copy 2

Ultrasystems

COAL MINE COMBUSTION PRODUCTS IDENTIFICATION AND ANALYSIS PROCEDURES AND SUMMARY

prepared for

UNITED STATES DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

by

ULTRASYSTEMS, INC.
2400 MICHELSON DR.
IRVINE, CALIFORNIA 92715

FINAL REPORT

on

CONTRACT NO. HO133004

COAL MINE COMBUSTION PRODUCTS
IDENTIFICATION AND ANALYSIS

SEPTEMBER 1978

(this page replaces old Title Page)

REPORT DOCUMENTATION PAGE

1. Report No.	2.	3. Recipient's Accession No.

4. Title and Subtitle Coal Mine Combustion Products Identification and Analysis Procedures and Summary	5. Report Date September 1978 6.
7. Author(s) K. L. Paciorek, R. H. Kratzer, J. Kaufman, and J. H. Nakahara	8. Performing Organization Report No. SN-8220-F
9. Performing Organization Name and Address Ultrasystems, Inc. 2400 Michelson Drive Irvine, California 92715	10. Project/Task/Work Unit No. 11. Contract or Grant No. HO133004
12. Sponsoring Organization Name and Address Office of the Assistant Director - Mining Bureau of Mines, Department of the Interior Washington, D. C. 20241	13. Type of Report Final 14.

15. Supplementary Notes

16. Abstract

The primary objective of this final phase of Contract No. HO133004 was to provide a description of all experimental assemblies and procedures used throughout this project in such a detail as to permit duplication of the tests in any other laboratory. A further objective was to summarize and evaluate all results generated throughout the duration of this program and to tabulate all the materials and data in such a manner as to allow this report to be used as a reference index for specific compositions or groups of compositions regarding potential hazards arising from their use in underground coal mining operations.

The report also contains an updated survey of the literature on thermal oxidative degradation of compositions investigated under this contract.

17. Originator's Key Words Mining Materials Thermal Oxidative Degradation Procedures and Techniques Toxic Hazards Toxic Load Factors	18. Availability Statement

19. U. S. Security Classif. of the Report	20. U. S. Security Classif. of This Page	21. No. of Pages	22. Price
Unclassified	Unclassified	130 + vii	

FOREWORD

This report was prepared by Ultrasystems, Inc., Chemicals and Materials Research Department, Irvine, California, under USBM Contract No. HO133004. The investigations were performed by K. L. Paciorek, program manager, R. H. Kratzer, J. Kaufman, and J. H. Nakahara. The contract was initiated under the Coal Mine Health and Safety Research Program. It was administered under the technical direction of the Pittsburgh Mining and Safety Research Center with Mr. T. Christos acting as the technical project officer. Ms. Sylvia Brown was the contract administrator for the Bureau of Mines.

This report is a summary of the work recently completed as part of this contract during the period 1 November 1977 to 1 September 1978. This report was submitted by the authors on 8 September 1978.

In view of the analytical nature of the work performed no subject inventions were made under this program.

TABLE OF CONTENTS

TABLE OF CONTENTS-Cont'd

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES-Cont'd

1. ABSTRACT AND SUMMARY

The primary objective of this phase of Contract No. HO133004 was to provide a description of all experimental assemblies and procedures used throughout this project in such detail as to permit duplication of the tests in any other laboratory. A further objective was to summarize and evaluate all results generated throughout the duration of this program and to tabulate all the materials and data in such a manner as to allow this report to be used as a reference index for specific compositions or groups of compositions investigated.

Consequently dimensional drawings of all apparatus utilized in the testing, both under quiescent and dynamic conditions, as well as for product characterization and separation have been prepared. The operational procedures employed in actual testing and product analysis have been fully described for ready process duplication.

To allow the report to serve as a material index the compositions tested were categorized into the following groups; a) Basic Polymers, b) Fibers, c) Additives, Flame Retardants, Plasticizers, and Preservatives, d) Conveyor Belts, e) Solvents and Fire Extinguishants, f) Hydraulic Fluids, g) Woods, and h) Miscellaneous Compositions, and references to specific reports given. The degradation data obtained for all the materials tested were reduced and tabulated to give toxic load values and toxicity contributions of major products formed upon thermal oxidative degradation. Comparative toxic load data were also included to permit comparison between quiescent and dynamic environments.

2. INTRODUCTION

Underground coal production makes it necessary to introduce a variety of combustible materials into the mine so that this operation can be carried out efficiently and safely. These include, among others, brattice cloth, ventilation pipe, conveyor belts, electrical insulation, wood, hydraulic fluids, lubricating and cutting oils, and fire extinguishants. Thus the ultimate goal of this program was to assess the potential hazard arising from the evolution of toxic products upon thermal oxidative decomposition of compositions employed in underground mining, to develop meaningful testing procedures and to provide a basis for realistic regulations for materials to be permitted in underground operations. To fulfill these requirements the thermal oxidative decomposition products of specific compositions were determined on a weight/weight basis and their potential toxic hazard was evaluated based on TLV and STEL.[1]

The materials studied under Phase I[2] of this contract were limited to four basic classes, namely, polyvinyl chloride and neoprene compositions, rigid urethane foams, and woods. Phase II[3] was devoted entirely to conveyor belting inasmuch as these devices are used in very large quantities in mines and thus present a grave hazard regarding toxic gas formation in the event of fire or local overheating. Phase III[4] involved the study of various pure components employed in conveyor belt manufacture and compounding to assist in selection of the best practical ingredients insofar as potential toxicity aspects are concerned. Phase IV[5] was directed at hydraulic fluids approved for underground use to determine the potential toxic hazard of the various classes of these materials and members within each class. The Phase V[6] efforts were centered on halogenated solvents, fire extinguishants and additives. The presence of halogen provides flame retardant characteristics; however, it contributes significantly to the formation of toxic products upon decomposition.

This Final Phase of the program was devoted to the detailed presentation of all experimental assemblies and procedures developed and/or employed under Contract No. HO133004. In addition the report generated is to constitute a summary and evaluation of testing data obtained for the various compositions and articles investigated during the preceding Phases.

3. TECHNICAL DISCUSSION

For ease of presentation this section has been divided into subsections dealing with the description of the specific degradation assemblies, the product separation procedures, the analytical methods, data summary of materials investigated under the other phases of the program, and a literature survey update.

3.1 STAGNATION BURNER ASSEMBLY

3.1.1 Apparatus Description

For studies performed in a dynamic environment a stagnation burner was utilized. Figure 1 depicts the actual experimental arrangement including the trapping system. Figures 2 and 3 present in detail the top, front and side views of the stagnation burner, the relative location of the four exit ports, and the stainless steel flexible metal hose pressure equalizing device. The cross-section of the stagnation zone is given in Figure 4. Regarding the component specifications (see Figure 4) the 2 gas heaters and the 2 auxiliary heaters are 120 volts, 500 watts, Part No. R-2265 from RAMA Corp., San Jacinto, California. The block heater is a specially manufactured General Electric Company cartridge heater (Cat. 7C885A106) 1.293 inch diameter, 5 inches long, 120 volts, 1250 watts. The stainless steel disc is Part No. D-1014-50100 S.S., 1.50" diameter x 0.125" sintered disc obtained from ANSCO Sintering Corp., Los Angeles, California.

All the tests involving the Stagnation Burner were performed after steady state was reached, i.e., after the gas and the heating block had attained constant temperature. The temperatures of the gas and the heating block were controlled independently and were measured by the thermocouples positioned as shown in Figure 4. These were calibrated using melting points of pure materials

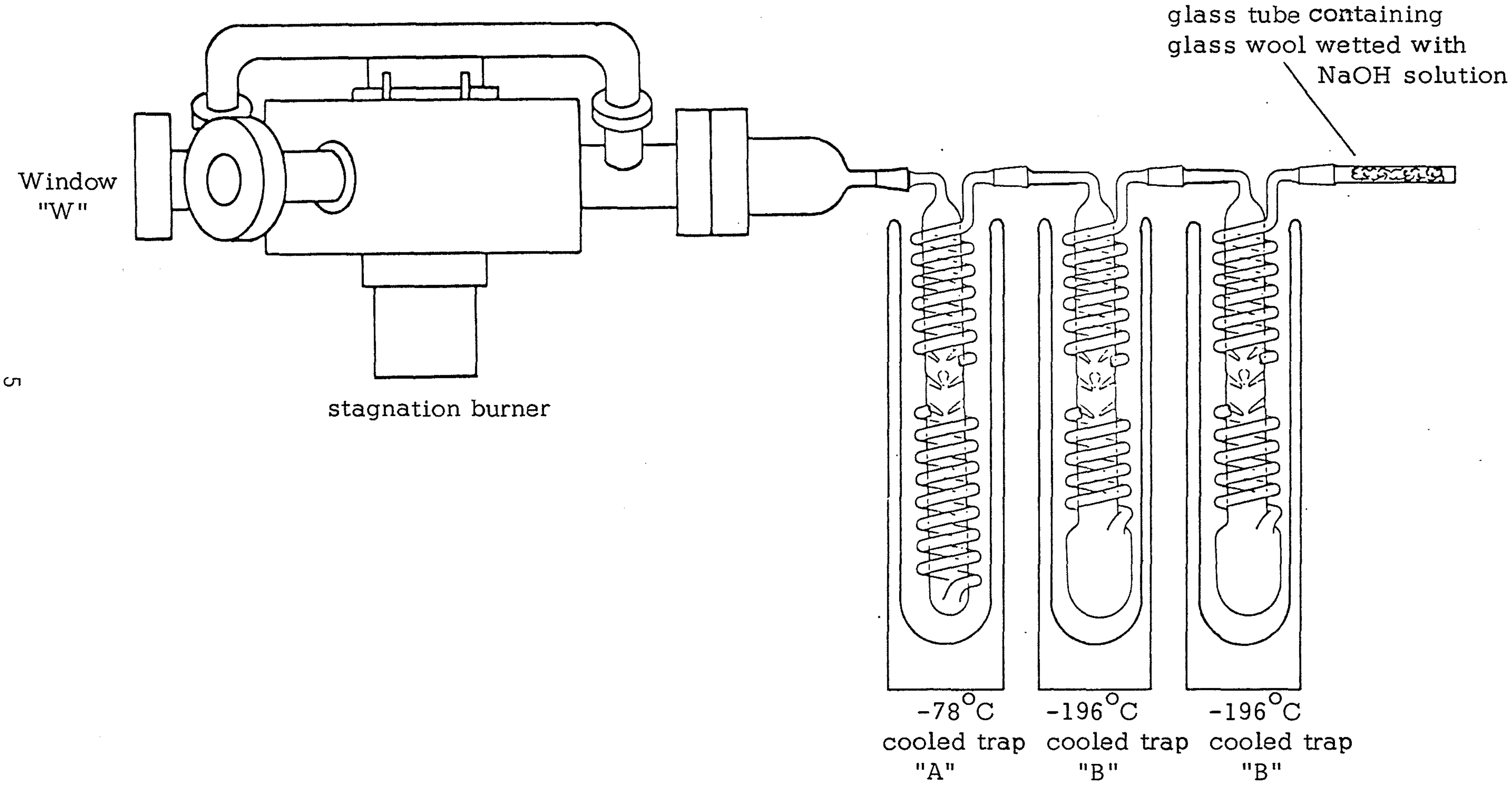


Figure 1: Stagnation Burner Arrangement

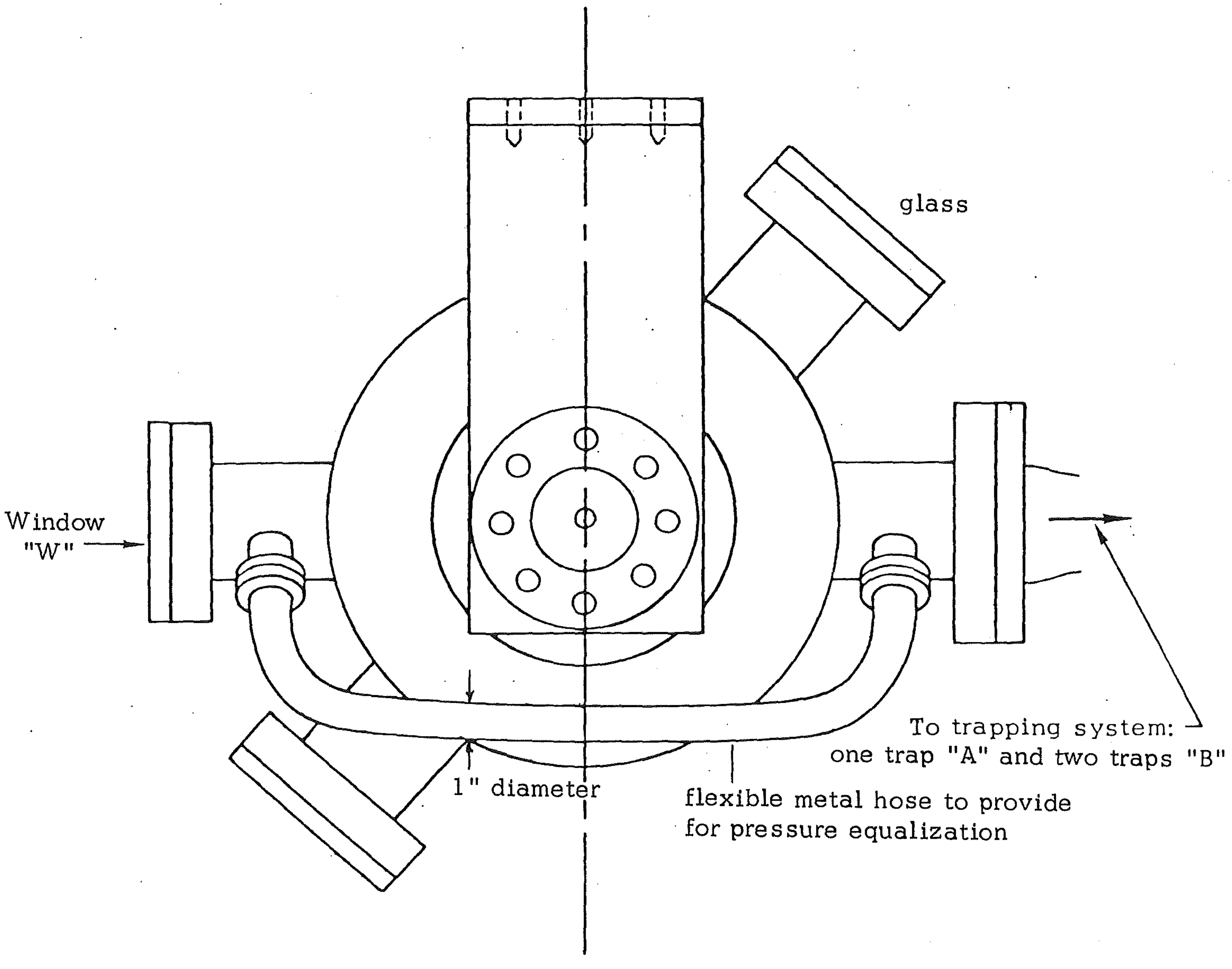


Figure 2: Top View of Stagnation Burner with Mounting System.

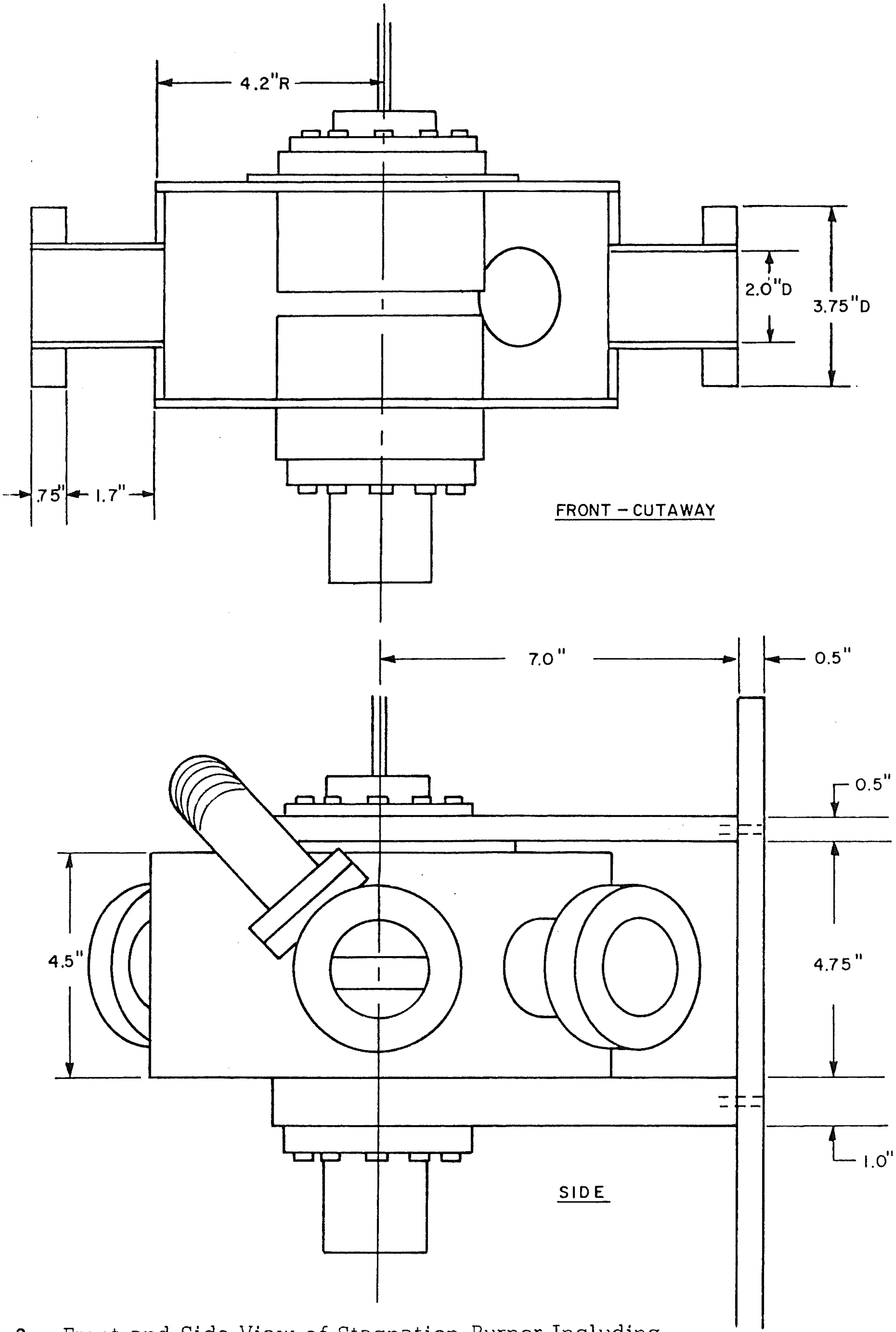


Figure 3: Front and Side View of Stagnation Burner Including Mounting System.

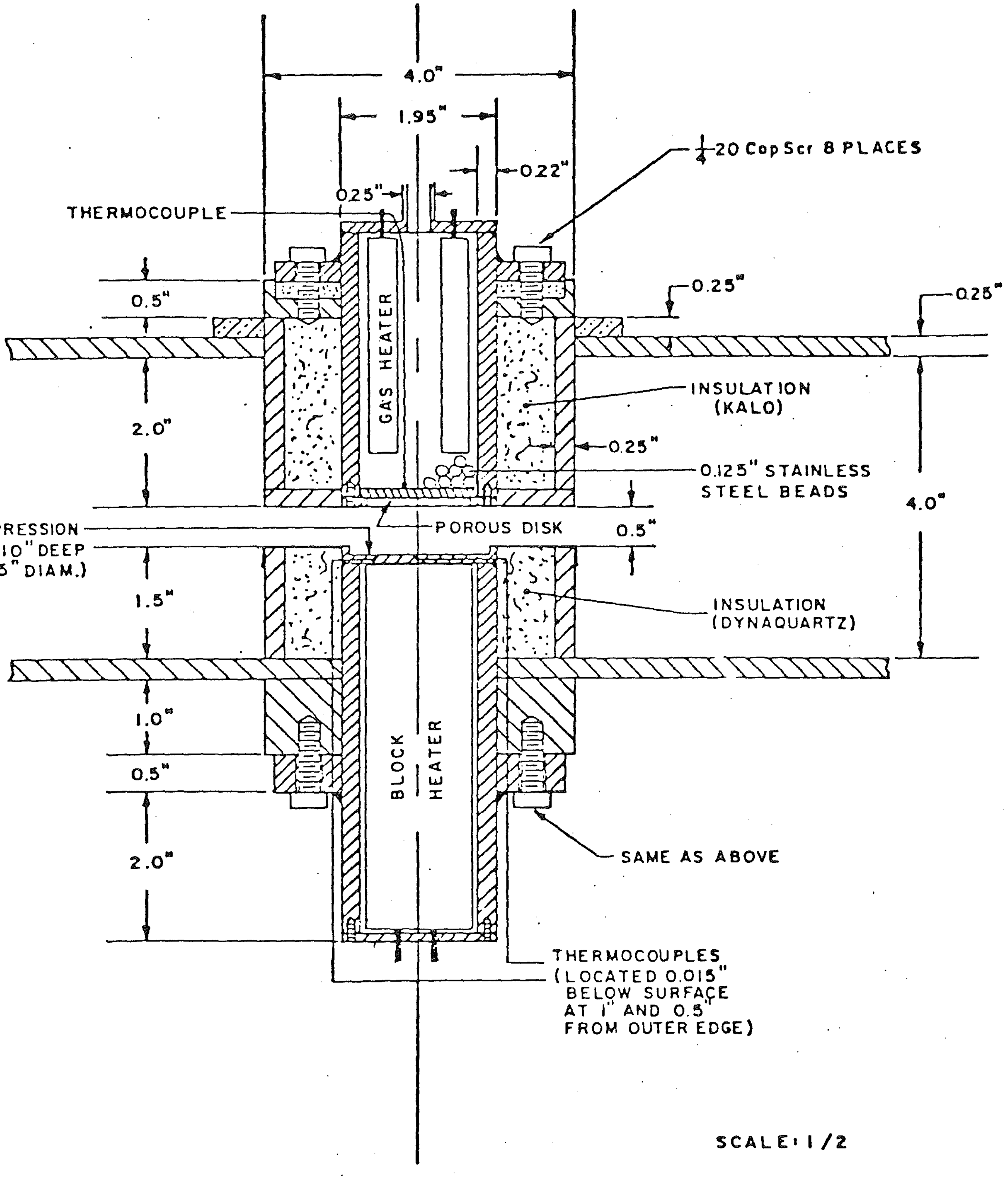


Figure 4: Detailed Drawing of Stagnation Zone with Gas and Block Heaters

in the temperature range of interest. The temperatures given are the temperatures recorded on a CEC Model 5-124A recording oscillograph. The gas inlet pressure was kept constant at 50 psi and the gas flow rate was measured by a turbine type flow meter. In view of the gas temperature range 200-550°C, the actual gas flow varied from 80-150 cc/sec.

A platinum insert tray was fabricated for the use with solid materials to avoid contamination of the heating block and to allow quantitative recovery of residues. For liquids and composite samples a 10 mm high platinum vessel was employed.

The detailed schematics of the traps utilized in the product collection train depicted in Figure 1 are given in Figures 5 and 6.

