitrogen in magnesium.

The immediate limitation on the use of magnesium in this work is the lack of downward electrical temperature control on the Leco induction heater. Without such control, further work on magnesium was abandoned.

## B. Iron

Iron and steel samples respond routinely to vacuum fusion and Kjeldahl methods of determining nitrogen. Since magnesium could not be used in the present apparatus, iron was chosen as the material with which to test the proposed method. An ingot iron, NBS sample 465, was obtained with an approximately known nitrogen content of 50 ppm. The nitrogen analysis supplied by the Bureau of Standards was obtained by vacuum fusion, but the value for this element was not certified.

The analysis of iron requires a furnace temperature of about 1900°C. With the crucible arrangement tried for magnesium (a graphite holder and a graphite crucible, no packing material), the crucible did not heat above 1400°C. When the crucible holder was replaced by graphite powder, a temperature of 2100°C was reached. Higher temperatures will require the use of carbon black as packing material, but the outgassing period may be extended.

A furnace bath of 10 g. of platinum was employed in an attempt to anticipate the use of a universal flux for other metals. Furnace blanks were collected before, between, and after the running of samples at a pyrometer-indicated temperature of 1800°C. (Pyrometer readings at this temperature were found to be approximately 100°C low.) Numerous blanks were collected over 30 minute periods and analyzed.

The nitrogen blank obtained at an indicated temperature of 1800°C was always in the range of 0.010 to 0.014 in.<sup>2</sup>/min. Over long periods of operation, it would vary  $\pm 0.001$  in.<sup>2</sup>/min. from a mean in the range cited, but a general upward shift of the mean occurred after a pressure bump blew graphite as far as the mercury diffusion pump. Even after a system clean-up, increases in the H<sub>2</sub> and CO blanks were also observed after this incident.

The analysis for nitrogen in quarter-gram samples of NBS-465 show a similar pattern. Fourteen samples were analyzed for nitrogen, four of these before the pressure bump. The results are tabulated on the following page. The samples were cut sequentially from one end of the sample rod.

TABLE IV

Determination of Nitrogen in Ingot Iron NBS-465

<u>Sample No.</u>	<u>ppm. N<sub>2</sub></u>
1	28.6*
3	44.7
6	34.8
7	40.8
-----	
8	14.7*
9	22.6
10	30.8
12	29.7*
19	21.9*
20	25.1
21	12.1
22	14.1
23	23.7*
24	21.1*

\* Grease contamination of sample.

Average of all 14 samples, 26.0 ppm.  $\pm$  36.5%

Average of first four samples, 37.0 ppm.  $\pm$  18%

Approximate nitrogen content as stated on NBS certificate, 50 ppm.

The precision of the first four samples and their reasonable agreement to the vacuum fusion data offered by the Bureau of Standards is more promising than those of the total series. The magnitude of the nitrogen blank is 40 to 60 per cent of the total sample peak, and this introduces a large portion of the imprecision. The use of larger samples or the attainment of a smaller blank would improve the signal to noise ratio appreciably and produce greater precision. The effect of the graphite bump was severe, and for some unknown reason it led to unaccountably low results even if the lower blank were used to calculate the analytical result.

The sample procedure was similar to that used in vacuum fusion analysis. Specimens were cut from the iron rod, cleaned with a file to produce smooth, bright surfaces, rinsed in reagent grade acetone and weighed. The clean samples

# Contrails

were stored in acetone until they were loaded into the apparatus. Several samples were contaminated by grease from the loading stopcock. The grease produced wild  $H_2$  and  $CH_4$  peaks, but there was no consistent effect on the nitrogen peaks, as is shown in Table IV by the results of the samples marked with an asterisk.

The hydrogen peaks in the blanks were consistent before the graphite bump at about  $0.002 \text{ in.}^2/\text{min.}$  After the graphite bump, the hydrogen blank decreased from  $0.007 \text{ in.}^2/\text{min.}$  to about  $0.004 \text{ in.}^2/\text{min.}$ , except when grease was introduced from the sample-loading stopcock. Because of this, hydrogen determinations were not attempted on Iron 465.

The CO content of the blank was inconsistent and high. Initially it ran about  $0.06 \text{ in.}^2/\text{min.}$ , but with continued operation of the same crucible it climbed to about  $0.10 \text{ in.}^2/\text{min.}$  After the graphite bump, the CO blank reached as high as  $0.16 \text{ in.}^2/\text{min.}$ , but it never became consistent at any level. For this reason, oxygen values have not been determined in the Iron 465 samples.