3.1.2 Stagnation Burner Operation

The experimental procedures employed were as follows: After temperature equilibrium was reached in the burner (block and gas temperatures) trap "A" (see Figure 5), cooled in a Dry Ice slush bath, was attached to the burner outlet followed by connecting two traps of the "B" type (see Figure 6) and attaching at the outlet a glass wool filled tube moistened with NaOH solution to prevent carbon dioxide from entering (see Figure 1). Subsequently the gas flow was measured, the window "W" opposite the burner exit (see Figure 1 and 2) removed and the two "B" type traps cooled with liquid nitrogen. After the boil off of liquid nitrogen ceased (the trap reached -196°C) the test sample contained in the platinum dish was placed on the heating block and the window "W" put back into place. All tests were run for 15 minutes. Trapping was so efficient that practically all the air which passed over the sample was condensed in the two "B" type traps together with all liquid nitrogen condensible

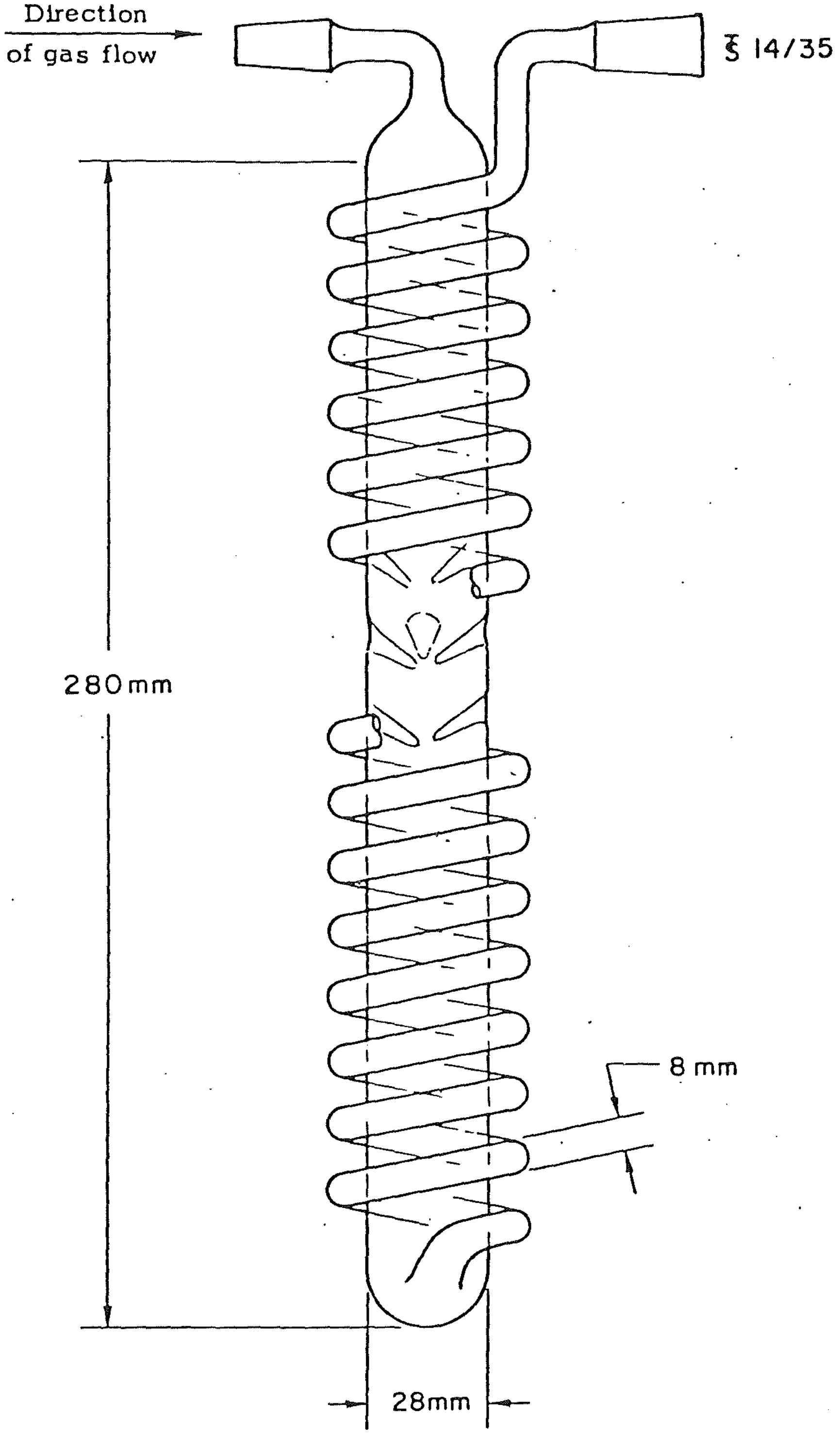


Figure 5: "A" Type Trap Cooled to -78°C

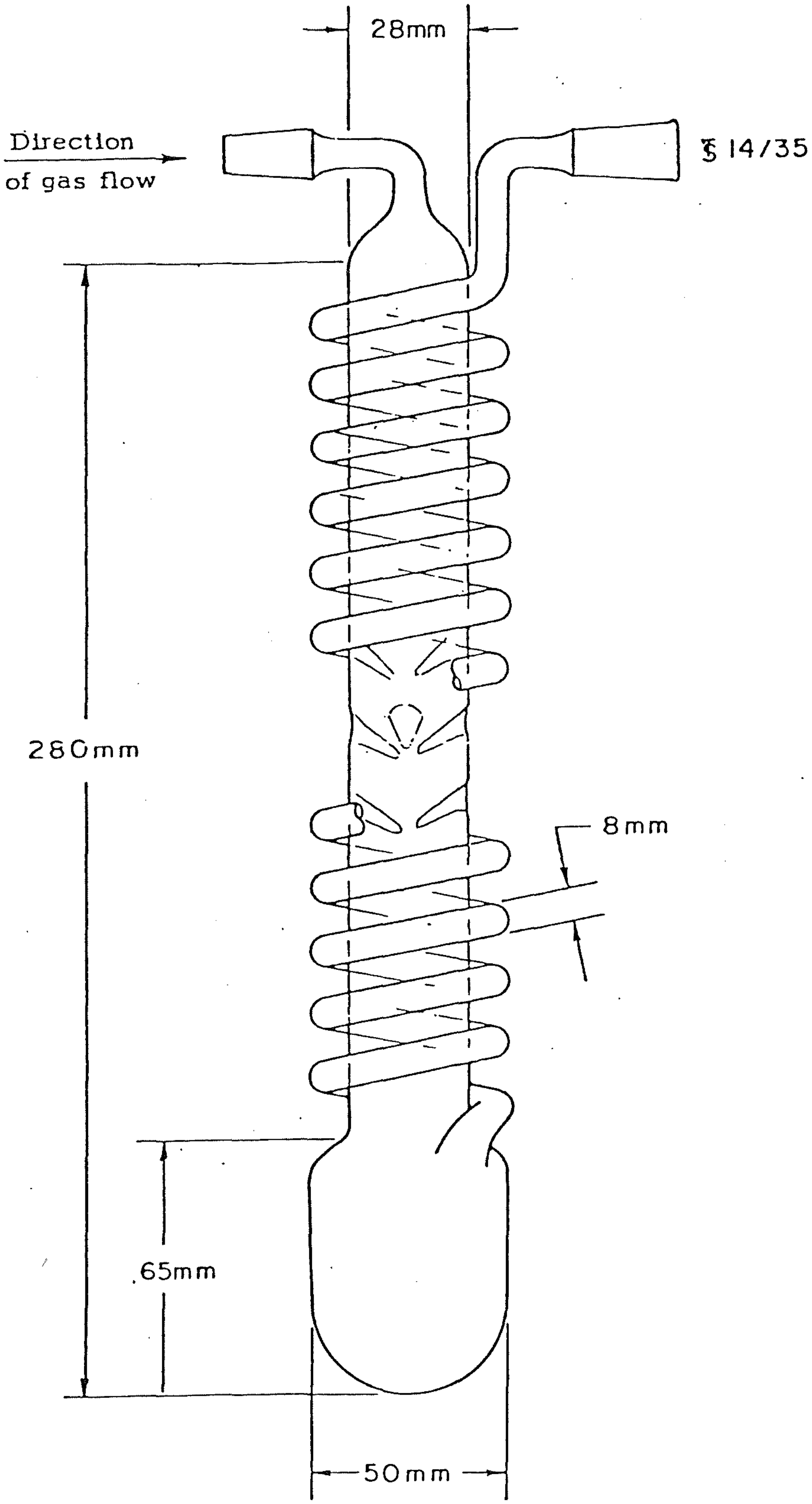


Figure 6: "B" Type Trap Cooled to -196°C

products. After completion of the test, the three traps were closed quickly with ground joint adapters, removed from the burner, and attached to a high vacuum system while still cooled to -78 and -196°C, respectively. Subsequently all noncondensibles (e.g., air, carbon monoxide, methane, argon) were pumped away through three more liquid nitrogen cooled traps. After removal of all noncondensibles, the condensible products were combined and subjected to fractional condensation as described in subsection 3.4.1.

3.2 SEALED SYSTEM

3.2.1 Standard Sealed System

The arrangement depicted in Figure 7A consists essentially of a 5 liter round bottom flask to which a quartz finger had been blown wherein the sample could be placed for decomposition. The flask was connected via a pair of standard taper joints to a stopcock through which air could be admitted or samples withdrawn. The volume V_1 sealed by stopcock "A" (see Figure 7A) was determined by measuring the amount of water contained in it, the volume between stopcocks "A" and "B" was determined using standard gas calibration procedures described fully in subsection 3.3.4.

3.2.2 Modified Sealed System

The sealed system depicted in Figure 7A was utilized for the degradation of relatively involatile liquids and solids and does not lend itself to the investigations of volatile materials. Accordingly the apparatus was modified as shown in Figure 7B. The tube-like projection shown in the center of the 5-liter bulb can be filled either with ice or cooled to lower temperatures depending on the volatility of the materials under study. This allows the evaporated liquid to be returned into the finger immersed into the 370°C bath.

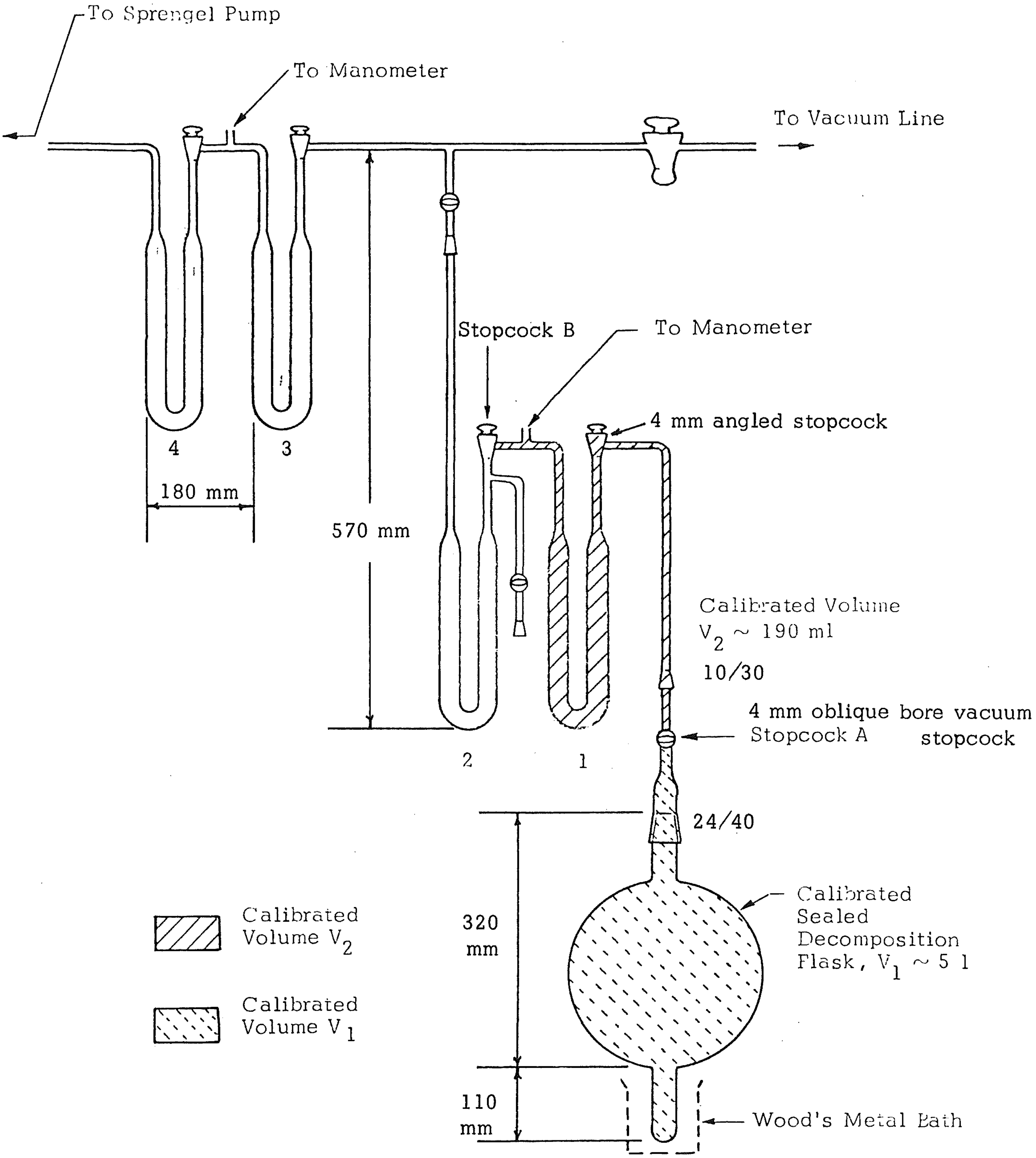


Figure 7A: Sealed System for Thermal Oxidative Degradations

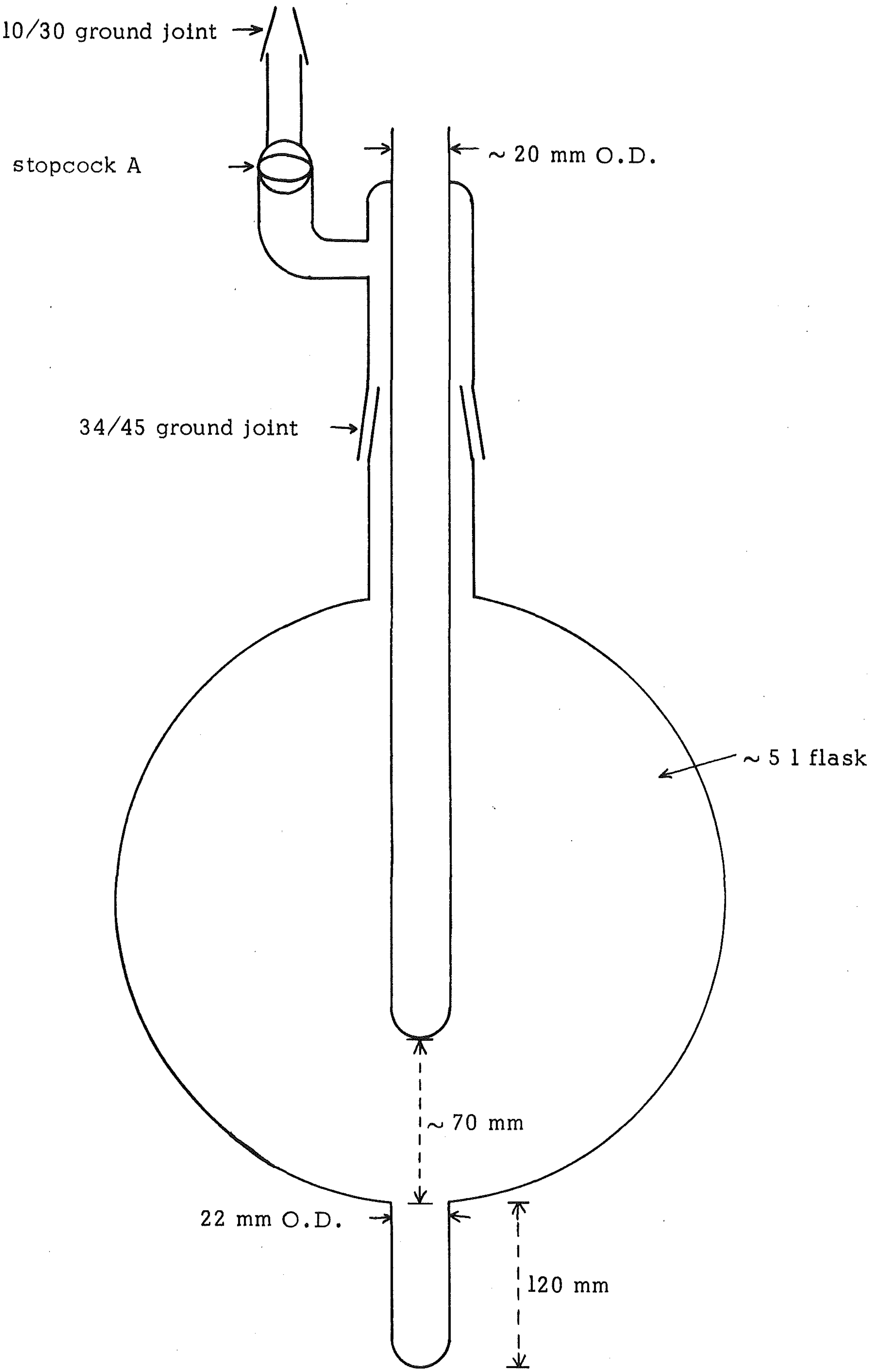


Figure 7B: Sealed System for Volatile Liquid Degradation

The samples studied in this apparatus were volatile at room temperature and thus were distilled into the evacuated 5-liter decomposition flask; then the apparatus was brought to room temperature and the air was introduced. Subsequently, the cooling finger (see Figure 7B) was filled with ice and the bottom finger-like projection was immersed into the Wood's metal bath which was preheated to the specified temperature. The volatiles workup was the same for both of the sealed degradation systems.

3.2.3 Sealed System Operation

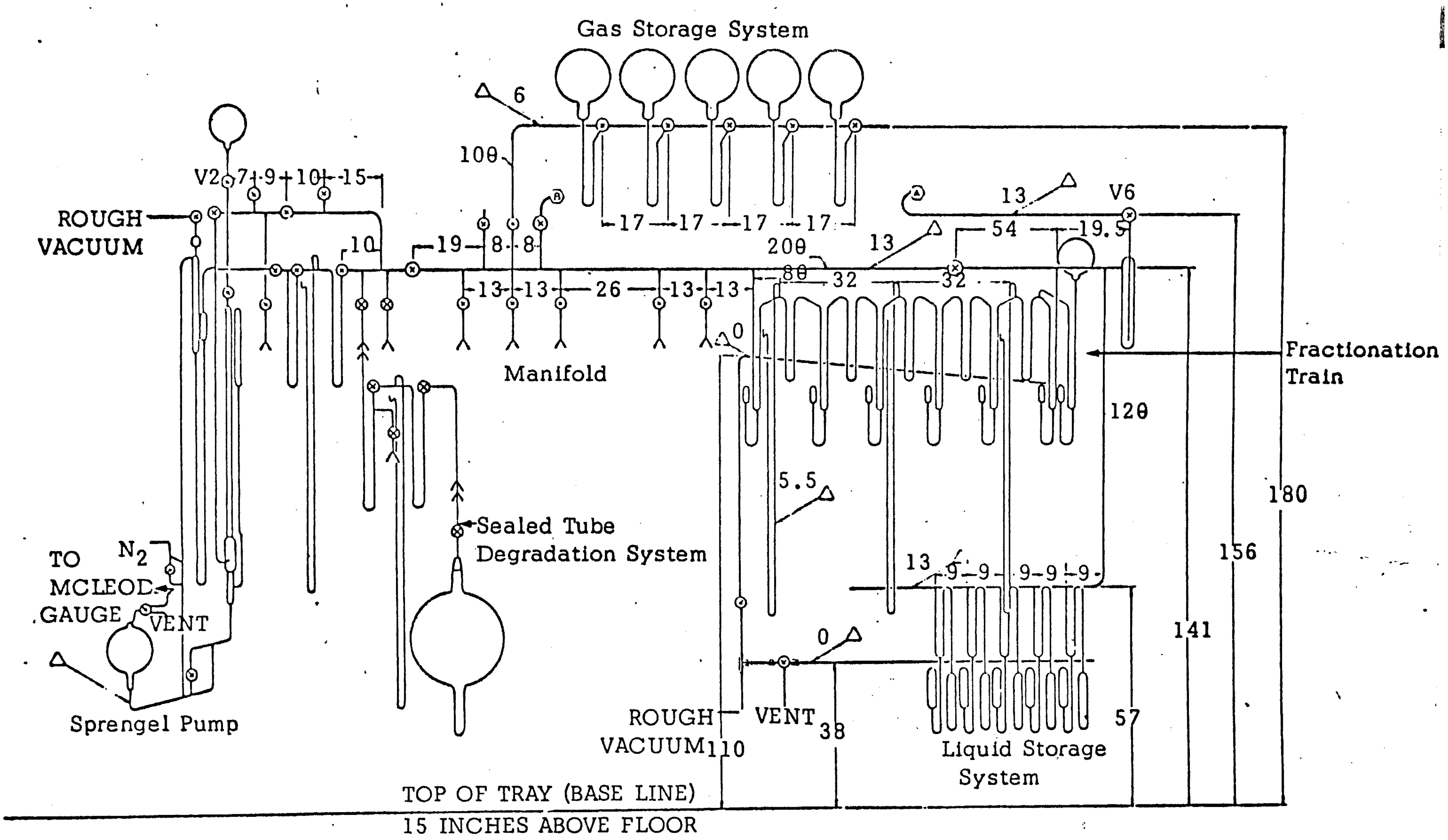
The general experimental procedure was to place a weighed sample of the material to be tested into the quartz heating finger, to seal the pair of ground joints with high temperature wax, and to evacuate the system on a high vacuum line (see section 3.3) to less than 0.1 mm Hg. Then the system was filled with pure, dry breathing air, which had been freed of carbon dioxide, to a known pressure and stopcock "A" (Figure 7A) was closed. By knowing the volume of the flask and by measuring the temperature and pressure of the air in it the total amount of gas and the number of mmoles of oxygen present could accordingly be calculated. The finger of the flask was then inserted into a Woods Metal Bath which was preheated to the desired constant temperature. The heating period in all the instances was 30 minutes. Subsequently, the flask was cooled by removing the bath of molten metal, the gases were expanded into the calibrated volume V_2 and the pressure and temperature were measured. The amount of expanded gaseous sample contained in volume V_2 was then isolated from the bulk left in volume V_1 by closing stopcock "A"; traps 1, 2, 3, and 4 (see Figure 7A) were cooled with liquid nitrogen and the noncondensibles were transferred quantitatively into the Sprengel pump (for description see subsection 3.3.6) where they were measured and then subjected to infrared and mass spectral analyses. The condensibles left in the four liquid nitrogen cooled traps (mainly in trap 2) were condensed back into volume V_2 (trap 1), measured and then condensed either onto frozen (-196°C) aqueous sodium hydroxide or water and analyzed for specific ions.

The bulk of the products left in volume V_1 was then freed from noncondensibles (air, CO, CH_4) by passing the volatiles through four liquid nitrogen cooled traps and discarding the noncondensibles. The materials condensed in these four traps were then combined and subjected to fractional condensation as described in subsection 3.4.1. The solid residue left in the finger of the reaction flask was removed and weighed whereas the involatile oils and tars deposited on the walls of the finger were investigated by infrared spectroscopy.

3.3 VACUUM LINE ASSEMBLY

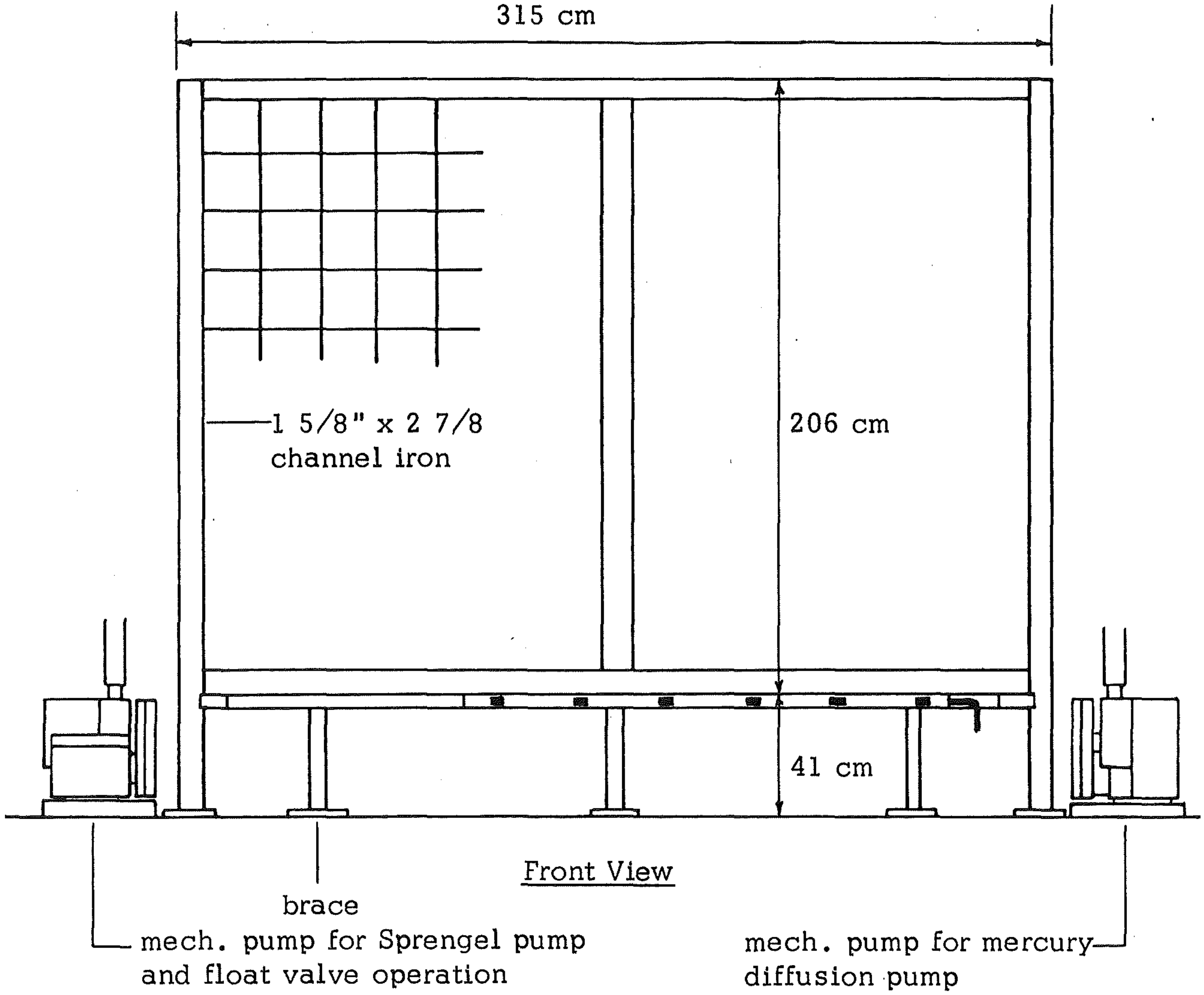
The vacuum system depicted in Figure 8 was employed to separate, measure and quantitate the volatiles produced on thermal oxidative degradation of samples both under dynamic (section 3.1) and quiescent (section 3.2) conditions. To facilitate the discussion the specific functional components have been boxed and labelled in Figure 8 and will be described in detail in subsequent schematics. Prior to proceeding to these components the dimensions of the metal rack and the lattice construction specifics are presented in Figures 9 and 10, respectively. These are self explanatory and do not require further clarification.

As noted in Figure 8 the outlet A (top right) leads to the pumping system which because of space limitations was installed on the "backside" of the rack. This system is composed of a mercury diffusion and high vacuum

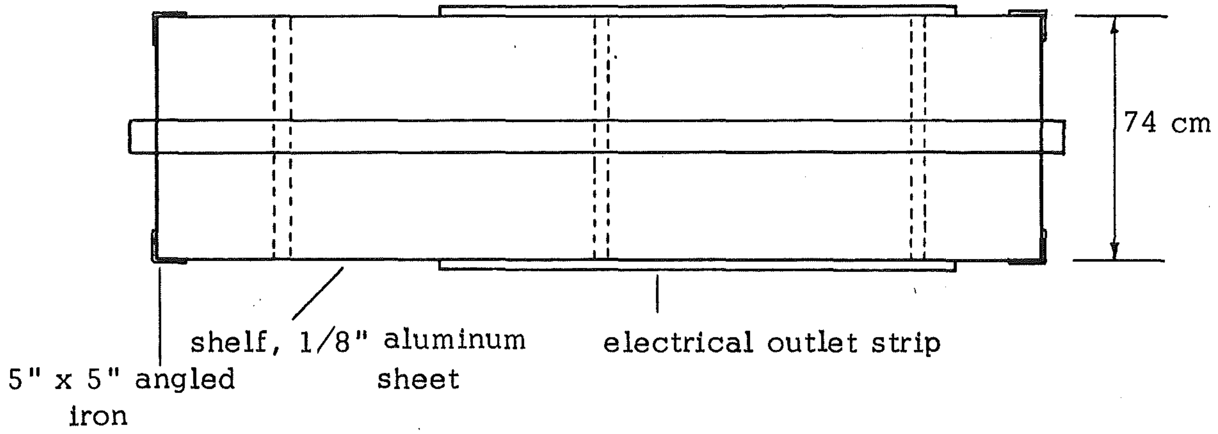


NOTE: ALL LENGTH MEASUREMENTS IN CENTIMETERS
DIAMETERS (θ) IN MILLIMETERS
△ DISTANCE TO NEAREST ROD
⬡ CONNECTIONS TO OPPOSITE SIDE OF FRAME (DIFFUSION PUMP SIDE)
ALL UNMARKED STOPCOCKS ARE V4
ALL TAPERED JOINTS ARE 10/30

Figure 8: Vacuum Line Component Systems



Front View



Top View

Figure 9: Vacuum Line Rack

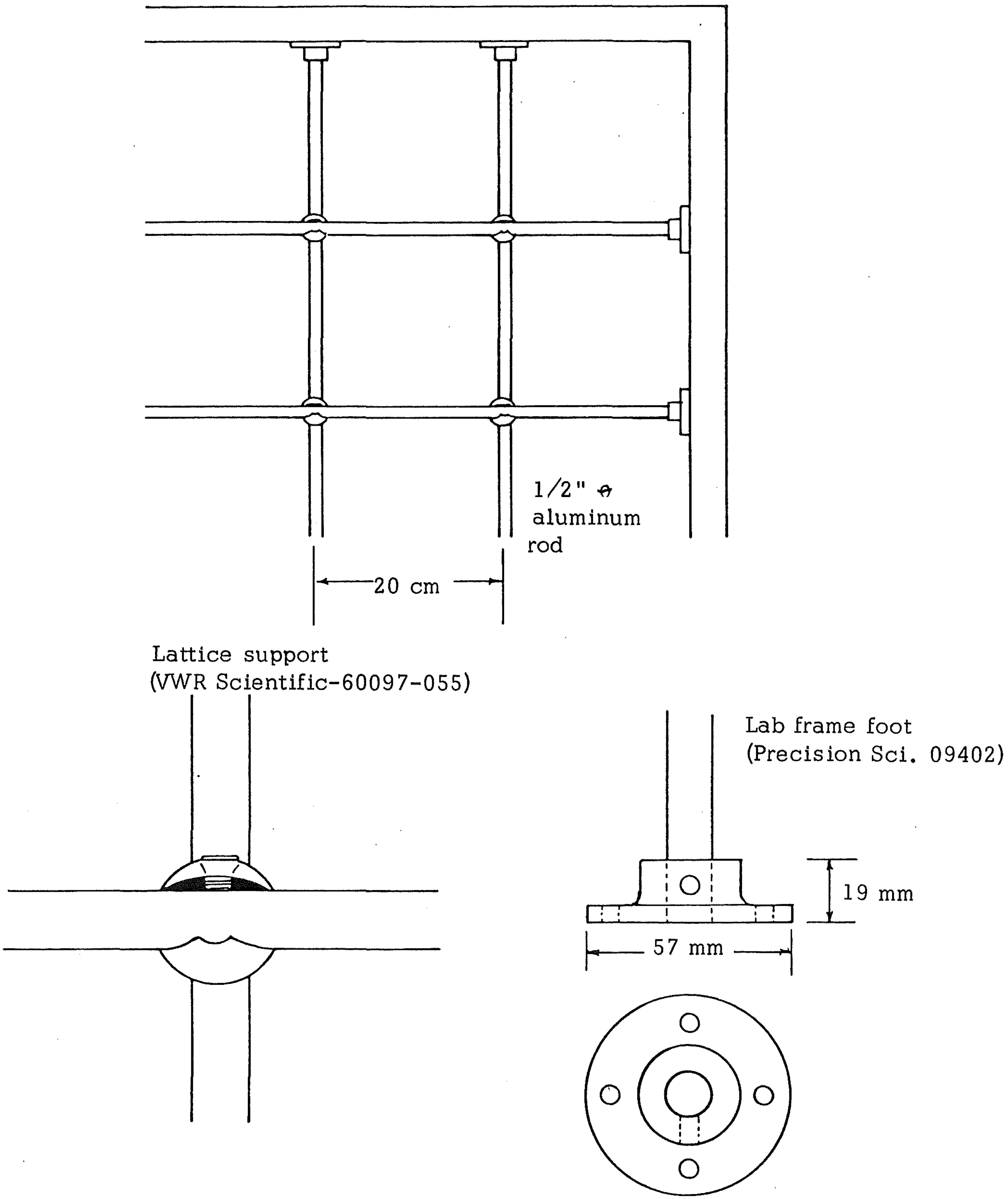


Figure 10: Vacuum Line Rack Lattice

mechanical forepump and capable of producing a vacuum of at least 10^{-4} mm Hg. Details of the pumping arrangement are presented in Figure 11 together with parts specifications. The trap depicted in Figure 11, when cooled with liquid nitrogen, protects the diffusion pump from vapors, which could be pyrolyzed in the presence of hot mercury vapors, thus decreasing pumping efficiency. It also prevents mercury vapors from entering the vacuum system. The two 2-mm oblique bore stopcocks shown in Figure 11 (shown as V2) aid in venting the trap and the mechanical forepump, respectively.

3.3.1 Gas Storage System

The uppermost section in Figure 8 depicts the gas storage assembly employed for storage of calibration and reagent gases condensible at -196°C. The Figure 12 schematic gives this in a greater detail, whereas an individual bulb is depicted in Figure 13. Typically, a quantity of purified calibration gas, known to give a pressure $<$ 760 mm when expanded within the storage bulb volume, is introduced into the bulb (see Figure 13) by condensation at -196°C in the U-trap portion followed by closing of the 4-mm stopcock and removal of the coolant.

3.3.2 Fractionation Train

The enlarged drawing of the fractionation train is given in Figure 14 and an individual section of the fractionation train showing the relative positions of a float valve, trap, and manometer is depicted in Figure 15. Figures 16-18 present the detailed schematics with dimensions of a mercury float valve, a mercury manometer, and a U-trap, respectively. The float valve in the fractionation train functions as the opening and closing device. To open the valve the line to the rough vacuum is pumped down followed by lifting of the