Small amounts of methane appeared in many but not all of the blanks, but the peak areas never exceeded  $0.003 \text{ in.}^2/\text{min.}$  When samples became grease contaminated, the  $CH_4$  peaks rose sharply.

Oxygen blanks, as such, were obtained routinely at a very consistent level of  $0.003 \text{ in.}^2/\text{min.}$  At first the appearance of unconverted oxygen was attributed to the evolution of the oxygen in molecular form--an unexpected phenomenon. A more logical conclusion, and one which was confirmed, was that the unconverted  $O_2$  peak was due to a small air leak outside of the hot zone of the furnace. This was demonstrated by the persistence of the  $O_2$  peak on a cold furnace blank.

The location of the leaks was difficult to establish. A helium leak detector did not indicate their presence, nor did a Tesla coil. The leaks were eventually found and partially eliminated by the use of plastic bags around individual sections of the apparatus to contain a static helium atmosphere. The system would be held for ten to thirty minutes before connecting to the leak detector. Sharp signals at several points in the system indicated minute leaks, two of which proved to be the major irremedial sources of oxygen. One of these was at the furnace base O-ring seal, and the other was at the sample-loading stopcock.

Redesign of the base seal on the furnace and of the sample loading device has been studied, but the expiration of the contract has prevented the accomplishment of these modifications.

## V. CONCLUSIONS

The results of the investigations carried out to date, while incomplete, allow a number of conclusions as to the general feasibility of the ideas proposed for the analysis of gases in metals as well as to the technical feasibility of the methods of approach which have been applied so far.

Since most of the effort on this program has been devoted perforce to the development of a suitable apparatus, the conclusions are restricted largely to the success of this phase of the investigation.

The principal result of the present work, in the opinion of the authors, has been the demonstration that the gases extracted from metals by a vacuum fusion method may be introduced into an evacuated sample loop and analyzed qualitatively and quantitatively by gas-solid chromatography using a 5A molecular sieve column. Furthermore, it has also been shown that gases extracted from a metal sample may be transferred conveniently and automatically into a collection vessel and transferred again as a unit into the gas chromatograph. The mechanical aspects of instrumenting the analysis system have been accomplished. Thus the general feasibility of gas-solid chromatography for the analysis of gases extracted from metals has been demonstrated. The sensitivity of measurements of individual gases in a gas sample has been shown to be of the order of 0.5 gamma for nitrogen, hydrogen, oxygen and carbon monoxide. This sensitivity corresponds to the determination of 1 ppm. of the individual gases in a half-gram sample of the metal. This limit is not achieved for nitrogen in the presence of a rather large nitrogen blank caused by small leaks in the furnace portion of the apparatus. Wide variations in hydrogen and carbon monoxide blanks at present preclude the determination of hydrogen and oxygen with any accuracy. The presence of molecular oxygen in the blank further demonstrates the presence of a leak in the system.

The design of the furnace section and the sample-loading device have been shown to be inadequate for vacuum operation, but relatively simple modifications can be made which will permit operation either in vacuo or under an inert gas atmosphere. The necessary changes are expected to reduce the size and variability of the furnace blank and to eliminate sample contamination by stopcock grease and thereby to restore the inherent sensitivity of the determination.

The feasibility of using the extraction and analysis method on refractory nitrides has not been demonstrated yet, but nothing in the results obtained to date indicates that the proposed method will not be successful. The use of inert-gas fusion in place of vacuum operation has not been attempted during the present period.

## VI. RECOMMENDATIONS

The results accomplished under the present contract are encouraging and justify continued effort to determine whether nitrogen may be extracted from refractory metals and analyzed. Both vacuum operation and inert-gas fusion merit continued study, and the requirements for future development are set forth below.

Apparatus modifications must be undertaken for either line of further study. The imperfect base seal can be improved by fabricating a bottom-sealing device to replace the side-sealing O-ring now in use. The proposed furnace base is shown in Figure 17. Room temperature vulcanizing (RTV) silicone rubber would be used to cast a series of gaskets for each furnace. With a high-walled base ring, the use of a deep gasket is expected to provide a leak-free seal which should give easy access to the furnace contents. The incorporation of an additional line with a needle valve will permit introduction of gas for absolute calibration of gas recovery and study of gettering effects of hot metal in and adjacent to the furnace.

The substitute loading device, for which no drawing is furnished, would be a toggle-operated vacuum valve connected directly to the crossarm above the furnace. This valve, available from the Vacuum Instrument Co., Huntington Station, New York, has been used successfully by the Titanium Metals Corporation of America, Henderson, Nevada.

The foregoing modifications are expected to provide leak-free operation under vacuum to produce a low and constant furnace blank which will permit proper evaluation of the vacuum fusion type of extraction of nitrogen and other gases. Continued experimentation with this form of the apparatus will also permit an investigation of the parameters limiting current vacuum fusion analytical procedures for determining nitrogen.

Inert-gas fusion may be used to replace vacuum fusion extraction, if the total amount of gas reaching the chromatographic analyzing column is reduced to an amount roughly equal to that produced by vacuum operation. There are two ways in which this can be accomplished.

If, after inert-gas sweeping, a fixed inert-gas atmosphere can be maintained in the furnace during fusion, a portion of the total gas can be expanded into the analyzing chromatographic system. Since a smaller fraction of extracted gas would be sampled, larger metal specimens would be required. The question of reabsorption of gases from the static atmosphere would have to be examined.

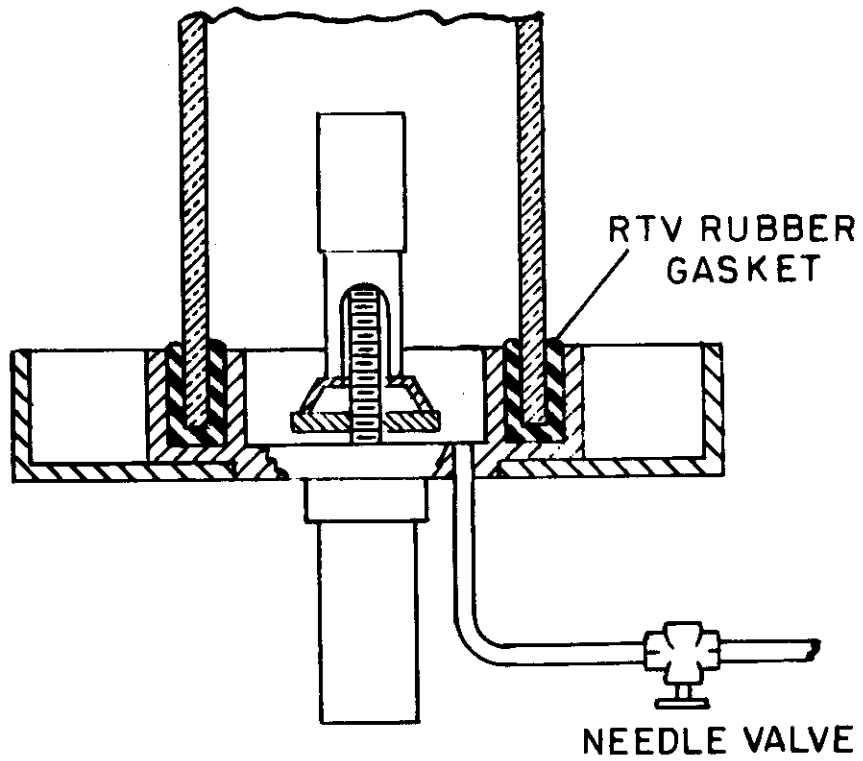


Figure 17. Proposed Furnace Base Seal

# Contrails

A continuously-sweeping inert-gas fusion would be more desirable from the standpoint of extraction efficiency and total gas analysis. The restriction on total gas introduced to the chromatograph could still be met, if a preliminary separation of carrier gas from the extracted gases is accomplished. Such a separation may be achieved by the use of a preadsorption column which is selective for the extracted gases. Displacement of these gases into the analyzing column would then provide a concentrated gas sample for complete analysis. If the latter separation can be accomplished, it should be possible to dispense with all vacuum pumps and transfer devices and operate solely with carrier gas and/or displacement gas as transfer agents.

The desired chromatographic separation of carrier gas from extracted gases might be achieved in several ways. A molecular sieve column operated in a dry ice-acetone cold bath would collect all of the gases exiting from the furnace. If the column temperature is raised, these gases could be flushed with helium into an analyzer column at the same pressure as the reference system. Alternately, a displacement gas could be used to remove all of the gas held on the preliminary column. The preliminary column would then require regeneration at elevated temperatures.

Another possible pre-separation might be accomplished with columns of activated charcoal or silica gel operating on a temperature cycle. The low adsorptivity of helium or argon on these materials might be used for the actual separation of carrier gas from extracted gases of greater chemical reactivity.

Futher studies of the furnace reaction will be needed before a method suitable for steel can be used for titanium, zirconium, niobium, tungsten and other refractory metals. Higher operating temperatures and a suitable flux system will be required and should be investigated.



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