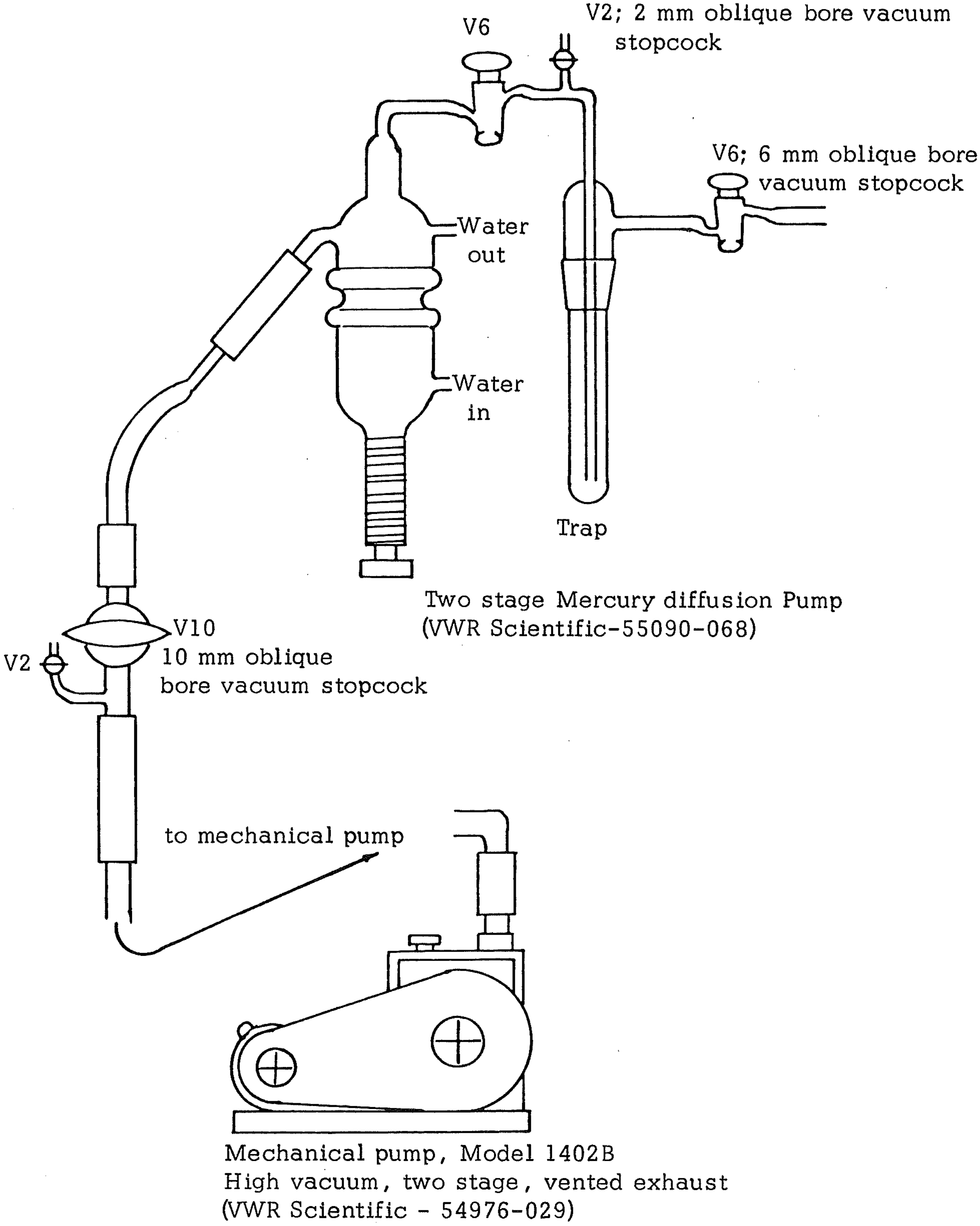


Figure 11: Pumping Assembly

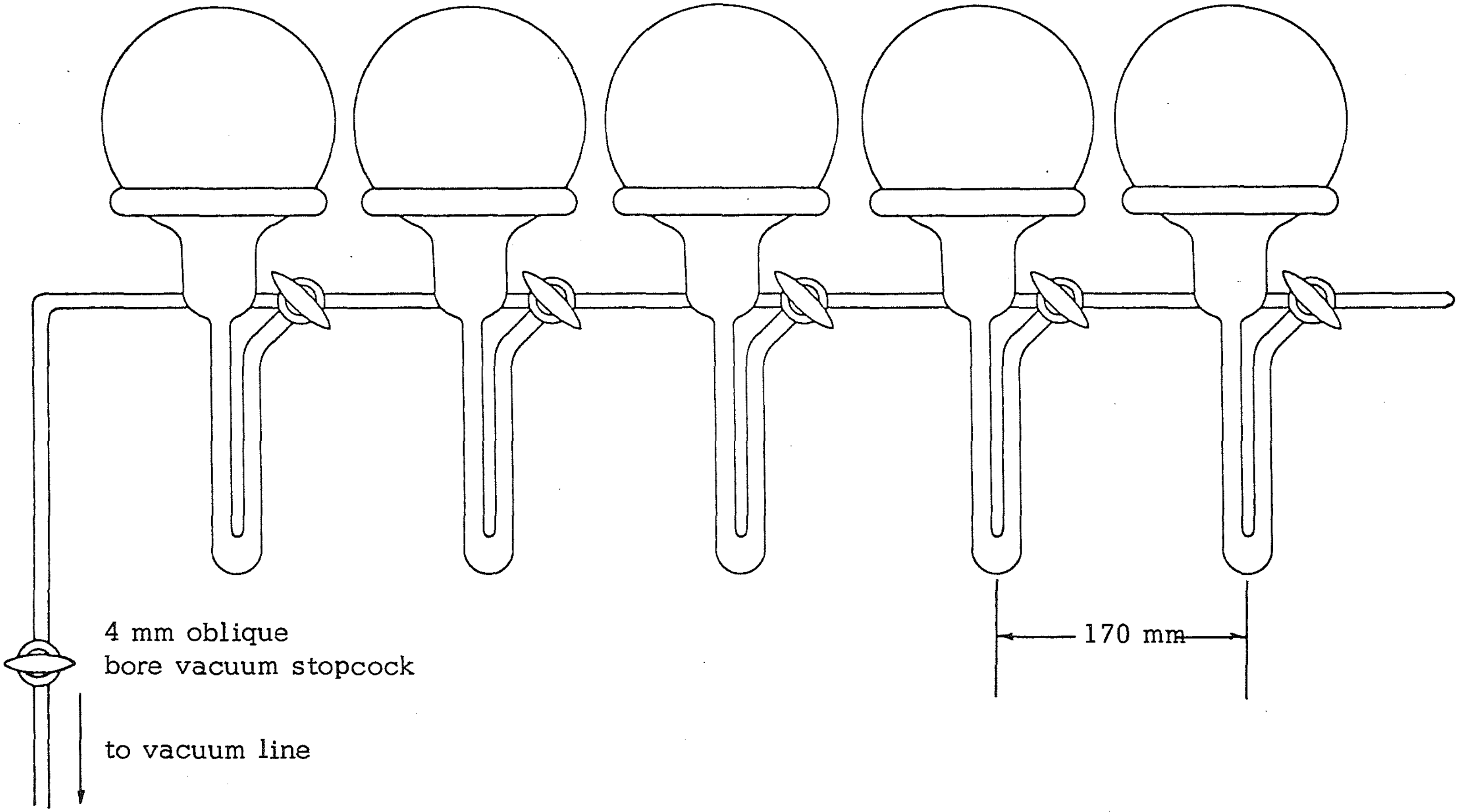


Figure 12: Gas Storage Assembly

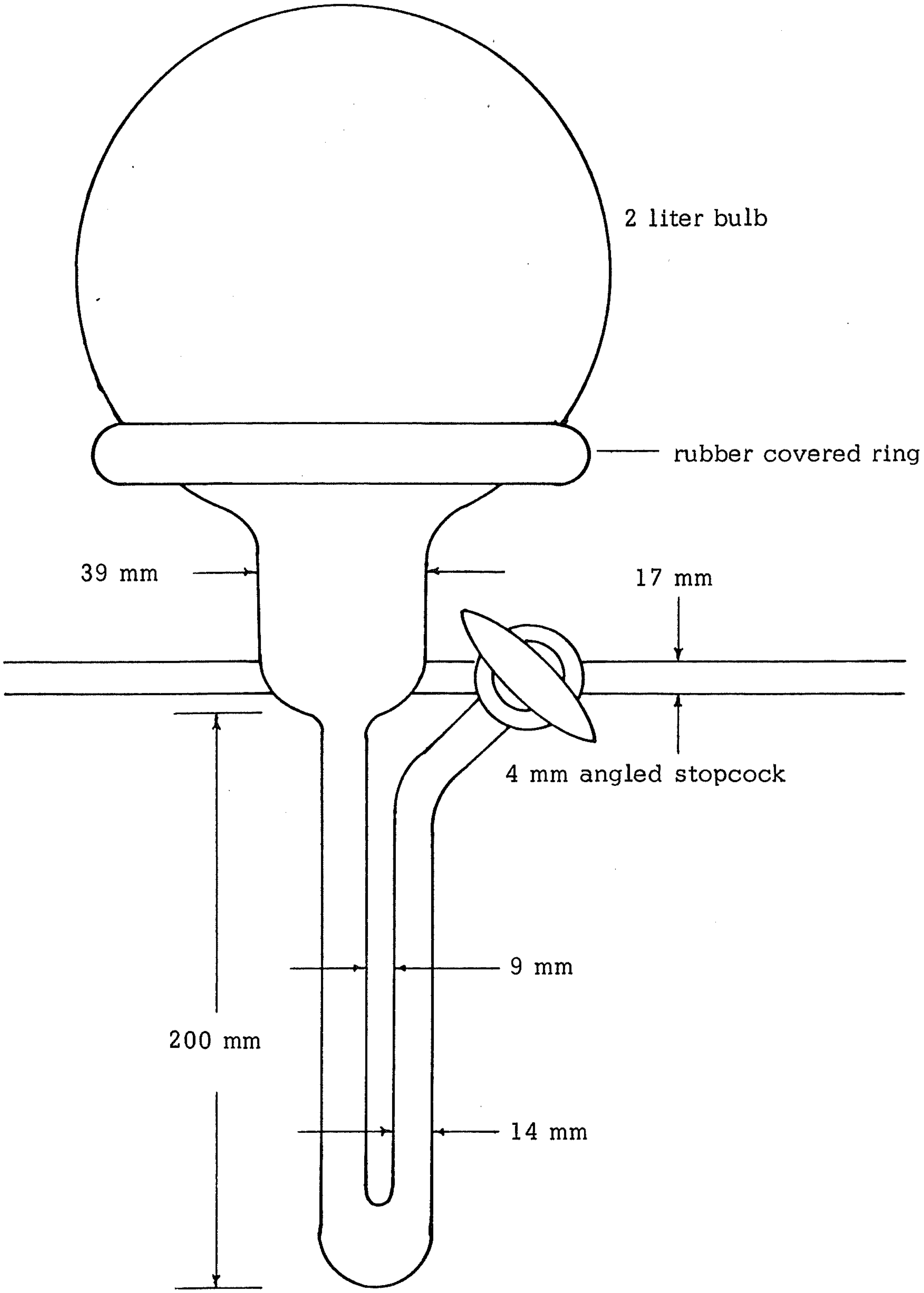


Figure 13: Gas Storage Bulb

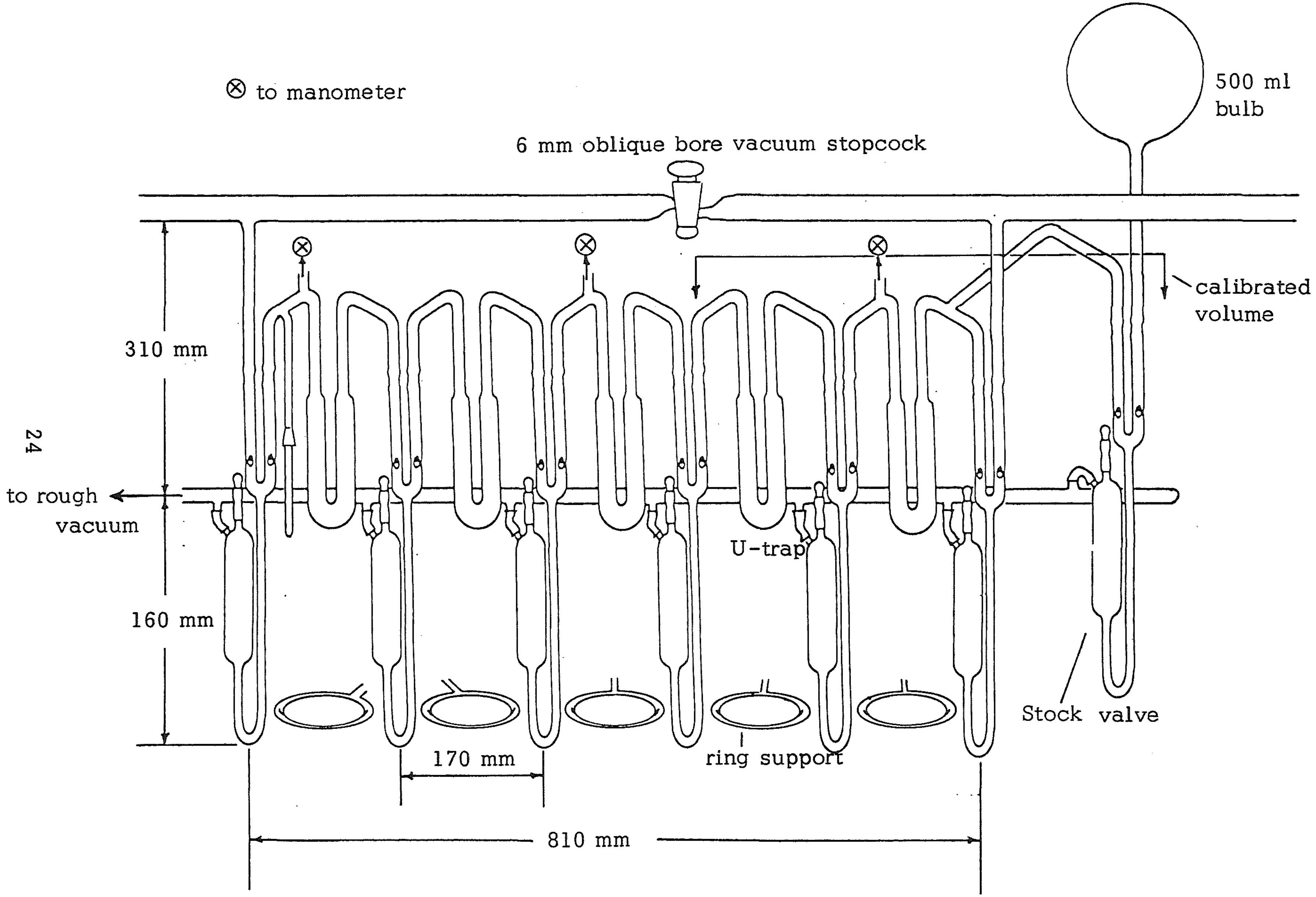


Figure 14: Fractionation Train

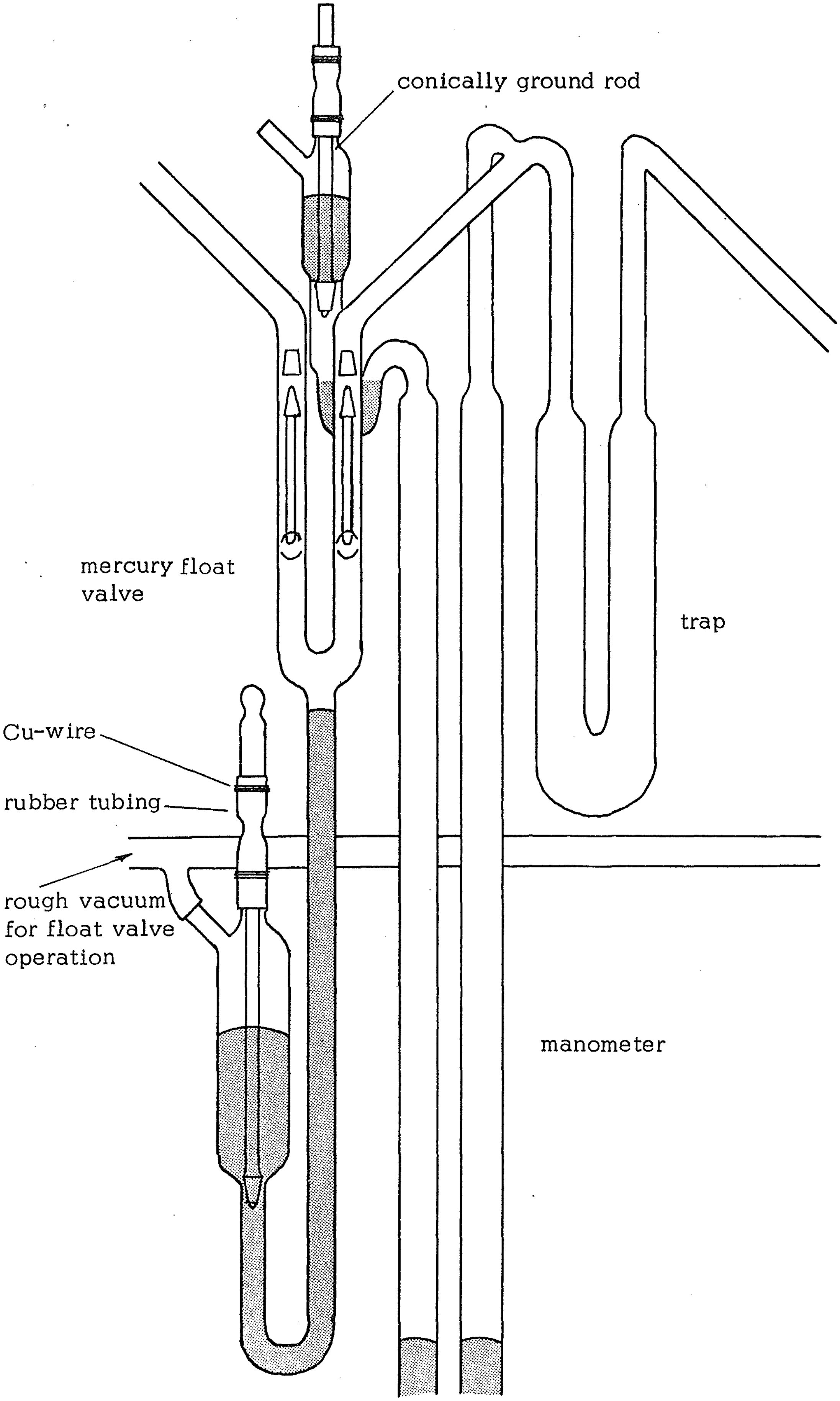


Figure 15: Complete Assembly of Stock Valve, Manometer, and Trap

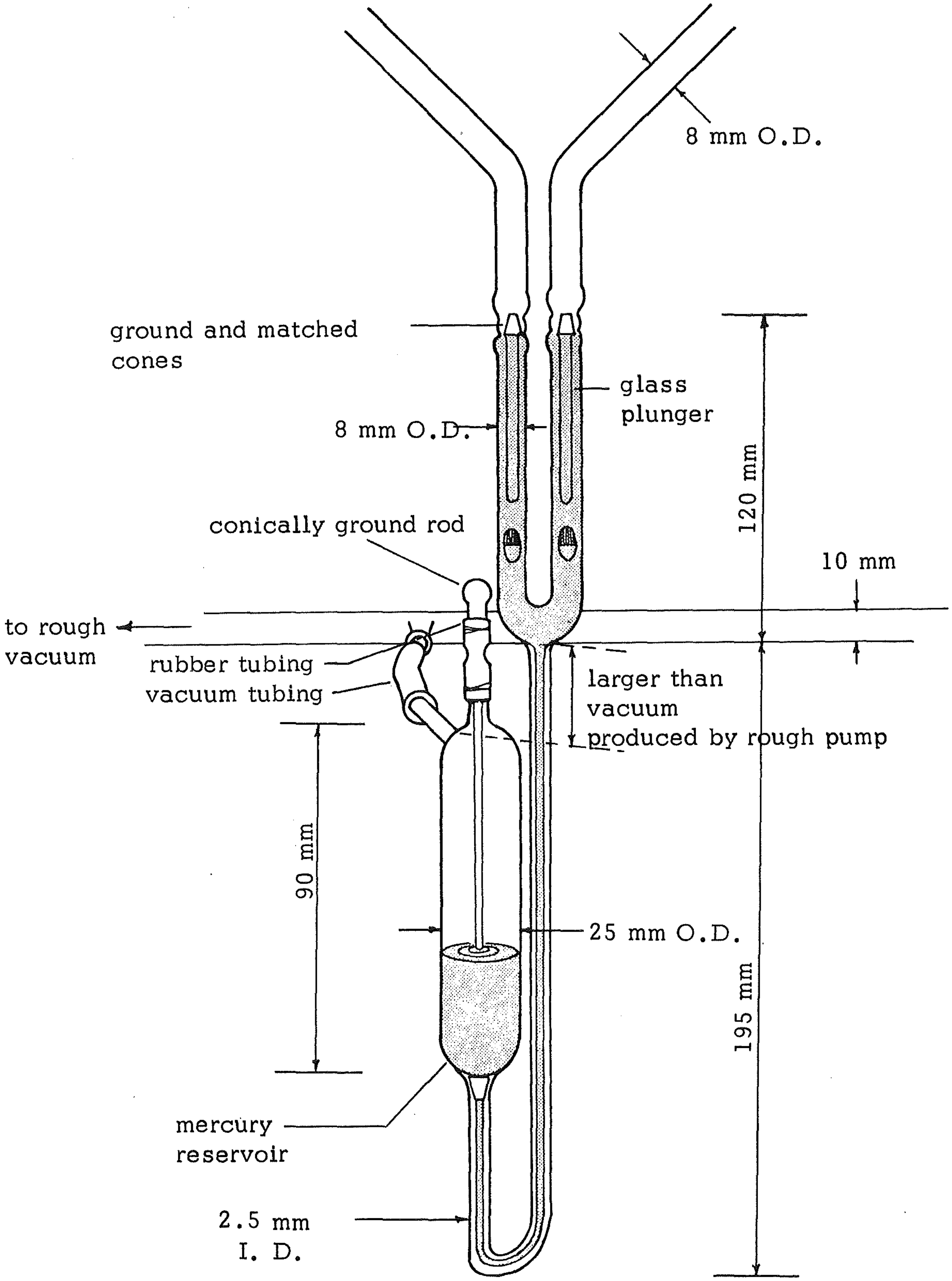


Figure 16: Stock Valve Arrangement

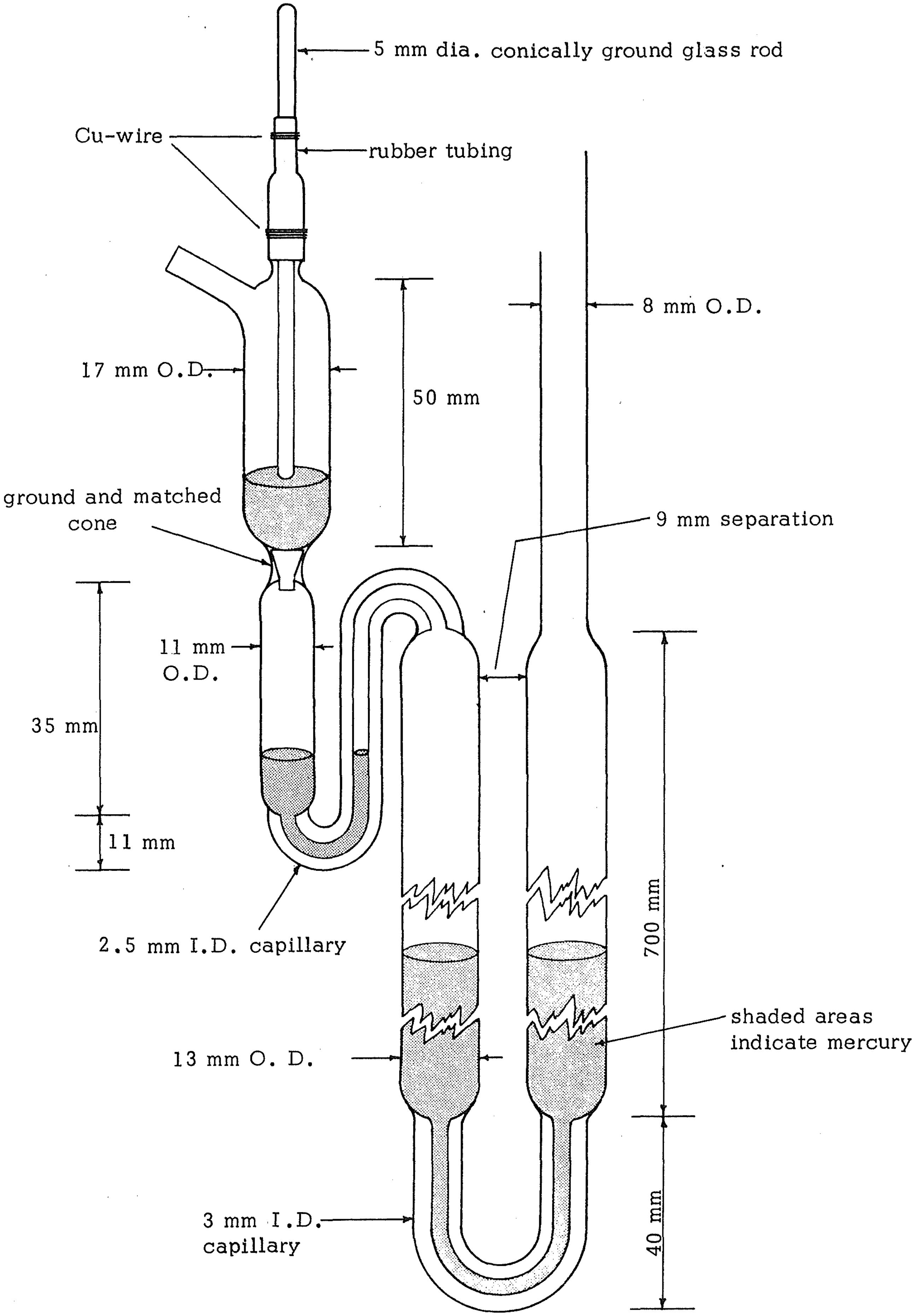


Figure 17: Manometer Assembly

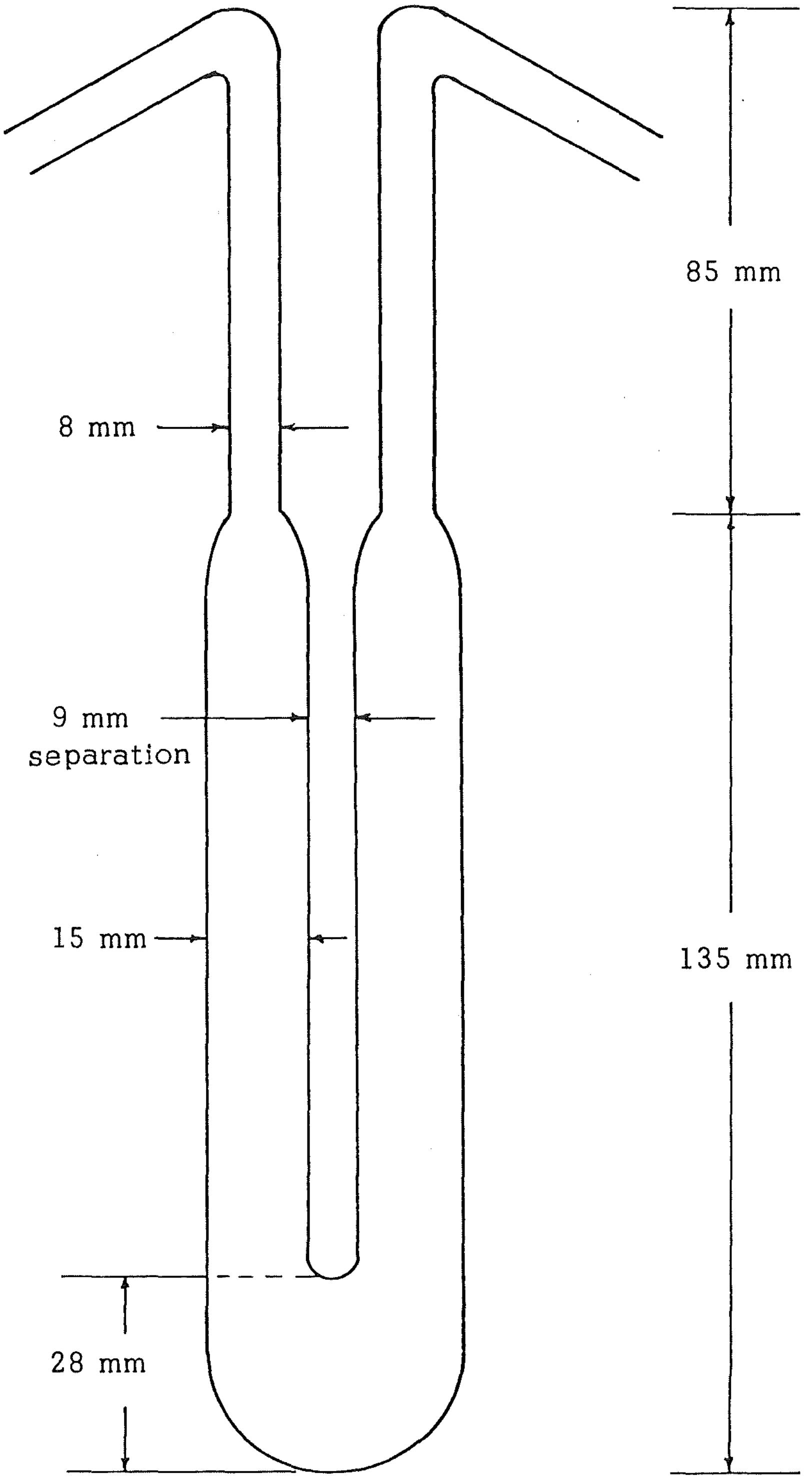


Figure 18: U-trap

glass rod (see Figure 16). This results in lowering of the mercury level in the valve, and opening of passage between adjacent traps. In order to assure efficient operation of the float valve it is essential that the conically ground rod shown in Figure 16 is tightly connected to the reservoir receiving the mercury upon valve opening and that the distance between the rough vacuum connection and the lowest part of the passageway is larger (in mm) than the rough vacuum produced by the pump (in mm Hg). This tight connection is made by stretching rubber tubing of appropriate inner diameter over the ground glass rod as well as over the neck of the mercury reservoir and securing the rubber tubing in this position by tying it to the rod and neck with copper wire. To close the valve requires bringing the rough vacuum line (see Figure 16) to atmospheric pressure, lifting slowly the conically ground rod and tapping the two glass plungers in the U-portion of the valve into place to produce a positive seal.

To produce a positive seal on the vacuum arm of the manometer (see Figure 17) the same principle is used as for sealing the mercury reservoir of the float valve, e.g. matched ground glass cone and stretched rubber tubing held in position with copper wire. In regard to the detailed diagram of the U-trap (Figure 18) it is only necessary to mention that the U-shaped bottom should be blown to produce a relatively thin glass wall so that mechanical stress introduced by repeated cooling and warming is kept to a minimum.

3.3.3 Liquid Storage

The enlarged drawing of the liquid storage system is depicted in Figure 19 with the individual trap-valve assembly given in Figure 20. The liquid transfer operation into the storage is analogous to that described for the gas storage with the exception that no pressure precaution required with

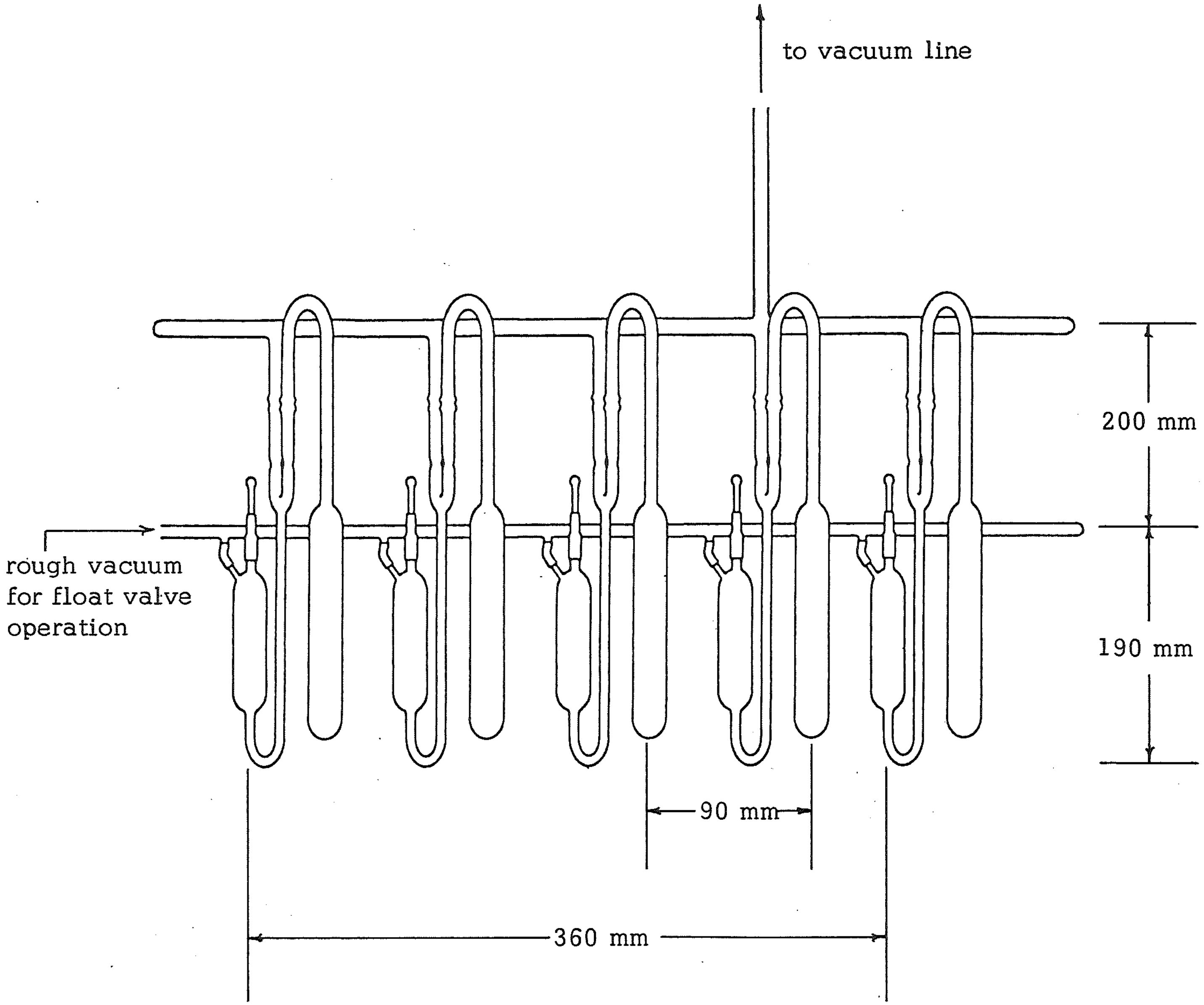


Figure 19: Liquid Storage Assembly

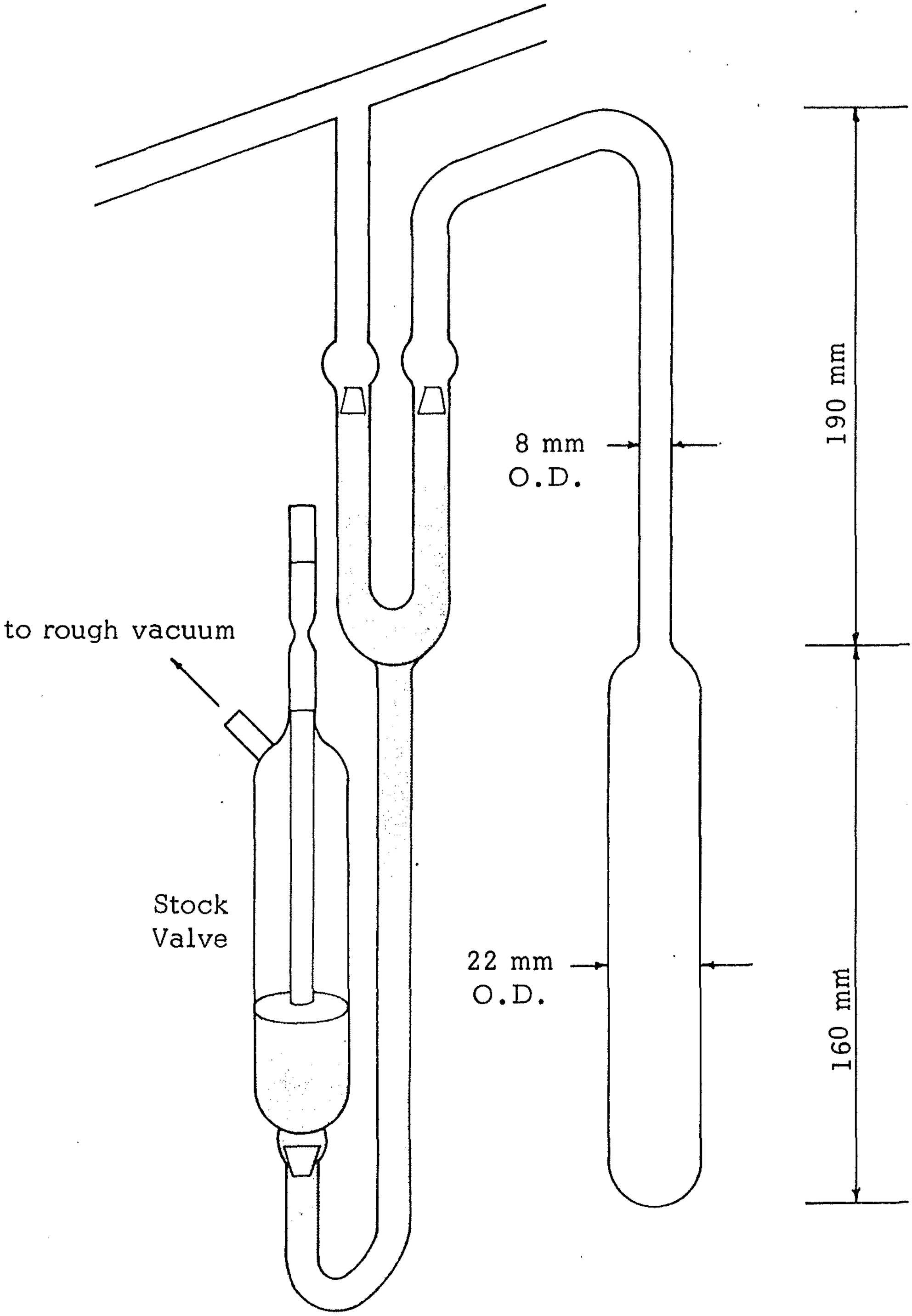


Figure 20: Volatile Liquid Storage

gases (i.e. materials below room temperature) needs to be taken, although the storage must never be filled completely with liquid.

3.3.4 Transfer Manifold Arrangement

In Figure 21 is presented the detailed schematics of the inlet-outlet manifold arrangement which is located as shown in Figure 8 on both sides of the fractionation train. It provides for material introduction and withdrawal from the line, including among others, filling and emptying of the infrared cell (see subsection 3.3.7). Since these ground joint equipped in- and outlets are located on both sides of the fractionation train the work-up of a product mix fractionally condensed at five successively lower temperatures (the number of traps in the fractionation train) is greatly accelerated.

3.3.5 McLeod Gauge

The McLeod Gauge schematic is given in Figure 22; its operation is fully described by Sanderson.[7] In the vacuum line employed for the investigations described in this report the McLeod gauge was, due to space limitations, installed on the same side of the rack as the pumping system as indicated in Figures 8 and 21. In general, it should always be installed at the farthest possible distance from the diffusion pump thereby assuring that the entire vacuum system is properly evacuated and degassed.

3.3.6 Sprengel Pump

The schematic of the Sprengel pump with all critical dimensions is given in Figure 23. Its operation has been fully described by, among others, Bartocha, Graham, and Stone[8] and need not be included here. It is, however, worth mentioning that the pump must be securely supported due to the large weight of the mercury contained in it and that all connecting glass lines to the vacuum

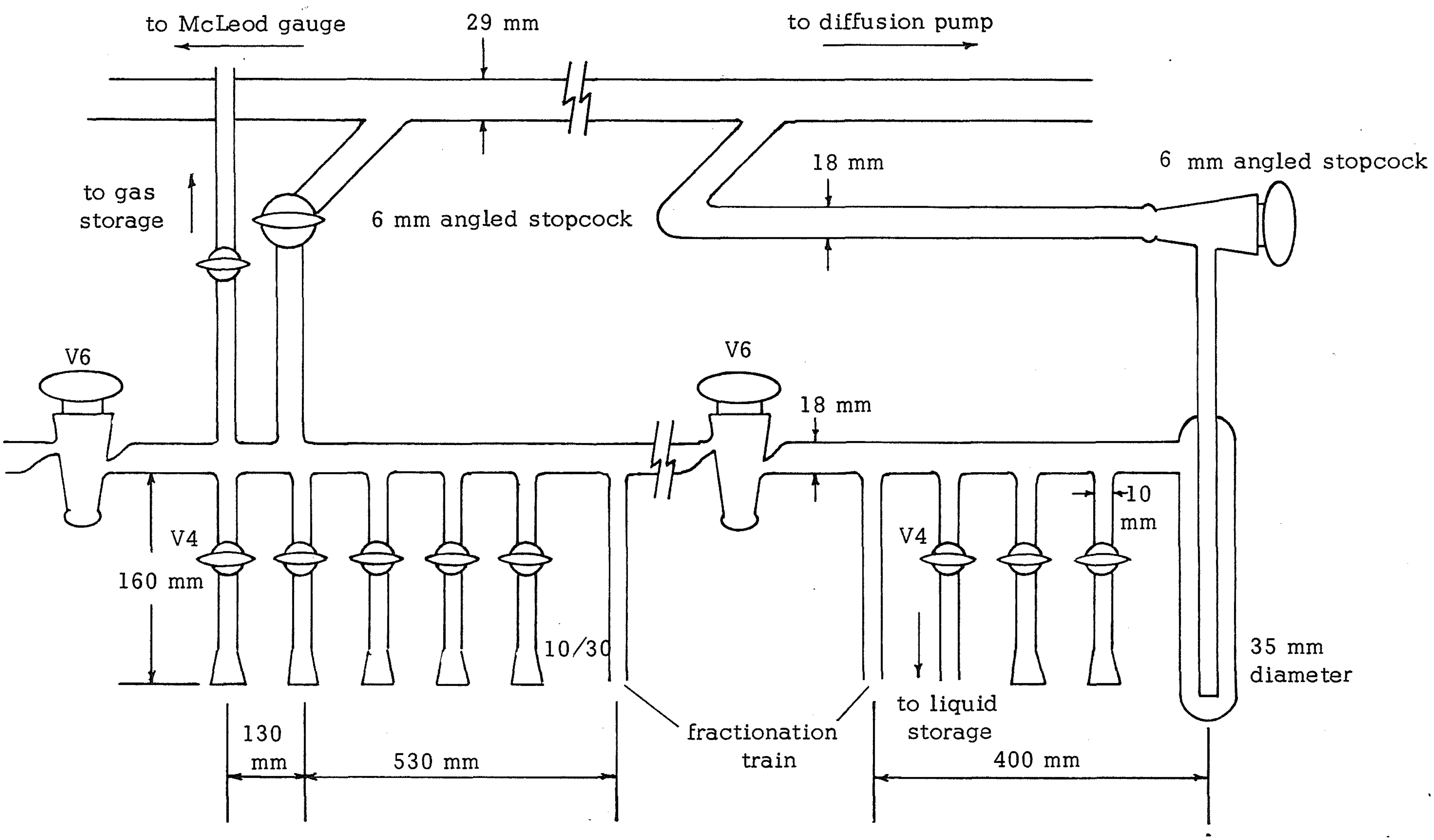
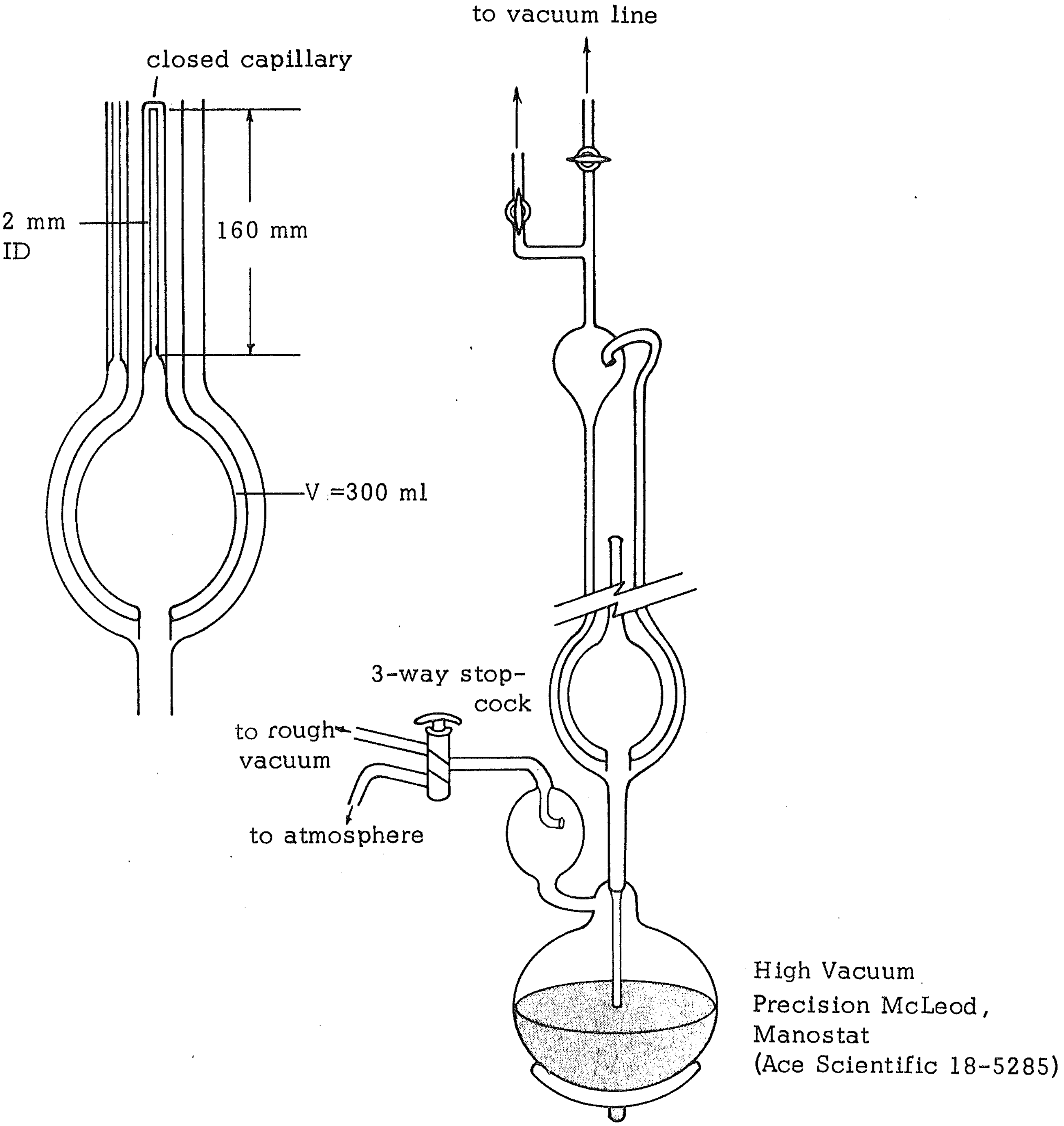


Figure 21: Transfer Manifold



High Vacuum
Precision McLeod,
Manostat
(Ace Scientific 18-5285)

Figure 22: McLeod Gauge

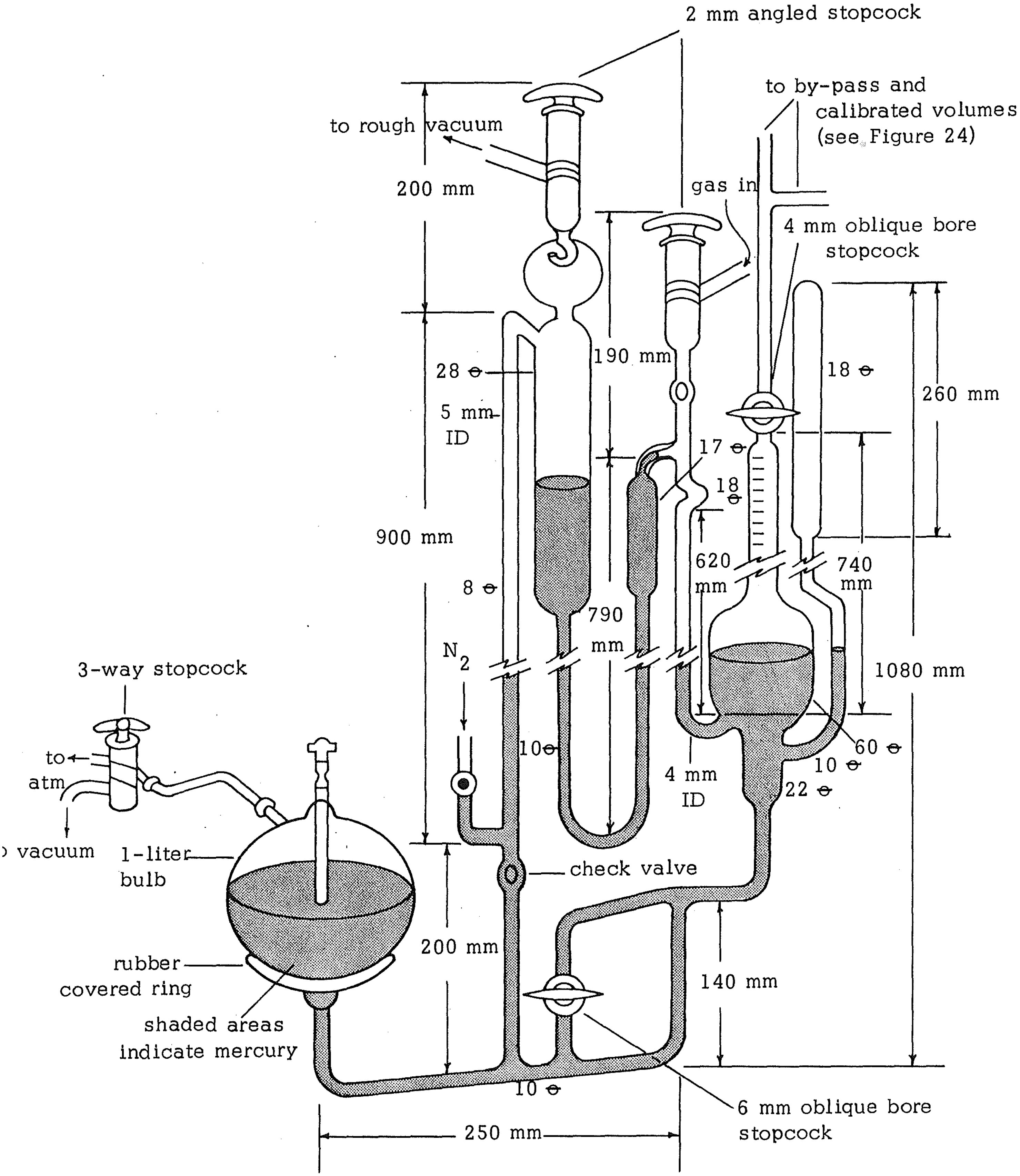


Figure 23: Sprengel Pump

system must be thoroughly annealed after filling with the required quantity of mercury. It must also be mentioned that the admission of the gas to be collected has to be done gradually to avoid pressure surges, if this gas stands under relatively high (e.g. $>$ 500 mm Hg) pressure.

Since the Sprengel pump was designed for the accurate collection and measurement of small gas samples the gas burette normally has a volume of 100 ml. In order to quantitatively measure larger gas samples ($> \sim$ 60 ml STP) it is therefore necessary to provide additional sampling volumes as shown in Figure 24. By installing above the gas burette the three bulbs as shown in Figure 24 four additional calibrated volumes in addition to the gas burette itself become available so that any quantity of gas can conveniently be collected and measured. To allow sample withdrawal (after measuring the total gas volume) for identification and determination of the composition by e.g. infrared, gas chromatographic, or mass spectral analysis, the outlet A (see Figure 24) is provided in the connecting line between the gas burette and the additional sample volumes.

3.3.7 Gas Infrared Cell Assembly

The infrared gas cell, although not an integral part of the vacuum system is a necessary component for determining infrared spectra of gases and highly volatile liquids. The schematic given in Figure 25 is self explanatory. In actual operation the infrared cell is attached to any of the inlets on the manifold (see subsection 3.3.4, Figure 21 or Figure 24) and evacuated. The known quantity of sample is then condensed in the finger cooled to -196°C. After closing the 4 mm and the manifold stopcocks the sample is warmed up to room temperature and the spectrum is recorded. To return the sample into the vacuum system, if desired, the cell is attached to the manifold, the volume between the

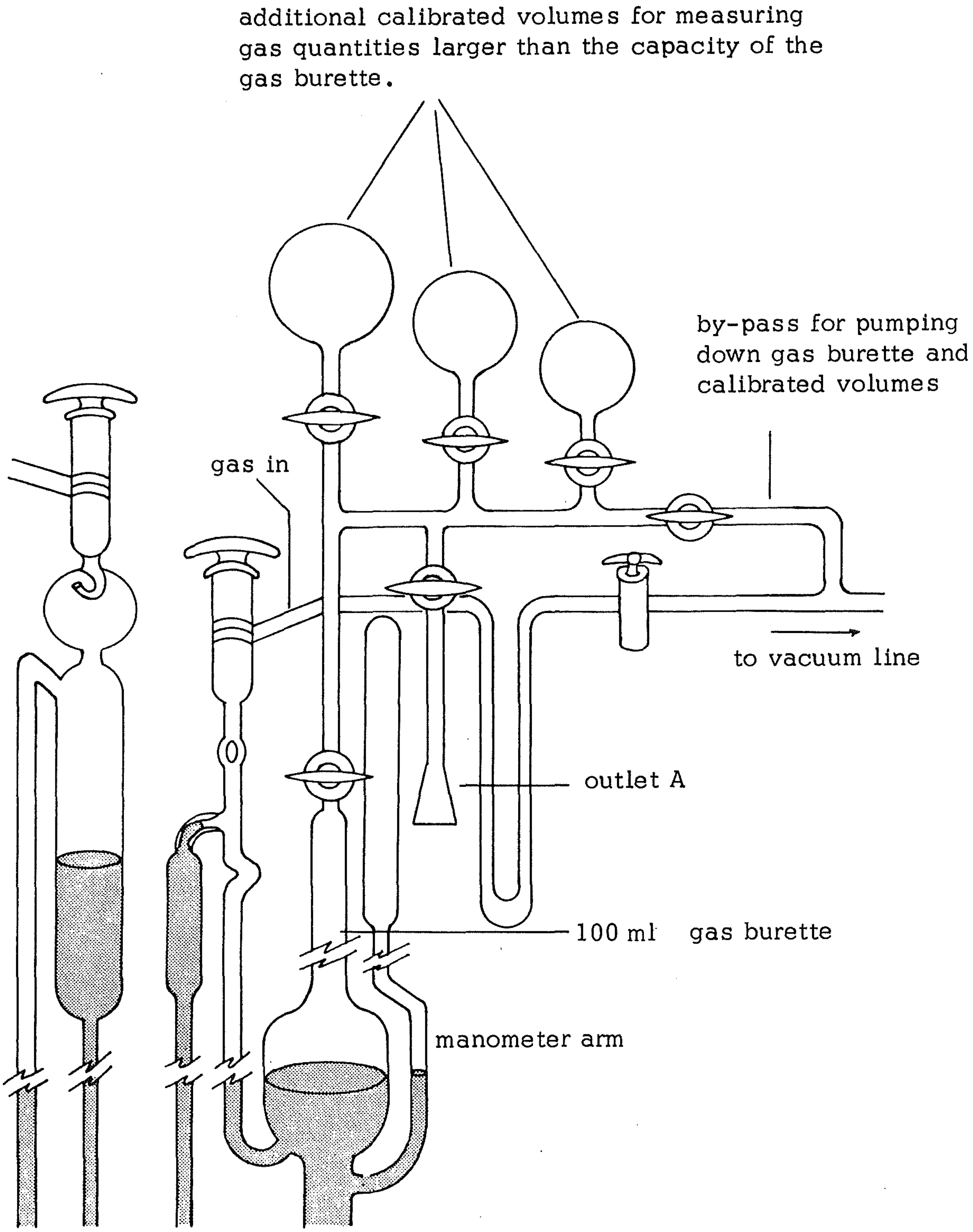


Figure 24: Sprengel Pump and Additional Measuring Volumes

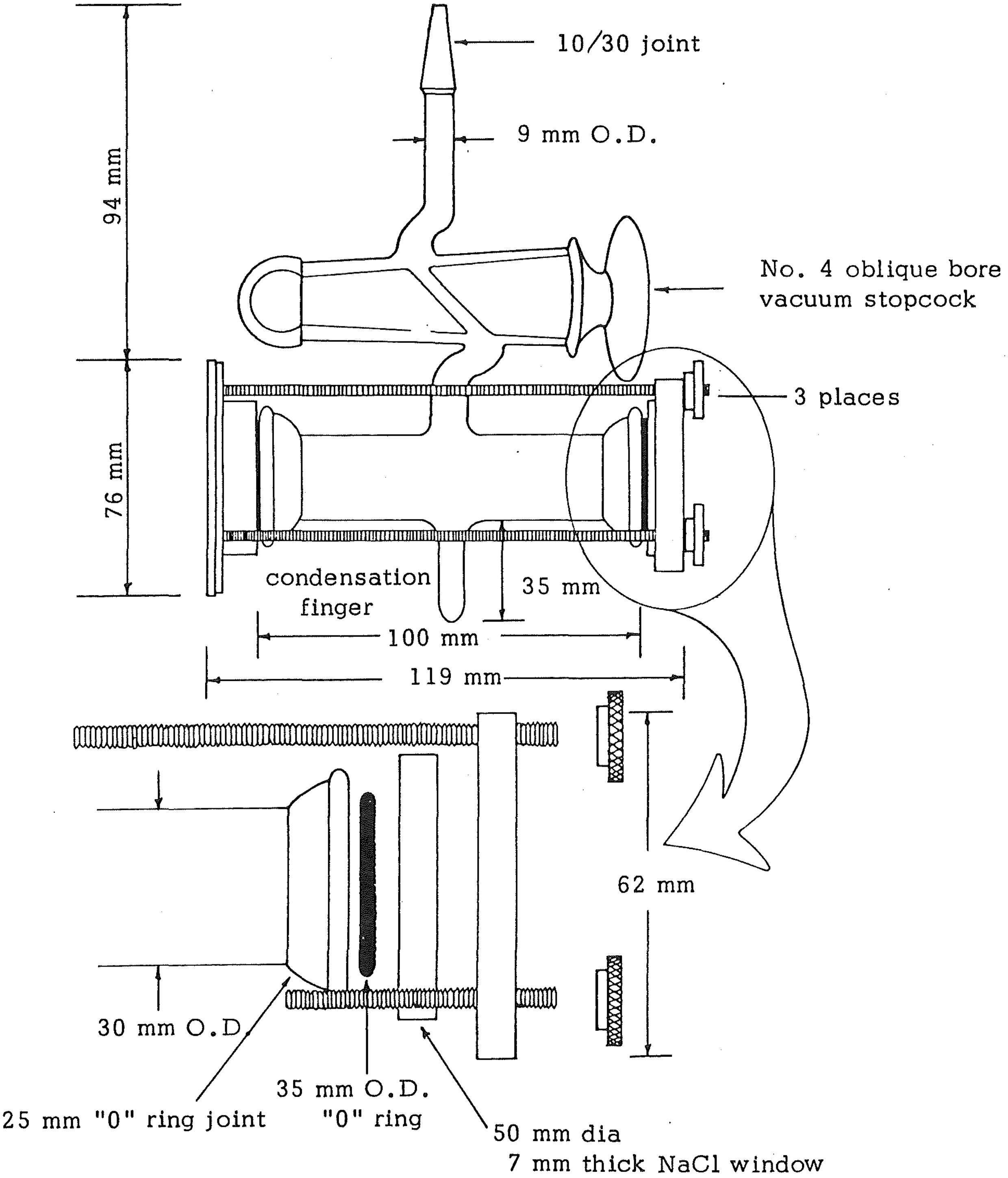


Figure 25: Gas Infrared Cell Assembly

4 mm stopcock and manifold stopcock is evacuated, and then the material present in the infrared cell is transferred quantitatively into the vacuum line by condensation.

3.3.8 Sample Ampoule

A sample ampoule, as is the gas infrared cell, is not an integral part of the vacuum line system, yet is required for any vacuum line operation whenever sample weight determinations and analyses such as gas chromatography, mass spectrometry, etc. are required. The schematic given in Figure 26 depicts a typical ampoule. For gases the volume of the ampoule is chosen so that the pressure of the gas within the ampoule is sufficiently lower than its vapor pressure to ensure behavior as ideal gas. This also applies to high vapor pressure liquids which most conveniently are handled in the gaseous state. For low vapor pressure liquids, e.g. those condensed at 0° or $-23^{\circ}C$, it is advantageous to make the ampoule volume as small as possible so that the volume of the gas phase above the liquid is comparatively small. It should be mentioned, however, that the volume <u>must</u> be larger than the volume of the liquid sample after warming to room temperature, e.g. to assure space for a gas phase, because otherwise explosion upon warming up will invariably result. The transfer process for condensible gases as well as liquids is analogous to that described for the gas infrared cell given in subsection 3.3.7.

3.3.9 Vacuum Line Operation and Calibration

The general methods and procedures employed in high vacuum line operations have been described in detail by Sanderson[7] and especially by Alfred Stock,[9] who contributed greatly to the development of procedures as well as devices. A special operation which was found to be necessary during

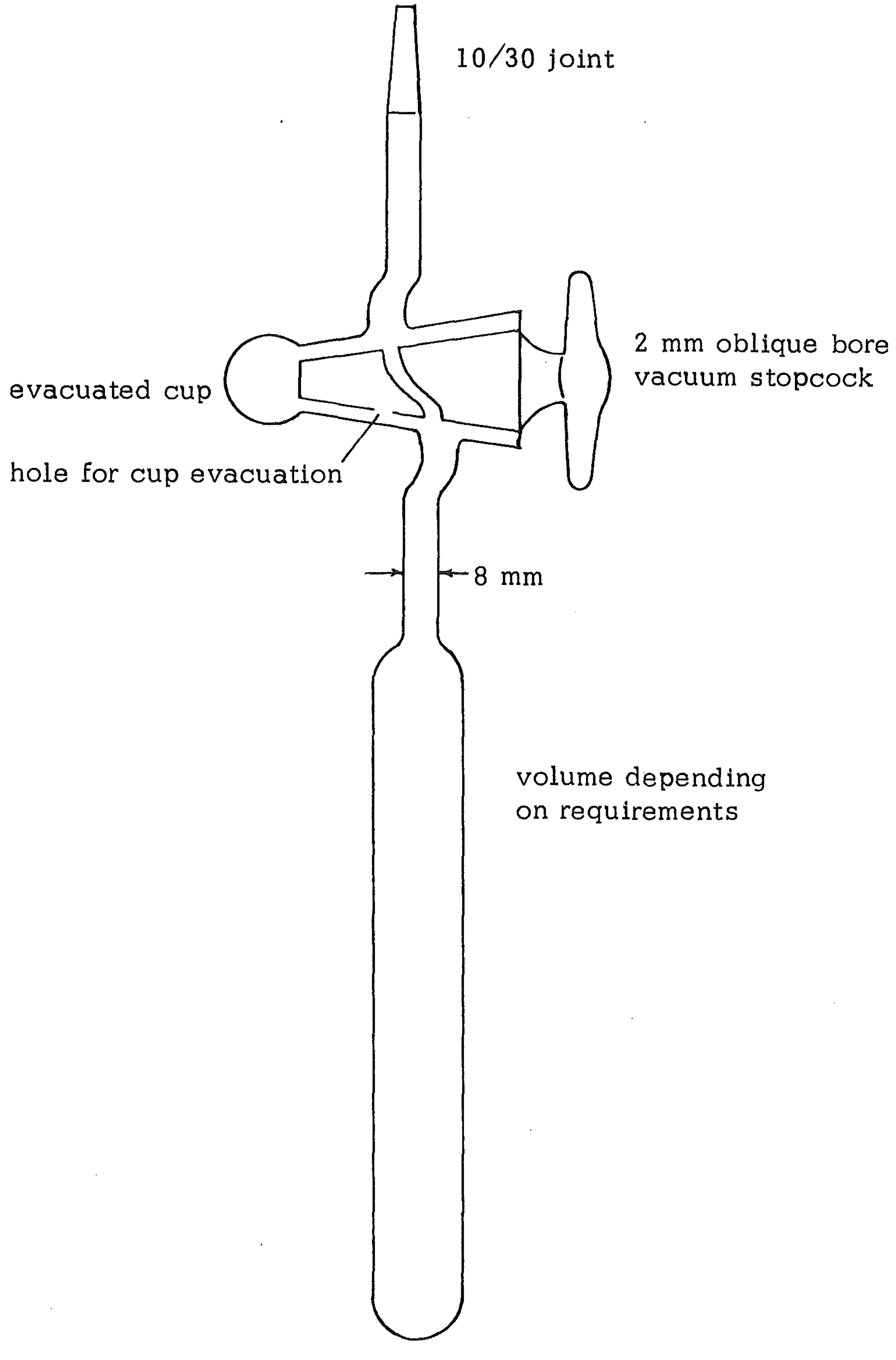


Figure 26: Sample Transfer and Storage Ampoule

this program was the degreasing of all stopcocks and ground joints after work-up of each degradation sample to assure that no products of intermediate volatility are retained in the grease (APIEZON-N) and carried over into the next product separation. After regreasing and evacuation the entire system exposed to the laboratory air was thoroughly flamed and degassed, as is common practice.

The major advantages of employing high vacuum techniques in an investigation such as the one performed under this contract are the quantitative material handling capability, which allows establishing mass balances, including e.g. oxygen uptake, the capability of separating complex product mixtures into fractions of different volatility, which are less difficult to analyse quantitatively, and the quantitative measurement on a weight as well as volume basis of all volatile materials including gases not condensible at liquid nitrogen temperature.

For the quantitative measurement of gases, selected volumes of the high vacuum system must be calibrated. The gas burette of the Sprengel pump is usually calibrated by the manufacturer by weighing in mercury at a constant temperature in 0.5, 1, and 5 ml increments. All other volumes in the vacuum system must be calibrated in the laboratory and recalibrated after each cleaning of the vacuum line which involved the mercury in the manometers or cutting of the line. Since the latter operations are necessitated frequently when working with the products of thermal oxidative degradation it is most convenient to determine the volume of a reference container with extreme accuracy and to use this container as a standardized volume. For a vacuum system as the one employed during this program it is best to use as the reference volume, a $\sim$ 250 ml thin glass wall bulb equipped with stopcock and a ground joint for ready attachment to the vacuum system.

As mentioned, this reference volume must be calibrated with utmost care and a minimum of five determinations must result in values deviating from the mean by not more than 0.1% in the case of a ~ 250 ml flask. It should be mentioned that the volume of the stopcock bore is included in the volume of the flask. This reference volume determination can be carried out by determining the difference between the weights of the evacuated (ground joint degreased) and mercury filled flask and dividing this weight difference by the density of mercury at the temperature the weight was taken. Employing distilled water instead of mercury is also acceptable since the weight of the bulb filled with water can normally be determined with greater accuracy than the weight involving mercury. A second method is to fill the calibrating flask at a known temperature (measured to $0.1^{\circ}C$) to a given pressure (determined to the nearest 0.1 mm Hg) of vapor tension pure carbon dioxide, to again determine the weight difference between the evacuated and "filled" stage, to divide this figure by the molecular weight of carbon dioxide, and to multiply by 22.414, the number of ml in one mmol of gas. Since the temperature and pressure of the carbon dioxide contained in the flask had been determined, the volume of the flask can be calculated, using the equation of state for ideal gases, as follows:

$$\frac{P_n V_n}{T_n} = \frac{P_1 V_1}{T_1}$$

where P_n = 760.0 mm Hg

$V_n = \frac{\text{weight } CO_2}{\text{MW } CO_2} \times 22.414$

$T_n = 273.16^{\circ}K$

P_1 = pressure of CO_2 in mm Hg

T_1 = temperature of CO_2 in $^{\circ}K$, e.g. $273.16 + t^{\circ}C$,

V_1 = volume of flask to be determined.

Having this reference volume calibrated in this manner all volumes in the vacuum line, e.g. the addition volumes to the Sprengel pump, the two right hand traps and the 500 ml expansion volume of the fractionation train (see Figures 8 and 14), or the trap in the sealed degradation system (see Figure 7A) can be calibrated using the same technique. In each instance three measurements should be within 0.3% of the mean value. Accordingly, the reference volume is filled with pure carbon dioxide, its pressure and temperature are recorded, which is followed by quantitative transfer of the gas into the volume to be determined by condensation at liquid nitrogen temperature. After removal of the liquid nitrogen bath and allowing the gas to completely equilibrate, pressure and temperature are again measured and the unknown volume calculated as above.

The volumes thus determined, however, will increase with increasing pressure due to the additional volume created in the manometer limb by the receding mercury. Inasmuch as constant bore glass tubing is used for the contruction of the manometer the additional volume created is a constant per unit of pressure, e.g. a factor of the dimension ml/mm Hg. This factor x is readily determined by successive volume determinations at increasingly higher pressures. Accordingly, volume V_1 at a pressure P_1 and volume V_2 at a higher pressure P_2 are determined as described above. Both these volumes are composed of two parts, the volume of the trap at zero pressure, v_o, and the volume of receded mercury, e.g. v_1 at pressure P_1. Since this volume v_1 is a linear function of pressure it can be expressed as $v_1 = P_1x$, so that the determination of this factor x is readily accomplished using a set of simultaneous equations, e.g.:

$$V_1 = v_o + x\,P_1$$
$$V_2 = v_o + x\,P_2$$

resulting in

$$v_o = V_1 - x\,P_1$$
$$V_2 - V_1 = x\,(P_2 - P_1)$$

and solving for x:

$$x = \frac{V_2 - V_1}{P_2 - P_1} \left[\frac{\text{ml}}{\text{mm Hg}}\right]$$

Obviously, for any volume measurement performed in the thus calibrated system this volume correction factor must always be added to the trap volume at zero pressure, e.g. $V = V_o + x\,P$.

3.4 PRODUCT SEPARATION AND ANALYSIS

3.4.1 Vacuum Line Separations

The stagnation burner and sealed system operations were described in sections 3.1 and 3.2, respectively. In each instance the volatile condensibles were separated from the involatile residues and noncondensibles indicated with the exception that in the case of the sealed system a measured portion of the mixture of condensible volatiles and noncondensibles was removed from the total sample (see subsection 3.2.3) to allow the measurement of the noncondensibles with the aid of the Sprengel pump followed by their analysis using infrared spectroscopy and mass spectrometry. The condensible volatiles contained in this portion of the total sample were separated from the noncondensibles using condensation at -196°C, weighed and subjected to wet analysis.

The bulk of the degradation products mixture was in each instance freed from the noncondensibles (e.g. the components of air, CO, CH_4, or H_2) by evacuation of the sealed system through four liquid nitrogen cooled traps. The products condensed in these four traps were then quantitatively collected in trap 1 of the degradation assembly (see Figure 7A) before being subjected to fractional condensation in traps kept at 0, -23, -78, and -196°C, using the fractionation train depicted in Figure 14. This fractionation was continued until all products had evaporated out of trap 1. Subsequently the vapor pressures of the -23 and -78°C fractions were measured and the volume of the -196°C fraction was determined. Knowing the volume and weight of the -196°C fraction the average molecular weight can be calculated which can be used as a correlation with the average molecular weight derived from the identification and quantitation of all components of this fraction, thus providing an independent assessment of the accuracy of this analysis.

After thus measuring the volumes of all fractions present in the gaseous state (liquid nitrogen noncondensibles and -196°C fraction) each of the five fractions was transferred into a pre-weighed evacuated ampoule (see Figure 26) for determination of the weight and analysis by the methods described below.

3.4.2 Gas Chromatographic and Mass Spectral Analyses, Combined GC/MS

In all the GC/MS analyses a mass spectrometer scanning rate of 2 sec/decade was employed, the mass: charge ratio scanned was from m/e = 12 to m/e = 500. The identification of species was performed using the spectra library of the data system and scan printout, followed by manual search and identification. The library search utilizes a reference tape containing the mass spectra of over 6,000 organic compounds based on the "Atlas of Mass Spectral Data".[10] In the manual analysis of spectra the reference works by Cornu and

Massot,[11] the Mass Spectrometry Data Centre,[12] and Stenhagen[13] were employed in addition to the above referenced Atlas.

The noncondensibles were subjected to mass spectral analysis mainly to determine oxygen, nitrogen, CO, and CH_4 using oscillograph output. The carbon monoxide content was further checked by gas infrared analysis; this was accomplished by expanding a portion of the noncondensibles collected in the Sprengel pump into the gas infrared cell, measuring the pressure, and comparing the absorbance at 4.58 μ with that of a standard.

Knowing the total quantity of gas contained in the sealed system (volume V_1) up to stopcock B (see Figure 7A), as well as the quantity of gas contained in volume V_2 (comprising the sample used for collection of noncondensibles and for wet analysis) and having established the quantity of noncondensibles present in volume V_2 by the Sprengel pump technique (see subsection 3.3.6) the total oxygen consumption and CO and CH_4 production was thus calculated.

The initial step in the analysis of all fractions obtained by vacuum line separation as described in subsection 3.4.1 was to record the mass spectrum of the gas phase of each fraction prior to gas chromatographic analysis. The same applied to the liquid portion of all the fractions. The "bulk" mass spectral analysis, prior to gas chromatography, pinpoints clearly the major products present and allows the detection of constituents which might be retained by the gas chromatographic columns. This method in conjunction with infrared spectroscopy and gas chromatography, assures that all components present in measurable quantities will be detected. All the mass spectral determinations were performed using a DuPont Model 21-491B mass spectrometer coupled to a DuPont 21-094-91 data acquisition and processing system with library search capability. After carrying out these "bulk" mass spectral analyses all fractions obtained via high vacuum separation were subjected to combined GC/MS (gas chromatography/mass spectroscopy).

The $-196^{\circ}C$ fractions contained no liquid portion and thus were examined by mass spectrometry, infrared spectroscopy, gas chromatography, and GC/MS as gases only. The $0^{\circ}C$ fractions had negligible vapor pressures and were therefore analyzed as liquids only using the above delineated methods. The -23 and $-78^{\circ}C$ fractions consisted of both gas and liquid phases and these phases had to be analyzed separately. To obtain weight factors for the liquid and gas phases the weight of the liquid portion was determined after the ampoule was cut apart and the weight of the gas phase was taken as the difference between the total and liquid weights. Samples from the liquid phases were withdrawn with micro syringes for gas chromatographic analyses and the remaining liquid was reweighed and analyzed for Cl^- and CN^- by titration.

Gas chromatographic separations were conducted using two basic instrumentations, a Loenco Model 70 and the GC/MS combination. The Loenco Model 70 dual column gas chromatograph was equipped with a calibrated gas inlet system; the effluent stream of the sample column was split 1:10 between a flame ionization and a thermal conductivity detector operated at 100 ma. The GC/MS combination consisted of a modified single column Varian Aerograph gas chromatograph with the effluent stream split 1 : 1.34 between the flame ionization detector and the inlet to the mass spectrometer. Two columns were employed in these analyses: (i) a 1/8" x 10' stainless steel column packed with 4% OV-101 on Chromosorb G, 80/100 mesh and (ii) a stainless steel 1/8" x 8' column packed with Porapak Q, 80/100 mesh. The helium flow used was 37 ml/min and the temperature was programmed from 50 to $220^{\circ}C$ at $7^{\circ}C$/min in the case of Porapak Q column and at 5°C/min in the case of the OV-101.

All organic liquid layers were investigated using the GC/MS combination and the OV-101 column in the Varian Aerograph. All other fractions and parts of fractions, e.g., the gas phase of the -78°C fraction or the aqueous layers, were run over Porapak Q columns twice using first the Loenco Model 70 gas chromatograph and then the GC/MS combination. This duplication was necessary since the latter is equipped only with a flame ionization detector, which does not detect important species such as HCl, HCOOH, COS, SO_2, CS_2, CO_2, and water, all of which had to be quantitated in order to obtain an overall mass balance. The Porapak Q column installed in the GC/MS combination was used mainly for identification purposes, whereas the quanitative determinations were made using the Loenco Model 70.

Retention times and area factors for all definitely identified products were obtained by calibrating with substances of known purity. Only those decomposition products were considered definitely identified for which retention time, infrared, and the mass spectral breakdown patterns were found to be in agreement. All the quantitations were based on the responses of the flame ionization and thermal conductivity detectors. In the instances when specific compounds were not available to obtain the area factors by calibration with a standard of known purity the latter were calculated based on carbon-content and functional resemblance to standards on hand. The mass spectrometry in the GC/MS mode was utilized only as a material identification device not as a quantitative tool. This was not true with respect to gases such as nitrogen, oxygen, CO and CO_2 where mass spectrometric output was employed in calculating the partial pressure or percent of a given gaseous component. However, this required a calibration run just prior to and after each sample analysis to obtain reliable factors and utilizing the recording oscillograph, not computer output.

3.4.3 Miscellaneous Analyses

Infrared spectral analysis performed on gases was utilized both for supplementary component identification and as a quantitative technique, the latter specifically to determine CO, N_2O, CO_2 and PH_3. Infrared spectroscopy was also employed to differentiate between stereoisomers and in certain instances positional isomers. The former are indistiguishable using mass spectrometry; this also applies to some positional isomers.

For the gas samples 10 cm gas cells were employed. All condensed phases were run squeezed between sodium chloride windows, if necessary using silver spacers. The spectra were recorded using a Perkin-Elmer Model 21 double beam infrared spectrophotometer.

Hydrogen halides do not lend themselves to infrared, mass spectral and gas chromatographic analyses and had to be determined by wet analysis as mentioned in subsections 3.4.1 and 3.4.2. To determine hydrogen halides quantitatively in gaseous samples a measured quantity of gas was condensed onto ice at -196°C, using the vacuum line technique, and the halide ion was determined by Volhard titration because the results obtained using specific ion electrodes were found to be erratic and unreliable due to the presence of the other components of the mixture.

In the cases where free ammonia was present in the -196°C fractions it was determined, in addition to infrared spectroscopy and mass spectrometry, by acid titration on an aliquot of the -196°C fraction which had been condensed onto water at liquid nitrogen temperature. Cyanide ion was determined using Liebig's method of titration in the presence of potassium iodide. However this method was found to be of low sensitivity. In conjunction with the generally low cyanide concentrations and the small sample sizes available the results for CN^- obtained by titration normally were of the same order as the experimental error of the method.

3.4.4 Involatile Products and Residues Analyses

The involatile residues left in the heating finger of the sealed system and those deposited on the walls of the 5-liter bulb as well as the residues left on the platinum tray and in the trapping arrangement of the stagnation burner were quantitatively collected and weighed to establish an overall mass balance.

In the case of the sealed system care was taken to separate the residues in the finger from the deposits on the wall which consisted of compositions volatile at the degradation temperature, yet involatile at room temperature. These deposits, after weighing, were subjected to infrared spectral analysis and, when feasible, to gas chromatography. Whenever the residues in the degradation finger were liquids (as in the case of phosphate esters) or materials other than chars, these were treated in the same manner as the deposits on the walls so that the quantity of products such as phosphoric acid as well as the quantity of unreacted test material, e.g. phosphate ester, could be determined.

In the case of the stagnation burner the materials involatile at the degradation temperature remained on the platinum tray, whereas the components volatile at the decomposition temperature, but involatile at room temperature, were retained in the -78°C trap (see Figure 1). The latter were subjected to the same analysis as described above for the deposits formed on the walls of the 5-liter bulb.

3.4.5 Thermal Analysis of Test Samples

Thermogravimetric analyses and/or differential thermal analyses have been performed on all the materials studied to determine thermal characteristics of these compositions, e.g. boiling point, melting point, rate of evaporation, degradation onset temperature, and extent of degradation at specific temperatures. Thermogravimetric analyses were also employed to aid in finding out the composition of certain samples; this was especially useful in those instances where infrared spectral techniques and gas chromatography could not be utilized, i.e. in the case of conveyor belt samples.

The thermogravimetric analyses were conducted in air using a DuPont 990-951 thermal analysis system programmed from 20 to 600°C at a heating rate of 10°C/min. The differential thermal analyses (DTA) were performed in air, using the same instrumentation by programming at 5°C/min from 20 to 400°C.

3.4.6 Calculations

Since the weight of all the fractions and the quantity (in mg) of the components of each fraction were determined as discussed in the preceding subsections the products could be calculated in mg of product/g of sample subjected to the test. The results obtained from infrared and mass spectral analyses on gases were in mmoles or volume percent and had to be transformed into mg data based on the component's molecular weight and total fraction volume.

3.5 LISTING OF MATERIALS STUDIED AND TOXIC LOAD DATA SUMMARY

3.5.1 Material Listing

In Tables I-VIII are compiled the materials investigated under

TABLE I

LIST OF BASIC POLYMERS STUDIED

Uncured Neoprene Rubber;[4] neoprene gum WRT; manufactured by duPont de Nemours and Company.

Cured Neoprene Rubber;[4] neoprene gum WRT; manufactured by duPont de Nemours and Company, product cured according to standard recipe.

Uncured Styrene-Butadiene Rubber;[4] SBR gum 1502, manufactured by Firestone Tire and Rubber Company.

Cured Styrene-Butadiene Rubber;[4] SBR gum 1502, manufacured by Firestone Tire and Rubber Company and cured according to recipe given in Table

Polyvinyl Chloride Resin;[2] polyvinyl chloride resin manufactured by U. S. Rubber Company; pressed into pellets.

TABLE II

LIST OF FIBERS STUDIED

Nylon 6 Resin;[3] prepared by Dr. J. Smith of Allied Chemical Corporation.

Nylon 6, 6 Fiber;[4] nylon type 728, 1260 denier; manufactured by duPont de Nemours and Company.

Dacron Polyester Fiber;[4] dacron polyester type 68, 1000 denier, manufactured by duPont de Nemours and Company.

Rayon Fiber;[4] viscose rayon tire cord; manufactured by FMC Corporation.

TABLE III

LIST OF ADDITIVES, FLAME RETARDANTS, PLASTICIZERS, AND PRESERVATIVES STUDIED

Diphenyl Phthalate Plasticizer;[4] manufactured by Monsanto Company.

Di-(2-ethyl hexyl)sebacate Plasticizer;[4] obtained from Pfaltz and Bauer, Inc.

Dioctyl Phthalate Plasticizer;[3] obtained from Analabs, Inc.

Tributyl Phosphate Plasticizer;[4] No. 2957, Lot No. D2A; obtained from Eastman Kodak Company.

Tritolyl Phosphate Flame Retardant Plasticizer;[4] No. 1483, Lot No. 691A, obtained from Eastman Kodak Company.

Tri-p-tolyl Phosphate Flame Retardant Plasticizer;[4] MCB T6565 TX 1565; obtained from MCB Manufacturing Chemists.

Tris (dichloropropyl)phosphate Flame Retardant;[4] Fyrol FR-2; manufactured by Stauffer Chemical Company.

Tris(2-chloroethyl)phosphate Flame Retardant;[6] No. 11966-0, Lot No. 022557; obtained from Aldrich Chemical Company.

Tris(2,3-dibromopropyl)phosphate Flame Retardant;[6] No. 17168-9, Lot No. 022637; obtained from Aldrich Chemical Company.

Chlorinated Hydrocarbon (liquid);[3] Unichlor 70L-190; manufactured by Neville Chemical Company.

Chlorinated Hydrocarbon (solid);[6] Chlorowax 70; manufactured by Diamond Shamrock Chemical Company.

Dimethyl Chlorendate;[6] Lot No. B12-417-1, manufactured by Velsicol Chemical Corporation.

Methyl Pentachlorostearate;[6] No. MPS-500, manufactured by Hooker Chemical Corporation.

TABLE III (cont'd.)

LIST OF ADDITIVES, FLAME RETARDANTS, PLASTICIZERS, AND PRESERVATIVES STUDIED

Pentachlorophenol;[6] No. P260-4, Lot No. 122047, obtained from Aldrich Chemical Company.

Decabromodiphenyl Oxide;[6] No. DE-83P, Ref. No. H-1482, manufactured by Great Lakes Chemical Corporation.

TABLE IV

LIST OF CONVEYOR BELTS STUDIED

E-1, neoprene-fire resistant;[3] manufactured by B. F. Goodrich Company. Contains: polychloroprene, zinc oxide, magnesium oxide, polyethylene lubricant, carbon black, chlorinated hydrocarbons, phosphorus, fatty acid, phthalate plasticizers.

F-7; (BFG No. 200 NF Caricoal) BFG Neocaricoal 200/NF; (ISG 206);[3] based on TGA the polymer component is neoprene.

F-10; Acme HNCO Used Cotton Nylon/7; (ISG 209);[3] based on TGA the polymer component is neoprene.

E-2; PVC-fire resistant;[3] manufactured by B. F. Goodrich Company. Contains: polyvinyl chloride, antimony oxide stabilizer, calcium oxide, plasticizers, thickener, coloring agent.

F-3; H New Scan (Scan PVC); (ISG 202);[3] based on TGA the polymer component is PVC.

F-6; Scandura PVC Used; (ISG 205);[3] based on TGA the polymer component is PVC.

Fenner-American; Fenner American; PVC Impregnated;[6] received from the Bureau of Mines.

Scandura;Scandura Gold Line II, Mesa No. 28-1-5-77;[6] fire resistant, obtained from the Bureau of Mines.

E-3; SBR-fire resistant;[3] manufactured by B. F. Goodrich Company. Contains: polystyrene-butadiene, zinc oxide, antimony oxide, chlorinated hydrocarbons, tackifying resins, polyethylene lubricant, carbon black, mineral pigments, antiozonant, phosphorous, antioxidant, fatty acid.

F-9; Bridge/Nylon SBR New 43, (ISG 208);[3] based on TGA the polymer component is SBR.

E-4; Grade 2-NR/SBR-non-fire resistant;[3] manufactured by B. F. Goodrich Company. Contains: polystyrene-butadiene, zinc oxide, tackifying agents, fatty acid, antiozonant, carbon black, processing oil (petroleum base).

TABLE V

LIST OF MISCELLANEOUS COMPOSITIONS STUDIED

4A; neoprene composition;[2] manufactured by U. S. Steel Corporation (labeled D0500W).

3A; hose conduit No. 1949;[2] composed of neoprene polymer reinforced with polyester; manufactured by H. K. Porter, Thermoid Division.

6A; brattice cloth No. 1800y;[2] composed of nylon scrim laminated with thin PVC layer; manufactured by C. R. Daniels.

13A; reinforced plastic fabric rip-proof No. 75 clear III;[2] nylon reinforced PVC, manufactured by Griffolyn Company, Inc.

9B; No. 3 nylon (Glasstex);[2] (composition: PVC-Antimony Trioxide ?); manufactured by Johnston-Morehouse-Dickey Company.

7A; O'Koseal 200;[2] composed of PVC, manufactured by O'Konite Cable (subsidiary of LTV).

10B; No. 4 plastic 15Y;[2] (appearance: solid yellow plastic, composition: PVC-Antimony Trioxide ?); manufactured by Johnston-Morehouse-Dickey Company.

1B; polyurethane rigid foam;[2] (resin component-CCl_3F 22%; polyols, amines, catalyst 78%. Activator component-CCl_3F 5%, isocyanate polymeric, MDI type 94%) manufactured by Callery Chemical Company.

2B; polyurethane rigid foam;[2] composition same as 1B.

16A; polyurethane rigid foam;[2] urethane-isocyanurate No. 4 foam; manufactured by Callery Chemical Company.

TABLE VI

LIST OF SOLVENTS AND FIRE EXTINGUISHANTS STUDIED

Tetrachloroethylene;[6] No. 1-9465, Lot No. 514861, obtained from J. T. Baker Chemical Company.

1,1,2-Trichloroethane;[6] MCB TX 1085 P7412, obtained from MCB Manufacturing Chemists.

Trichloroethylene;[6] No. 8600, Lot No. DHM, obtained from Mallinckrodt Chemical Works.

Bromotrifluoromethane;[6] Halocarbon 13B1,obtained from Linde Division, Union Carbide Corporation.

TABLE VII

LIST OF HYDRAULIC FLUIDS STUDIED

Ucon Hydrolube 275 CP;[5] water-ethylene glycol mixture; manufactured by Union Carbide Corporation.

Citgo Glycol FR-20XD;[5] water-ethylene glycol mixture; manufactured by Cities Service Oil Company.

SNFH Fluid;[5] water-synthetics (glycols) mixture; manufactured by Ore-Lube Corporation.

Duro-FR-HD;[5] oil-water emulsion; manufactured by Atlantic Richfield Company.

Quintolubric 822-300;[5] non-phosphate synthetic esters; manufactured by Quaker Chemical Corporation.

Fyrquel 220;[5] synthetic phosphate esters; manufactured by Stauffer Chemical Company.

Pydraul 50E;[5] synthetic phosphate esters; manufactured by Monsanto Corporation.

Pydraul MC;[5] mixture of phosphate esters, mineral oils, etc.; manufactured by Monsanto Corporation.

TABLE VII (cont'd.)
LIST OF HYDRAULIC FLUIDS STUDIED

Dasco FR 300;[5] mixture of phosphate esters, mineral oils, etc.; manufactured by D. A. Stuart Oil Company, Ltd.

Phosphate-hydrocarbon mixture;[5] 50% by weight triphenylphosphate/n-octacosane.

TABLE VIII
LIST OF VARIOUSLY TREATED SOUTHERN YELLOW PINE SAMPLES STUDIED

1D; Untreated;[2] standard southern yellow pine.

2D; Pentachlorophenol-Treated;[2] standard southern yellow pine treated with oil-borne preservative (pentachlorophenol); 0.37 lbs/cu.ft.; impregnation by Koppers Company.

3D; Cresote-Treated;[2] standard southern yellow pine treated with cresote (coal tar distillate); 10.6 lbs/cu.ft.; impregnation by Koppers Company.

4D; Minalith-Treated;[2] standard southern yellow pine treated with fire retardant type-C, Minalith [$(NH_4)_2HPO_4$, 10%; $(NH_4)_2SO_4$, 60%; $Na_2B_4O_7$, 10%; H_3BO_3, 20%]; 0.4 lbs/cu.ft.; impregnation by Koppers Company.

5D; CCA-Treated;[2] standard southern yellow pine treated with water borne preservative-CCA (CrO_3, CuO, As_2O_5); 0.40 lbs/cu.ft.; impregnation by Koppers Company.

Contract HO133004 together with the pertinent details of origin, composition and report reference. For ease of search these have been segregated into the following groups namely:

1) Basic Polymers
2) Fibers
3) Additives
4) Conveyor Belts
5) Miscellaneous Compositions
6) Solvents and Fire Extinguishants
7) Hydraulic Fluids
8) Woods

The reference given next to each material pertains to a specific report generated under Contract HO133004 (see Section 4) where the details of thermal oxidative behavior including decomposition products separation and analysis are described for this material.

3.5.2 Summary of Potential Toxic Load Data of Materials Studied

The degradation data obtained for compositions investigated under Contract No. HO133004 was reduced and tabulated in order to make it readily usable and accessible to compare the potential toxic hazards of given classes of materials. The grouping of these data is in the same order as the Listing of Materials given in the preceding section.

Pertinent information relating to the materials' thermal oxidative behavior was included in these tabulations. Also the major products formed upon degradation were listed to provide information as to the type of species produced in large amounts by a given composition. Whenever applicable comparisons between static and dynamic testing were presented. The detailed information on all the products is given in the referenced original reports. The toxic load is expressed in (mg/g)/TLV and (mg/g)/STEL based on the 1977 values recommended by the American Conference of Governmental Industrial Hygienists.[1] The total toxic load as reported is the sum of the toxic loads of the individual products formed, for which TLV and/or STEL values are available. The value mg/g (mg of specific product formed per g of composition employed) is an absolute figure solely dependent on the material and degradation conditions; thus any future changes in TLV and STEL or the use of other new factors can be readily accommodated. This is not the case with animal tests and other related data.

Neoprene and styrene-butadiene elastomers together with polyvinyl chloride resins are utilized in conveyor belt manufacture. Examining Table IX it is apparent that the chlorinated materials present a more than two orders of magnitude greater potential hazard than the non-chlorinated elastomers. Furthermore, even at 370°C, the extent of degradation as measured by weight loss was higher than 25% with hydrogen chloride accounting for the bulk of the weight loss.

The fibers, for which the data are presented in Table X constitute the carcass portion of the belting; consequently, their potential contribution to the overall toxic load hazard of a given belt is of importance. It is apparent that substantial differences exist even between the types of nylon fiber with Nylon-6 resin exhibiting apparently a much lower toxic load than Nylon 6,6. It should be pointed out that although the toxic load of Dacron Polyester does not change greatly from 370° to 420°C, the species responsible for the toxicity do, i.e., formaldehyde's contribution decreases (1.62 to 0.14 (mg/g)/TLV). This is of importance in hazard assessment since in the case of a fire, different

TABLE IX

BASIC POLYMERS

TOXIC LOAD DATA [a]

	Toxic Load		Main Toxic Species		Weight Loss	Volatiles	Main Products	
Sample	(mg/g)/TLV	(mg/g)/STEL	Compound	Toxic Load (mg/g)/TLV	mg/g	%[b]	Compound	mg/g
Neoprene Rubber [4] (uncured)	44.93	44.81	HCl CO	44.7 0.11	429	87.6	HCl C_2-species	313 22.5
Neoprene Rubber [4] (cured)	24.59	24.52	HCl CO	24.4 0.06	268	67.9	HCl H_2O	171 33.2
Styrene-Butadiene Rubber [4] (uncured)	0.10	0.09	Styrene Benzene	0.03 0.01	67.5	98.9	Styrene 1,3-Butadiene	13.8 11.2
Styrene-Butadiene Rubber [4] (cured)	0.09	0.08	Cresol CS_2 C_2-benzenes	0.03 0.01 0.01	62.9	68.0	H_2O CO_2 C_2-benzenes	18.8 4.69 4.15
Polyvinyl Chloride Resin [2]	80.59	80.27	HCl Benzene	78.7 1.48	658	88.1	HCl Benzene	551 47.5

a) All the degradations were performed at 370°C using a 2 or 5 liter sealed system, wherein only the finger-like projection was at the designated temperature. b) Percent of weight loss; the remainder being room temperature involatile tars and oils.

TABLE X
FIBERS
TOXIC LOAD DATA [a]

Sample	Toxic Load		Main Toxic Species		Weight Loss	Volatiles	Main Products	
	(mg/g)/TLV	(mg/g)/STEL	Compound	Toxic Load (mg/g)/TLV	mg/g	%[b]	Compound	mg/g
Nylon 6 Resin [3]	0.01	0.01	SO_2	0.01	24.0	22.1	H_2O CO_2	18.4 4.86
Nylon 6,6 Fiber [4]	0.71	0.46	NH_3 CO	0.68 0.02	54.4	20.4	CO_2 H_2O	24.0 15.7
Dacron Polyester Fiber [4]	2.07	1.73	Formaldehyde CO	1.62 0.38	56.1	87.4	CO CO_2	20.6 14.0
Dacron Polyester Fiber [4,c] (420°C)	2.62	0.81	CO Acrolein Acetaldehyde Formaldehyde	1.14 1.04 0.21 0.14	287	53.0	CO_2 CO	155 62.6
Rayon Fiber [4]	0.97	0.32	Furfural CO Formaldehyde	0.36 0.45 0.11	466	77.1	H_2O CO_2	333 85.4

a) All the degradations except when noted otherwise were performed at 370°C using a 2 or 5 liter sealed system wherein only the finger-like projection was at the designated temperature. b) Percent of weight loss; the remainder being room temperature involatile tars and oils. c) This test was conducted at 420°C.

regions are at different temperature levels; consequently, the same conveyor belt, depending on the temperature at a given point along the belting, may produce different types of products. Thus it is obvious that an increase in the degradation (i.e., combustion) temperature must not be necessarily equated with an increase in toxic product formation. At these high temperatures certain toxic species such as e.g., formaldehyde can be transformed, e.g. into $CO + H_2$ and, provided heat and oxygen are available, further reacted into CO_2 and H_2O. This type of reasoning also applies to acrolein.

Additives such as plasticizers, flame retardants or antioxidants are employed extensively in elastomer formulations such as conveyor beltings. Based on the information given in Table XI the variation in the potential toxic load among these products is three orders of magnitude. However, it has to be noted that some of the additives, specifically dioctyl phthalate, tributyl phosphate, tritolyl phosphate, and pentachlorophenol themselves represent a greater toxic hazard than the products formed on their thermal oxidative degradations. Interestingly, in a number of other compounds the major toxic species responsible for the overall toxic load are not those readily expected. This is in particular true in tris(dichloropropyl)phosphate wherein acrolein, not hydrogen chloride, is the major toxic component and in the case of tris-(2-chloroethyl)phosphate wherein large quantities of vinyl chloride were produced; but, since at present no assigned TLV or STEL factor exists, the contribution of vinyl chloride has not been included in the total toxic load.

The results compiled in Table XII for the conveyor beltings in the case of the halogenated polymer based belts reflect in large measure the findings obtained for the parent polymers. This is to be expected since these basic ingredients do account for a major portion of the belting and hydrogen

TABLE XI

ADDITIVES, FLAME RETARDANTS, PLASTICIZERS, AND PRESERVATIVES TOXIC LOAD DATA [a]

Sample	Toxic Load [c]		Main Toxic Species		Weight Loss	Volatiles	Main Products	
	(mg/g)/TLV	(mg/g)/STEL	Compound	(mg/g)/TLV	mg/g	%[b]	Compound	mg/g
Diphenyl Phthalate [4]	0.24	0.12	Phenol CO	0.23 0.01	6.3	39.4	Phenol CO_2	4.38 1.32
Di-(2-ethylhexyl)sebacate [4]	0.10	0.06	2-Ethyl-1-hexene CO	0.06 0.04	104	76.9	2-Ethyl-1-hexene CO_2	84.7 6.85
Dioctyl Phthalate [3]	32.47 [200]	8.17 [100]	Phthalic anhydride C_8-ene	32.3 0.08	139	13.9	Phthalic anhydride C_8-ene	194 119
Tributyl Phosphate [4]	0.64 [200]	0.54 [200]	C_4-species C_4-alcohol Crotonaldehyde	0.38 0.17 0.04	618	102.4	C_4-species C_4-alcohol	540 25.9
Tritolyl Phosphate [4]	0.07 [10,000]	0.06 [3333]	Cresols Phenol	0.05 0.02	4.0	51.8	Cresols H_2O	1.17 0.933
Tri-p-tolyl Phosphate [4]	0.07 [10,000]	0.07 [3333]	Cresols	0.07	3.1	91.2	Cresols H_2O	1.59 0.642
Tris(Dichloropropyl)-phosphate [4]	112.18	51.50	Acrolein HCl	90.8 20.9	660	96.8	1,3-Dichloropropene CO_2	301 146
Tris(2-chloroethyl) phosphate [6]	8.62	7.59	HCl 2-Chloroethanol 1,2-Dichloroethane	3.61 2.68 1.52	563	75.0	1,2-Dichloroethane Vinyl Chloride	305 135
Tris(2,3-dibromopropyl) phosphate [6]	13.40	13.05	HBr HCl Acrolein	12.4 0.52 0.34	628	98.3	Dibromopropenes Tribromopropanes HBr	219 152 124
Chlorinated Hydrocarbon (liquid) [3]	71.95	71.83	HCl Benzene CO	71.4 0.24 0.13	551	77.1	HCl H_2O	500 9.21
Chlorinated Hydrocarbon (solid) [6]	83.07	82.97	HCl HBr	81.6 1.21	648	93.9	HCl CO_2	571 19.2
Dimethyl Chlorendate [6]	1738.8	593.32	Hexachlorocyclopentadiene HCl	1718 20.1	640	89.9	Hexachlorocyclopentadiene Dimethyl fumarate HCl	189 155 141
Methyl pentachlorostearate [6]	39.20	39.13	HCl Methyl chloride Benzene	38.7 0.30 0.11	459	99.7	HCl Methyl chloride CO_2	271 63.4 53.4
Pentachlorophenol [6]	4.11 [2,000]	4.11 [667]	HCl Benzene	4.10 0.01	204	95.1	Octachlorodibenzo-p-dioxin HCl	171 28.7
Decabromodiphenyl oxide [6]	-	-	-	-	3.8	-	H_2O CO_2	0.294 0.138

a) All the degradations were performed at 370°C using a 2 or 5 liter sealed system wherein only the finger-like projection was at the designated temperature. b) Percent of weight loss; the remainder being room temperature involatile tars and oils.

c) The values in the brackets apply to the toxic load of the starting material itself assuming complete evaporation; the toxic load of the products does not include the contribution of the staring material, if any was recovered.

TABLE XII
CONVEYOR BELTS
TOXIC LOAD DATA [a]

	Toxic Load		Main Toxic Species		Weight Loss	Volatiles	Main Products	
Sample	(mg/g)/TLV	(mg/g)/STEL	Compound	Toxic Load (mg/g)/TLV	mg/g	%[b]	Compound	mg/g
E-1 (Neoprene FR) [3]	17.22	17.07	HCl CO	16.7 0.17	229	50.3	HCl H_2O	117 31.4
F-7 (Neoprene) [3]	12.94	12.63	HCl 2-Chloroethanol	11.5 0.72	226	50.9	HCl H_2O	80.7 58.0
F-10 (Neoprene) [3]	10.13	9.99	HCl Acetic Acid	9.71 0.14	279	58.5	H_2O HCl	111 68.0
E-2 (PVC-FR) [3]	18.42	18.40	HCl Benzyl Chloride 2-Chloroethanol	12.8 3.20 2.22	308	49.4	HCl H_2O	89.6 60.6
F-3 (PVC) [3]	22.86	22.83	HCl Benzene 2-Chloroethanol	22.2 0.43 0.12	309	73.6	HCl C_8-species	156 81.5
F-6 (PVC) [3]	14.69	14.30	HCl Phenol	13.6 0.92	391	73.5	H_2O HCl	140 95.0
Fenner American (PVC) [6]	19.11	18.99	HCl Benzene Phenol	18.6 0.23 0.22	345	83.0	HCl H_2O	130 66.9
Scandura (PVC) [6]	26.21	26.19	HCl 2-Chloroethanol Benzene	25.4 0.43 0.30	379	66.6	HCl H_2O	178 19.0
E-3 (SBR FR) [3]	0.66	0.47	HCl CO	0.40 0.22	130	46.2	H_2O CO_2	71.4 18.7
E-5 (SBR) [3]	2.20	2.11	HCl CO HCN	2.01 0.07 0.04	90.5	44.6	H_2O HCl	33.9 14.1
F-9 (SBR) [3]	6.22	6.22	HCl Formic Acid Cresols	5.63 0.32 0.08	130	68.4	HCl H_2O	39.4 20.2
E-4 (SBR NFR) [3]	2.37	2.32	HCl CO 2-Chloroethanol	2.27 0.04 0.01	120	69.6	H_2O CO_2	42.8 25.5

a) All the degradations were performed at 370°C using a 2 or 5 liter sealed system wherein only the finger-like projection was at the designated temperature. b) Percent of weight loss; the remainder being room temperature involatile tars and oils.

chloride evolution occurs at relatively low temperature. Furthermore in these materials hydrogen chloride is usually the major toxic component liberated on heat treatment although the contribution from additives, i.e. phenols, cannot be ignored. In the case of beltings it is of interest that for the beltings based on non-halogenated rubbers, e.g. SBR, the major toxic component obtained on degradation was again hydrogen chloride, which is due to the use of chlorinated additives as flame retardants (see Table XI).

In Table XIII are presented the data pertinent to miscellaneous compositions studied such as foams, brattice cloth, or hose conduit. Since most of these are composed in part of halogenated polymers (PVC and Neoprene), hydrogen chloride was found to be the major toxic species. It should be noted however, that in view of the forthcoming change in TLV values of benzene, the benzene contribution will be raised most likely by a factor of five. Regarding the urethane foams, at least in two of the compositions tested, aniline presented a major toxic hazard on degradation. This is in agreement with literature data (see subsection 3.6.1). The hydrogen chloride in these foams most likely originates from the flame retardants use, e.g. halogenated phosphate esters.

Certain compositions were subjected to degradation both under static (sealed system) and dynamic (stagnation burner) conditions. A comparison of the toxic load data thus obtained is given in Table XIV. Although the stagnation burner tests were carried out at 400°C and the sealed system experiments at 370°C the toxic load values are very close, with the stagnation burner actually showing a lower toxic load. The reason for these findings is that the major toxic product formed from these materials is hydrogen chloride which is evolved below 370°C. The lower "production" or more precisely "collection"

TABLE XIII

MISCELLANEOUS COMPOSITIONS

TOXIC LOAD DATA [a]

Sample	Toxic Load		Main Toxic Species		Weight Loss	Volatiles	Main Products	
	(mg/g)/TLV	(mg/g)/STEL	Compound	Toxic Load (mg/g)/TLV	mg/g	%[b]	Compound	mg/g
4A (Neoprene)[2]	16.12	15.80	HCl CO	15.7 0.35	377	64.3	CO_2 HCl	138 110
3A (Neoprene)[2]	9.54	9.40	HCl CO SO_2	9.24 0.13 0.05	145	39.3	HCl CO_2	64.7 26.6
6A (PVC-nylon)[2]	25.21	25.12	HCl CO Benzene	24.9 0.09 0.16	295	43.7	HCl CO_2	174 29.1
13A (PVC-nylon)[2]	37.20	37.11	HCl Benzene	36.2 0.83	426	63.4	HCl Benzene	254 26.7
9B (PVC-nylon)[2]	30.74	30.60	HCl Benzene CO	29.4 1.12 0.16	525	67.1	HCl Benzene	206 35.8
7A (PVC)[2]	38.50	38.41	HCl Benzene CO	37.6 0.79 0.10	447	66.7	HCl Benzene	264 25.4
10B (PVC)[2]	43.68	43.38	HCl Benzene CO	42.9 0.61 0.11	487	70.5	HCl CO_2	300 33.7
1B (Polyurethane rigid foam)[2]	7.75	7.43	HCl Aniline p-Toluidine 2-Chloroethanol	3.31 3.08 0.47 0.43	439	47.4	CO_2 $CFCl_3$	144 89.2
2B (Polyurethane rigid foam)[2]	5.98	5.53	Aniline HCl NH_3 2-Chloroethanol p-Toluidine	3.52 0.54 0.59 0.37 0.36	417	48.3	CO_2 Aniline	149 66.9
16A (Polyurethane rigid foam)[2]	3.43	2.79	HCl CO	2.47 0.63	443	63.4	CO_2 CO	192 34.5

a) All the degradations were performed at 370°C using a 2 or 5 liter sealed system wherein only the finger-like projection was at the designated temperature. b) Percent of weight loss; the remainder being room temperature involatile tars and oils.

TABLE XIV

HALOGENATED POLYMERS
STAGNATION BURNER-SEALED TUBE SYSTEM
COMPARISON OF TOXIC LOAD DATA

Sample	Toxic Load		Main Toxic Species		Main Products	
	(mg/g)/TLV	(mg/g)/STEL	Compound	Toxic Load (mg/g)/TLV	Compound	mg/g
Neoprene Rubber (uncured) ^{a,4}	44.93	44.81	HCl	44.7	HCl	313
			CO	0.11	C_2-species	22.5
Neoprene Rubber (uncured) ^{b,2}	43.04	43.04	HCl	42.9	HCl	300
			SO_2	0.07	CO_2	48.0
Neoprene Rubber (cured) ^{a,2}	24.59	24.52	HCl	24.4	HCl	171
			CO	0.06	H_2O	33.2
Neoprene Rubber (cured) ^{b,2}	26.54	26.46	HCl	25.6	CO_2	116.0
			SO_2	0.49	HCl	181
4 A (Neoprene) ^{a,2}	16.12	15.80	HCl	15.7	CO_2	138
			CO	0.35	HCl	110
4 A (Neoprene) ^{b,2}	14.80	14.74	HCl	14.2	CO_2	1050
			SO_2	0.44	HCl	99.4
3 A (Neoprene) ^{a,2}	9.54	9.40	HCl	9.24	HCl	64.7
			CO	0.13	CO_2	26.6
			SO_2	0.05		
3 A (Neoprene) ^{b,2}	6.59	6.55	HCl	6.41	HCl	44.9
			H_2S	0.04	CO_2	32.7
			SO_2	0.04		
Polyvinyl Chloride Resin ^{a,2}	80.59	80.27	HCl	78.7	HCl	551
			Benzene	1.48	Benzene	47.5
Polyvinyl Chloride Resin ^{b,2}	61.55	61.54	HCl	60.2	HCl	421
			Benzene	1.31	CO_2	49.2
					Benzene	39.4
7 A (PVC) ^{a,2}	38.50	38.41	HCl	37.6	HCl	264
			Benzene	0.79	Benzene	25.4
			CO	0.10		
7A (PVC) ^{b,2}	21.61	21.60	HCl	21.0	HCl	147
			Benzene	0.59	CO_2	31.6
6A (PVC-nylon) ^{a,2}	25.21	25.12	HCl	24.9	HCl	174
			CO	0.09	CO_2	29.1
			Benzene	0.16		
6 A (PVC-nylon) ^{b,2}	24.67	24.66	HCl	24.1	HCl	169
			Benzene	0.53	CO_2	23.2
13 A (PVC-nylon) ^{a,2}	37.20	37.11	HCl	36.2	HCl	254
			Benzene	0.83	Benzene	26.7
13 A (PVC-nylon) ^{b,2}	27.49	27.48	HCl	26.3	HCl	184
			Benzene	1.11	Benzene	33.3
9 B (PVC-nylon) ^{a,2}	30.74	30.60	HCl	29.4	HCl	206
			Benzene	1.12	Benzene	35.8
			CO	0.16		
9 B (PVC-nylon) ^{b,2}	23.29	23.28	HCl	22.2	HCl	155
			Benzene	1.07	Benzene	32.0

a) The degradations were performed at 370°C using a 2 or 5 liter sealed system wherein only the finger-like projection containing the sample was at the designated temperature. b) The degradations were performed at 400°C using the stagnation burner arrangement.

of hydrogen chloride, reflected in the lower toxic load figures for stagnation burner runs, is due to absorption of hydrogen chloride by the metal walls of the stagnation burner assembly. In the case of the sealed system the all glass apparatus allows essentially quantitative product collection and thus results in more accurate data.

Halogenated aliphatics are used in cleaning and degreasing formulations employed in underground operations. The toxic load data for selected chlorinated compounds are given in Table XV. Based on this compilation, at least under the conditions employed, tetrachloroethylene presents the least toxic hazard. Trifluorobromomethane, a widely used fire extinguishant, has been included in this series. It was recovered essentially unchanged after the test.

Hydraulic fluids are of importance in underground coal mining in view of the increased use of heavy machinery. It is obvious from the results given in Table XVI that regarding both toxic load and degree of decomposition Quintolubric 822-300 and Fyrquel 220 are far superior to the other fluids tested.

Wood is used extensively in mines to provide roof support and its potential contribution to toxic offgassing in case of fire or even local overheating is of importance. The effect of the various treatments, which are in use to render wood fire and rot resistant, on the potential toxic load thus needed to be assessed. From the data given in Table XVII it would appear that these treatments have minimal effect on the potential toxic load both under static and under dynamic conditions. In the majority of instances the values obtained in the sealed system and in the stagnation burner were relatively closely comparable. The discrepancy observed in the case of untreated pine is most likely

TABLE XV

SOLVENTS AND FIRE EXTINGUISHANTS
TOXIC LOAD DATA[a]

Sample	Toxic Load[b]		Main Toxic Species		Main Products	
	(mg/g)/TLV	(mg/g)/STEL	Compound	Toxic Load (mg/g)/TLV	Compound	mg/g
Tetrachloroethylene[6]	4.85 [1.49]	4.85 [1.00]	$COCl_2$	4.85	CO_2 $COCl_2$	1.42 0.97
1 1,2-Trichloroethane[6]	303.2 [22.2]	298.2 [44.4]	$COCl_2$ HCl CO	198.0 99.4 5.71	HCl CO	696. 314.
Trichloroethylene[6]	618.4 [1.87]	615.7 [1.25]	$COCl_2$ HCl Hexachloroethane	580 34.7 1.43	HCl $COCl_2$	243. 116.
CF_3Br[6]	- [0.16]	- [0.13]	-	-	-	-

a) All the degradations were performed at 370°C using totally immersed sealed ampoules. b) Values in the brackets apply to the toxic load of the starting material assuming complete evaporation; the toxic load of the products does not include the contribution of the starting material, if any was recovered.

TABLE XVI

HYDRAULIC FLUIDS
TOXIC LOAD DATA[a]

	Toxic Load		Main Toxic Species		Weight Loss	Volatiles	Main Products	
Sample	(mg/g)/TLV	(mg/g)/STEL	Compound	Toxic Load (mg/g)/TLV	mg/g	%[b]	Compound	mg/g
Ucon Hydrolube 275CP [5]	0.08	0.04	Ethylene glycol CO	0.04 0.03	364	81.1	H_2O Ethylene glycol	347 9.83
Citgo Glycol FR-20XD [5]	0.09	0.05	Ethylene glycol CO	0.04 0.03	233	83.6	H_2O Ethylene glycol	212 10.3
SNFH Fluid [5]	0.01	0.01	Ethylene glycol	0.01	208	80.6	H_2O 1,2-Propanediol Ethylene glycol	200 3.59 2.70
Duro FR-HD [5]	0.10	0.02	CO Acrolein	0.06 0.02	418	92.7	H_2O CO	400 3.50
Quintolubric 822-300 [5]	0.10	0.04	Acrolein CO	0.07 0.02	25.6	77.7	H_2O C_{11}-species	8.39 1.52
Quintolubric 822-300[c,5] (420°C)	0.08	0.05	CO C_6-species	0.03 0.02	83.6	95.0	C_{11}-species H_2O C_7-species	9.74 8.32 8.32
Fyrquel 220 [5]	0.08	0.07	Cresols Biphenyl Phenol	0.03 0.03 0.02	5.4	38.8	Xylenols H_2O	2.04 1.16
Fyrquel 220[c,5] (420°C)	0.08	0.07	Cresols Phenol	0.05 0.02	7.9	52.6	Xylenols H_2O Cresols	4.11 1.04 1.02
Pydraul 50E[c]	0.41	0.20	Phenol Acrolein CO	0.38 0.01 0.01	17.2	75.2	Phenol C_4-species	7.12 2.55
Pydraul 50E[c,5] (420°C)	1.83	0.94	Phenol C_6-species	1.79 0.02	67.6	79.9	Phenol C_6-species	34.1 6.99
Pydraul MC[c]	0.59	0.30	Phenol C_8-species CO	0.54 0.02 0.01	48.9	98.4	C_8-species Phenol	25.0 10.3
Pydraul MC[c,5] (420°C)	10.57	4.66	Phosphine Phenol	6.95 3.49	161	81.0	Phenol C_8-species	66.3 24.7
Dasco FR 300 [5]	2.34	0.88	Acrolein Phenol	1.73 0.56	53.3	76.4	Propionaldehyde Phenol	12.2 10.6
Dasco FR 300 [c,5] (420°C)	1.18	0.51	Acrolein Phosphine Phenol	0.43 0.35 0.27	61.9	64.1	H_2O Propionaldehyde	10.5 5.88
Triphenylphosphate-Hydrocarbon Mixture[c,5] (420°C)	1.32	0.63	Phenol Acrolein	1.14 0.14	53.9	85.4	Phenol H_2O	21.6 7.72

a) All the degradations except when noted otherwise were performed at 370°C using a 2 or 5 liter sealed system wherein only the finger-like projection was at the designated temperature. b) Percent of weight loss; the remainder being room temperature involatile tars and oils. c) This test was conducted at 420°C.

TABLE XVII

VARIOUSLY TREATED SOUTHERN YELLOW PINE SAMPLES

TOXIC LOAD DATA

Sample	Toxic Load		Main Toxic Species		Main Products	
	(mg/g)/TLV	(mg/g)/STEL	Compound	Toxic Load (mg/g)/TLV	Compound	mg/g
Untreated-Pine (6 D) [a,2]	4.70	2.06	Acrolein	2.48	H_2O	277
			CO	0.88	CO_2	116
			Formaldehyde	0.79		
			Acetic Acid	0.29		
Untreated-Pine (1 D) [b,2]	1.72	1.08	Acrolein	0.84	H_2O	486
			Formaldehyde	0.70	CO_2	200
Pentachlorophenol-Treated (2 D) [a,2]	6.99	4.68	Acrolein	4.84	H_2O	268
			CO	0.82	CO_2	73.8
			Formaldehyde	0.61		
			Acetic Acid	0.31		
Pentachlorophenol-Treated (2 D) [b,2]	4.42	2.44	Acrolein	2.80	H_2O	334
			HCl	1.22	CO_2	227
			Formaldehyde	0.12		
Creosote-Treated (3 D) [a,2]	3.47	1.65	Acrolein	1.72	H_2O	243
			Formaldehyde	0.56	CO_2	77.7
			Acetic Acid	0.44		
			CO	0.38		
Creosote-Treated (3 D) [b,2]	3.05	1.30	Acrolein	2.36	H_2O	224
			Formaldehyde	0.24	CO_2	172
			Acetic Acid	0.12		
			Furfural	0.11		
Minalith-Treated (4 D) [a,2]	3.64	2.66	Formaldehyde	1.21	H_2O	306
			SO_2	1.15	CO_2	88.7
			CO	1.06		
Minalith-Treated (4 D) [b,2]	3.27	2.45	SO_2	1.72	H_2O	468
			Acrolein	0.88	CO_2	274
			Furfural	0.24		
			Formaldehyde	0.17		
CCA-Treated (5 D) [a,2]	3.93	1.78	Acrolein	1.88	H_2O	320
			Formaldehyde	0.80	CO_2	135
			CO	0.79		
			Furfural	0.21		
CCA-Treated (5 D) [b,2]	6.42	4.42	Formaldehyde	3.32	CO_2	591
			Acrolein	2.72	H_2O	410
			Furfural	0.16		
			Acetic Acid	0.11		

a) The degradations were performed at 370°C using a 2 or 5 liter sealed system wherein only the finger-like projection containing the sample was at the designated temperature. b) The degradations were performed at 400°C using the stagnation burner arrangement.

due to the different wood samples employed in the two experiments. Pentachlorophenol-treated wood would be expected to exhibit lower toxic load under stagnation burner conditions due to absorption of the evolved hydrogen chloride by the metal walls of this apparatus, as discussed for the halogenated polymers. In the case of the CCA-treated pine, glow was observed in the dynamic system and this is most likely responsible for higher volatiles production and thus toxic load. It must be stressed that one of the important toxic load constituents in wood is carbon monoxide as evident from the sealed system runs. No CO is listed for the stagnation burner tests, since no CO determinations were carried out in these experiments. Had these been obtained the toxic load would have been definitely higher than in the sealed system due to the higher temperatures involved, 370 versus 400°C, and the occurrence of glow in the 1 D, 2 D and 5 D samples.

3.6 LITERATURE DATA SUMMARY

Under Contract No. HO122009 [14] a literature survey was carried out on the thermal and thermal oxidative degradation of compositions used in underground coal mining operations with special emphasis on the nature and quantities of the products formed. During the various phases of Contract HO133004 literature data were gathered pertaining to materials under investigation; this information is scattered throughout the generated annual reports or has been obtained only recently. In addition some of the results of the studies carried out under the subject contract were published in the open literature. Consequently, it appeared worthwhile to include these data in this report to make the program summary more comprehensive.

3.6.1 Basic Polymers and their Formulations

Polyvinyl chloride probably is the most widely used of the halogenated polymers, due to economic considerations and other desirable characteristics. Based on the past survey [14] and on the studies conducted under this program [2,3] it can be safely said, in direct contradiction to the conclusions by Wagner, [15] that initially and at lower temperatures hydrogen chloride, not carbon monoxide, is the major species given off. It was also established unequivocally [16,17] that no phosgene, long postulated as an important constituent of the decomposition products, is formed on thermal and thermal oxidative degradation of polyvinyl chloride resins.

Recent studies and reviews of polyvinyl chloride resins show definitely that already at 180°C hydrogen chloride evolution occurs (the process being autocatalytic) but, whether this inital evolution is due to material irregularities, weak links, or end groups has not been definitely established. [18] This reaction is accelerated in oxidizing atmospheres. [19,20] For the pure resin, below 200°C, hydrogen chloride is the only product evolved. [21] However, this is not the case in the formulated material wherein the plasticizer is co-evolved[22-24] with hydrogen chloride. Hemmer et al [23] did not delve into the oxidation products of the plasticizers and other additives, but it was found under this program [3,4,25] and by others [15] that phthalate esters, which are probably the most commonly used plasticizers, when subjected to elevated temperatures produce CO, CO_2, unsaturated hydrocarbons and phthalic anhydride.

Neoprene, due to its high chlorine content, exhibits flame retardant characteristics and thus is employed in applications wherein fire resistance is of importance. Conflicting data exist in the literature regarding its thermal stability; some Russian workers [26] claim that this material is thermally stable up to 300°C whereas others [27] report degradation onset at 180°C. Based on TGA curves of the raw gum and cured compositions [28] the degradation onset for the former is around 220°C whereas for cured compositions that onset could be as low as 125°C. On the other hand whether the initial weight loss corresponds to hydrogen chloride evolution or to evaporation of some curing constituent has not been determined. Hydrogen chloride is the major degradation product at 370°C and it accounts for 80% of the chlorine present [4,26,28] with the rest liberated in the form of chlorinated materials, chloroprene (the monomer) being the major component of these.

The discussion of Butadiene-Styrene (SBR) rubber thermal oxidative degradation was included in the past review.[14] Studies performed under Contract No. HO133004 [4,29] have shown that at 370°C in air the oxygen consumption was low and the major products formed by the raw gum were 1,3-butadiene, its dimer, and styrene. In the cured material other hydrocarbons in addition to the three mentioned above became of importance.

Urethanes have been included in the basic polymer section although unlike the other polymers discussed the designation as urethanes embodies a number of widely differing compositions, wherein the thermal and thermal oxidative behavior is largely dependent not just on the urethane type bond but also on the other linkages present. A recent review delved into these aspects in considerable detail [30] and provides probably the best summary of the current understanding of the factors involved in the thermal and oxidative stability of urethanes.

In view of the relatively high nitrogen content the common belief is that hydrogen cyanide is one of the main decomposition products of urethanes thus making these materials especially "toxic". That this is not so was made evident by the literature review [14] conducted under Contract HO122009 and the studies carried out under Phase I of Contract HO133004.[2] This conclusion is further supported by recent publications.[31,32] Also, apparently in the case of polyurethanes derived from aromatic isocyanates, the quantities of isocyanates produced on thermal oxidative degradations are low[33] inasmuch as the major decomposition path is the production of aromatic amines and carbon dioxide.[34-38]

Urethanes of many commerically available isocyanates and primary and secondary alcohols start to decompose between 200-250°C. The major volatile liberated by the non fire-retardant compositions is carbon dioxide; however when halogenated flame retardant additives or co-reactants are included hydrogen halodes are invariably evolved.[2] The polyether urethanes, where at 200°C unzipping sets in, are significantly less stable oxidatively and thermally than the polyester based materials. This was shown by some early comparison studies[39] and more recent investigations.[30] Addition of suitable antioxidants can alleviate this undesirable characteristic to a certain extent. On the other hand traces of specific metal impurities such as e.g. copper, can catalyze the thermooxidative degradation of polyether urethanes significantly.[30] Highly cross-linked rigid polyurethanes, wherein isocyanate bonding is predominant, do exhibit thermal and thermal oxidative stability above 200°C.

There are a number of different kinds of polyamides and in a broad sense these can be divided into the aliphatic and aromatic compositions. By nylons one usually understands the aliphatic compositions as represented by nylon 6.6 (formed from adipic acid and hexamethylene diamine), nylon 6 (formed from ε-aminocaprolactam), nylon 6.10 (formed from hexamethylene diamine and sebacic acid) etc.

The previous review[14] covered the early work at the Bureau of

Standards as well as other pyrolytic investigations. The more recent studies carried out by Edel and Etienne [40] in air below 300°C on nylon 6.6 have shown that ammonia and carbon dioxide are the two major products produced under these conditions and that their evolution commences as low as 140 and 120°C respectively, with the rate becoming fast above 200°C. These data do essentially agree with the investigations conducted under the current program [4] where on oxidative degradation at 370°C carbon dioxide, ammonia and water were found to be the major products formed by nylon 6.6. Although the same major volatiles were produced by nylon 6 as by nylon 6.6, the former showed a lower weight loss [41] under analogous conditions [3] (10 versus 27%). For nylon 6 others [41] observed after 872 days at 260-5°C in the absence of oxygen, 17.4% volatilization; the gaseous products were evolved at the rate of 0.274 ℓ/kg-day and consisted of CO_2, NH_3, H_2O, CO and H_2.

Apparently, nylon 6.10 is also more thermally stable than nylon 6.6.[41] The thermal instability of nylon 6.6 has been ascribed to the ring closure tendency of the adipic acid component. [42] It has been reported previously [14] that hydrogen cyanide is produced by polyamides only above 400°C; more recent results by a Japanese investigation [43] confirm these stipulations.

3.6.2 Chlorinated Solvents

According to M. Schmeisser, et al., [44] pyrolysis of tetrachloroethylene, C_2Cl_4, at 1200-1300°C in vacuo in the presence of activated charcoal yields C, Cl_2, C_2Cl_2, C_2Cl_6, C_4Cl_6 and C_6Cl_6 as well as the unreacted starting material. At 700°C in the presence of carbon dioxide a similar product mixture was observed with the starting material predominating (50-60%). [45] Apparently, when exposed to sunlight, tetrachloroethylene produces phosgene;[46] exposure duration and extent of formation were not given. Under the current program [6] subjecting the material to 370°C gave as the only detectable products traces of phosgene and carbon dioxide.

No literature data pertaining to the thermal oxidative degradation of 1,1,2-trichloroethane was found. The thermal degradation [47] and the decomposition in the presence of small amounts of oxygen and/or chlorine [48] have been investigated. The kinetics of the pyrolysis at 360-500°C showed that both intramolecular as well as radical chain reactions take place with vinylidene chloride, $CCl_2 = CH_2$, and 1,2-dichloroethylene, $(CHCl)_2$, being the main products aside from hydrogen chloride. Addition of small amounts of oxygen and/or chlorine were found to increase the rate of thermal dehydrochlorination. [48] In the current investigation [6] degradation of 1,1,2-trichloroethane at 370°C in air resulted in the formation of small quantities of vinyl chloride, vinylidene chloride, cis- and trans-1,2-dichloroethylene, chloroform, trichloroethylene, and tetrachloroethylene, which is basically in agreement with the results of Teramoto [47] and those of Barton. [48] The major products, however, were hydrogen chloride, phosgene, carbon monoxide, and carbon dioxide. It therefore must be concluded that the primary reactions in the oxidative thermal degradation of 1,1,2-trichloroethane are dehydrochlorination and oxidation of the reaction intermediates formed.

The literature data regarding thermal and thermal oxidative degradation of trichloroethylene, C_2HCl_3, is very limited. Early studies performed under flow conditions in CO_2 atmospheres at 700°C gave a number of products, these being dichloromethane, dichloroethylene, chloroform, tetrachloroethylene, carbon tetrachloride, 1,1,1,2-tetrachloroethane, pentachloroethane, hexachloroethane, hexachlorobenzene, hexachlorobutene, carbon, and, of course, hydrogen chloride. [44] Based on the work of Erdmann, [49] apparently some oxidation does take place already at room temperature in air as indicated by the formation of phosgene and hydrogen chloride. At atmospheric pressure at 60°C the only products found were $COCl_2$, HCl, CO and $CHCl_2COCl$. At higher temperatures, 65-80°C, under pressure the reaction became much more complicated and given sufficient time all the oxygen was consumed. Later studies by Goodall and Howlett [50] showed that thermal degradations at 385-445°C using vessels whose walls were covered with a carbonaceous layer resulted in theoretical yields of HCl and hexachlorobenzene. Gonikberg and Zhulin [51] claim that heating trichloroethylene at temperatures below 190°C in a steel bomb gives as a main product 1,1,2,4,4-pentachloro-1,3-butadiene. Subjecting trichloroethylene to thermal oxidative degradation at 370°C in air [6] gave as the major products hydrogen chloride, phosgene, and carbon monoxide together with some dichloroethylenes, carbon dioxide, and hexachlorobenzene.

3.6.3 Woods

Wood is used extensively in mines as structural material. For this type of an application the wood has to be made flame retardant and must be treated against rot and decay. Under the previous contract a literature survey of the thermal oxidative behavior of cellulosic materials was compiled; [14] however, it was not specifically directed toward woods and no mention was made of impregnations and treatments of woods. Wood is composed of cellulose, lignin, hemicellulose, rosin, tannins, fats, waxes, and some coloring matter [52-54] and it is the degradation of all these constituents that leads to the variety of chemicals observed on pyrolysis of wood. A large number of investigations have been published and reviewed pertaining to wood degradation. [55,56] Of these probably the most useful and most inclusive is the compilation by the Canadian Wood Council. [56] The work done by Lipska [57,58] and others,[59] to mention just a few, although pertaining only to cellulose is nevertheless of direct application to wood studies since wood consists largely of cellulose. Regarding the effect of preservatives and flame retardants on wood's thermal oxidative behavior and the nature and relative concentration of volatiles the data in the literature are more limited. The extent of penetration is usually of the order of 3/4 - 1" depending on the type of wood, its water content and the method of impregnation. A number of theories have been advanced for the action of flame retardants in woods; to summarize briefly the current belief is that a flame retardant influences the mechanism of decomposition, lowers the temperature of decomposition onset and increases the char yield. Byrne et al [59] state that an effective flame retardant must act at temperatures below those at which cellulose would normally pyrolyze. The results obtained under Contract No. HO133004 [2,60] support these stipulations as shown by the pronounced effect of the Minalith treatment upon the degradation characteristics and product nature of the impregnated yellow pine. Other treatments such as pentachlorophenol, creosote and water borne CCA-preservative did not affect greatly the thermal oxidative behavior of the pine as compared to the untreated material.

3.6.4 Additives

A number of additives (see Table III, section 3.5) were studied under this contract. In the majority of instances no literature data could be found regarding the thermal and/or thermal oxidative behavior of these materials.

Phthalates represent an important class of plasticizers. The work performed by Hagen [61] and the studies reported by Wagner [15] show that the major species formed are phthalic anhydride and olefins. This has been discussed in the subsection 3.6.1 in connection with the decomposition studies of polyvinyl chloride compositions.

Phosphate esters, in view of their flame retardant and plasticizing action are widely used as additives, yet with the exception of the work carried out on tricresyl and triphenyl phosphates by Hagen [61] and by Japanese workers[62] on tris(2,3-dibromopropyl)phosphate, no other studies seem to be reported. The investigations performed under the current program [6,63] showed that: at 370°C in air tri-p-tolyl phosphate undergoes only minimal degradation; butene was the major product obtained in tributyl phosphate decomposition; hydrogen halides and halogenated C_2 - and C_3 - species were the main compounds formed by the halogenated phosphate esters. In the case of tris(1,3-dichloro-2-propyl)phosphate, acrolein, not hydrogen chloride, presented the greatest toxic hazard.

Pentachlorophenol is a widely employed wood preservative as well as flame retardant and pentachlorophenol-treated timber was studied under this program. [2] Pentachlorophenol itself is toxic and in view of the extreme toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) [64] and other members of the series [65] a literature survey pertaining to the toxic potential and ease of formation of octachlorodibenzo-p-dioxin was carried out. Based on the latest data this particular dibenzo-p-dioxin is relatively nontoxic. It has been reported that preparation of octachlorodibenzo-p-dioxin from pentachlorophenol requires catalysts [67,68] although others [69] claim to have obtained the latter by pyrolysis at 300°C. In the current investigation conducted at 370°C [6] hydrogen chloride and octachlorodibenzo-p-dioxin were the major products formed. Thus it is surprising that apparently combustion of pentachlorophenol-treated wood [70] does not result in the formation of octachlorodibenzo-p-dioxin; on the other hand, it is quite likely that interaction of the aromatic chlorines with cellulose-derived hydroxyl groups is under these circumstances the predominant reaction preventing the self-condensation of pentachlorophenol observed under the conditions employed in this study.

4. REFERENCES

1. Threshold Limit Values for Chemical Substances for 1976; American Conference of Governmental Industrial Hygienists

2. K. L. Paciorek, R. H. Kratzer, J. Kaufman, and J. H. Nakahara, Coal Mine Combustion Products - Identification and Analysis, Annual Report No. 1,Bureau of Mines, Contract No. HO133004, August 1973, PB 226,994/AS

3. K. L. Paciorek, R. H. Kratzer, J. Kaufman, and J. H. Nakahara, Coal Mine Combustion Products - Identification and Analysis, Annual Report No. 2, Bureau of Mines, Contract No. HO133004, August 1974

4. K. L. Paciorek, R. H. Kratzer, J. Kaufman, and J. H. Nakahara, Coal Mine Combustion Products - Identification and Analysis, Annual Report No. 3, Bureau of Mines, Contract No. HO133004, August 1975, PB 250,527/AS

5. K. L. Paciorek, R. H. Kratzer, J. Kaufman, and J. H. Nakahara, Coal Mine Combustion Products - Identification and Analysis, Annual Report No. 4, Bureau of Mines, Contract No. HO133004, September 1976, PB 267,658/AS

6. K. L. Paciorek, R. H. Kratzer, J. Kaufman, and J. H. Nakahara, Coal Mine Combustion Products - Identification and Analysis, Annual Report No. 5, Bureau of Mines, Contract No. HO133004, October 1977

7. R. T. Sanderson, Vacuum Manipulation of Volatile Compounds, John Wiley and Sons, Inc., New York, 1948

8. B. Bartocha, W. A. G. Graham and F. G. A. Stone, J. Inorg. and Nucl. Chem., 6, 119 (1958)

9. A. Stock, Hydrides of Boron and Silicon, Cornell University Press, Ithaca, New York, 1933

10. E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Atlas of Mass Spectral Data, John Wiley and Sons, Inc., New York, 1969

11. A. Cornu and R. Massot, Compilation of Mass Spectral Data, Heyden and Son Limited, London, 1966

12. Eight Peak Index of Mass Spectra, published by Mass Spectrometry Data Centre, AWRE, Aldermaston, Reading, England, 1970

13. E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Registry of Mass Spectral Data, John Wiley and Sons, Inc., New York, 1974

14. K. L. Paciorek, R. H. Kratzer and J. Kaufman, Coal Mine Combustion Products - Identification and Analysis, Final Report, Bureau of Mines, Contract No. HO122009, ICIS 03154, July 1972

15. J. P. Wagner, Fire Res. Abs. and Rev., January 1973

16. E. A. Boettner, Analysis of Volatile Degradation Products of Polymer Combustion, Polymer Conference, University of Detroit, June 16-20, 1969

17. E. A. Boettner, G. Ball and B. Weiss, J. Appl. Polym. Sci., 13, 377 (1969)

18. D. Braun, Gummi Asbest Kunstst., 24 (9), 902 (1971); 24 (10), 1116 (1971)

19. L. Valko, J. Polym. Sci., Part C, No. 16, 1979 (1967)

20. L. Valko, J. Polym. Sci., Part C, No. 16, 545 (1967)

21. A. Guyot, Jean-Paul Benevise and Y. Trambouse, J. Appl. Polym. Sci., 6 (19), 103 (1962)

22. G. A. Kleinenberg and D. L. Geiger, Private Communication

23. E. Hemmer, H. Jesse and H. Rhiem, Gummi Asbest Kunstst., 29 (5), 294 (1976)

24. E. Hemmer, H. Jesse and H. Rhiem, Gummi Asbest Kunstst., 29 (4), 204 (1976)

25. K. L. Paciorek, R. H. Kratzer, J. Kaufman, J. H. Nakahara, and A. M. Hartstein, J. Appl. Polym. Sci., 18, 3723 (1974)

26. R. M. Sorokina and A. L. Klebanski, Kauchuk i Resina, 25 (2), 18 (1966) [CA 64, 17834c (1966)]

27. J. Kalman et al., Muanyag Gumi, 5 (10), 381 (1968)

28. K. L. Paciorek et al., Amer. Ind. Hyg. Assoc. J., 36 (1), 10 (1975)

29. R. H. Kratzer, K. L. Paciorek, J. Kaufman, J. H. Nakahara, and A. M. Hartstein, J. Appl. Polym. Sci., 21, 2077 (1977)

30. H. J. Fabris, Adv. Urethane Technol., 4, 89 (1975)

31. K. Ashida et al., J. Cell. Plast., 10 (4), 181 (1974)

32. K. Sumi and Y. Tsuchiya, J. Fire and Flammability, 4, 15 (1973)

33. D. W. Skidmore and P. R. Sewell, Eur. Polym. J., 11 (2), 139 (1975)

34. V. A. Orlov and O. G. Tarakanov, Plasticheskie Massy, 6, 11 (1965)

35. V. A. Orlov and O. G. Tarakanov, Plasticheskie Massy, 5, 12 (1965)

36. V. A. Orlov and O. G. Tarakanov, Vysokomol, Soedin., 6, 1157 (1964)

37. V. A. Orlov, O. G. Tarakanov, and S. A. Sokolov, Vysokomol. Soedin. B, 11, 276 (1968)

38. M. L. Matuszak and K. C. Frisch, J. Polym. Sci., 11, 637 (1973)

39. A. Singh, L. Wessbein and J. C. Mollica, Rubber Age (N. Y.), 98 (12), 77 (1966)

40. G. Edel and H. Etienne, Bull. Inst. Text Fr., 24 (146), 23 (1970)

41. H. Hofmann and A. B. Darwish, Chemiefasern Text. Anwendungstech., 20 (10), 857 (1970)

42. F. Wiloth, Makromol. Chem., 144, 283 (1971)

43. T. Sugihara, Chem. Abstr., 85, 33640s (1976)

44. M. Schmeisser, H. Schroeter, H. Schilder, J. Massonne, and F. Rosskopf, Ber., 95, 1648 (1962)

45. O. Nicodemus, J. Prakt. Chem., 83, 312 (1909)

46. S. R. Gunewardene, Trop. Diseases Bull., 38, 38 (1941)

47. K. Teramoto, M. Kitabatake, and T. Onouchi, Kogyo Kagaku Zasshi, 67, (3), 460 (1964)

48. D. H. R. Barton, Nature, 157, 626 (1946)

49. E. Erdmann, J. Prakt. Chem., 85, 87 (1911)

50. M. Goodall and K. E. Howlett, J. Chem., Soc., 1954, 2596

51. M. G. Gonikberg and V. M. Zhulin, Chem. Abstr., 54, 1261 (1960)

52. T. C. Brauns, Lignin and Other Noncarbohydrates, in High Polymers, Vol. V, Cellulose and Cellulose Derivatives, 2nd ed., Part I, pg. 480; E. Ott, H. M. Spurlin, and M. W. Grafflin, Eds., Interscience Publishers, Inc., New York, 1954

53. C. B. Purves, Chain Structure, in High Polymers, Vol. V, Cellulose and Cellulose Derivatives, 2nd ed., Part I, pg. 54; E. Ott, H. M. Spurlin, and M. W. Grafflin, Eds., Interscience Publishers, Inc., New York, 1954

54. J. Marton, Lignin Structure and Reactions, Advances in Chemistry Series 59, R. F. Gould, Ed., American Chemical Society Publications, Washington, 1966

55. A. E. Lipska and N. J. Alvares, Chemical Constituents of Wood Smoke and Conjecture as to Their Role in Foam Destruction, paper presented at the Spring Meeting of Western States Section of the Combustion Institute, Denver, 1971

56. J. B. Fang, C. D. M. MacKay, and G. Bramball, Wood Fire Behavior and Fire Retardant Treatment, a review of Literature, November 1966, published by Canadian Wood Council, Ottawa, Canada (1966)

57. A. E. Lipska and F. A. Wodley, Isothermal Pyrolysis of Cellulose Kinetics and Gas Chromatographic Mass Spectrometric Analysis of the Degradation Products, paper presented at the Spring Meeting of the Combustion Institute, Los Angeles, 1968

58. A. E. Lipska, The Fire Retardance Effectiveness of High Molecular Weight, High Oxygen Containing Inorganic Additives in Cellulose and Synthetic Materials, paper presented at the Spring Meeting of the Combustion Institute, Arizona, 1973

59. G. A. Byrne, D. Gardiner, and F. H. Holmes, J. Appl. Chem., 16, 81 (1966)

60. K. L. Paciorek, R. H. Kratzer, J. Kaufman, J. Nakahara, and A. M. Hartstein, J. Fire and Flammability, 5, 243 (1974)

61. E. Hagen, Plaste und Kautschuk, 13, 140 (1966)

62. Y. Okamoto, N. Kimura, and H. Sukarai, Bull. Chem. Soc. Jap., 47, 1299 (1974)

63. K. J. L. Paciorek, R. H. Kratzer, J. Kaufman, J. H. Nakahara, T. Christos, and A. M. Hartstein, Amer. Ind. Hyg. Assoc. J., 39, (8), 633 (1978)

64. Chem. and Eng. News, 54 (35), 27 (1976)

65. B. A. Schwetz, et al., Environ. Health Prospect, 5, 87 (1973)

66. D. H. Norbach, J. F. Engblom, and J. R. Allen, Toxicology and Appl. Pharm., 32, 330 (1975)

67. M. Kulka, Belg. Patent 616,197, July 1962

68. J. Kaupp and H. Klug, Ger. Patent 1,092,480, November 1960

69. L. Denivelle, R. Fort, and Pham Van Hai, Bull. Soc. Chim., France, 1960, 1538

70. R. H. Stehl, et al., Advan. Chem. Ser., 120, 119 (1973)

APPENDIX

Tabluations of thermal oxidative degradation products, in mg/g, for all compositions investigated.

LIST OF TABLES

APPENDIX-Cont'd.

TABLE I

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF STYRENE-BUTADIENE AND NEOPRENE RUBBERS

Product	SBR Uncured mg/g	SBR Cured mg/g	Neoprene Uncured mg/g	Neoprene Cured mg/g
CO	n.d.	n.d	5.83	3.55
CH_4	0.67	0.89	4.28	1.87
H_2O	6.63	18.8	16.2	33.2
HCl			313	171
CO_2	0.95	4.69	20.8	22.9
SO_2	?	?	?	?
COS	0.13	0.14	-	0.09
CS_2	0.29	0.68	-	-
H_2S	T[e]	T	-	0.58
C_2-species	0.99	0.53	22.5	3.46
C_3-species	1.19	0.51	4.39	2.06
C_4-species	0.22	3.47	1.18	0.72
1,3-Butadiene	11.2	3.80	-	-
C_5-species	2.77	1.56	0.50	0.83
Isoprene	0.50	0.65	2.39	-
C_6-species	3.09	2.11	2.32	1.67
C_7-species	1.19	1.05	0.47	1.50
4-Vinyl-1-cyclohexene	8.98	1.73	-	-
C_8-species	0.64	1.05	0.45	0.47
C_9-species	-	-	0.11	0.06
C_{10}-species	-	-	0.49	0.04
C_{11}-species	-	-	-	0.04
Benzene	0.95	0.58	0.36	0.72
Toluene	3.40	2.25	0.90	0.96
C_2-benzenes	2.11	4.15	2.69	1.38
C_3-benzenes	0.34	1.04	2.44	0.37
C_4-benzenes	0.11	0.14	0.16	0.01
C_5-benzenes	0.01	0.11	-	T
C_6-benzenes	0.38	0.07	0.04	-
Styrene	13.8	2.79	-	-
Methylstyrenes	0.46	0.66	-	-
Dimethylstyrenes	-	-	-	0.46
Naphthalene	-	-	-	0.15
Tetrahydronapthalenes	-	0.08	-	0.05
Methyltetrahydronapthalenes	0.14	0.08	-	-
Dimethyltetrahydronapthalenes	0.01	-	-	-

TABLE I-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF STYRENE-BUTADIENE AND NEOPRENE RUBBERS

Product	SBR Uncured mg/g	SBR Cured mg/g	Neoprene Uncured mg/g	Neoprene Cured mg/g
Indene	0.01	0.02	?	?
Indan (2,3-dihydroindene)	0.05	0.37	0.20	0.70
Methylindans	0.03	0.10	0.12	0.98
Dimethylindans	-	0.03	-	0.11
Dimethylindenes	0.09	-	-	-
C_3-indenes	0.02	-	-	-
γ-Terpinene	-	-	-	0.03
Santene	-	0.05	-	0.04
Azulene	-	0.02	-	0.01
Methyl chloride	1.10	-	0.36	0.16
Vinyl chloride	-	-	0.21	-
Ethyl chloride	0.05	-	0.25	0.33
Chloropropenes	-	-	0.44	0.04
Chloropropanes	-	-	0.55	-
Chloroprene	-	-	8.40	0.55
Chloro-C_4-species	-	-	0.53	T
2-Chloro-2-butene	-	-	0.94	0.06
Dichloro-C_4-ene species	-	-	3.15	1.84
Dichloro-C_5-ene species	-	-	0.05	T
Chloroprene dimer	-	-	2.83	0.64
Chlorobenzene	-	-	0.53	0.48
Chlorotoluenes	-	-	1.42	0.87
Benzyl chloride	-	-	T	0.10
Chloro-C_2-benzenes	-	-	2.33	1.21
Chloro-C_3-benzenes	-	-	0.07	0.01
Dichlorobenzenes	-	-	0.30	-
Dichlorotoluenes	-	-	0.17	-
Dichloro-C_2-benzenes	-	-	-	0.01
Methanol	0.01	0.03	-	0.14
Ethanol	0.02	0.01	T	T
Propanols	T	T	-	-
Butanols	T	-	T	0.01
2-Chloroethanol	-	-	T	0.02
Phenol	-	0.04	-	0.01
Cresols	-	0.59	-	-

TABLE I-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF STYRENE-BUTADIENE AND NEOPRENE RUBBERS

Product	SBR Uncured mg/g	SBR Cured mg/g	Neoprene Uncured mg/g	Neoprene Cured mg/g
Methylbenzyl alcohols	0.02	0.28	-	0.22
1-Phenyl-1-ethanol	-	-	-	0.05
Acetaldehyde	0.01	0.02	0.10	0.36
Butyraldehyde	T	-	-	-
Acetone	0.04	0.07	0.36	0.22
Methyl ethyl ketone	-	0.04	0.03	0.03
Methyl furyl ketone	-	0.30	-	-
Ethyl furyl ketone	-	-	-	T
(4'-methyl-2'-furyl)-2-cyclopentane-2-one	0.11	-	-	-
2-Ethyldimedone	-	T	-	-
Allyl benzyl ether	-	-	0.31	-
Formic acid	-	-	-	0.05
Acetic acid	0.06	T	-	0.35
Propionic acid	0.02	-	-	-
Methyl formate	T	-	-	-
Methyl acetate	T	-	-	-
2-Acetylthiophene	-	T	-	-

e) T = < 0.005 mg/g.

TABLE II

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF SELECTED FIBERS

Products	Nylon 6,6 mg/g x 10^2	Dacron[b] mg/g x 10^2	Dacron[c] mg/g	Rayon mg/g
CO	86.2	2060	62.6	25.0
CH_4		159	3.45	0.35
H_2O	1570	550	11.8	333
CO_2	919	1400	155	85.4
	(2400)[d]	-	-	-
COS	-	-	-	0.341
CS_2	-	-	-	T[e]
NH_3	82.5	-	-	-
	(1230)[f]	-	-	-
C_2-species	1.56	50.4	6.35	0.21
C_3-species	1.03	13.2	0.50	0.24
C_4-species	0.78	9.73	0.26	T
C_5-species	0.11	-	-	-
C_6-species	0.19	0.37	-	0.02
C_7-species	0.62	-	0.04	0.10
C_8-species	0.27	6.27	0.07	-
C_9-species	3.91	-	-	-
C_{10}-species	1.13	-	-	-
C_{11}-species	-	-	-	0.02
C_{12}-species	-	-	-	0.01
C_{13}-species	-	-	-	0.04
Benzene	1.59	10.1	0.65	0.02
Toluene	1.40	4.62	0.15	0.03
C_2-benzenes	0.32	2.45	0.06	0.01
C_3-benzenes	-	-	-	0.04
Styrene	-	-	0.06	-
Napthalene	-	-	0.08	-
Biphenyl	-	-	0.02	-
Methanol	2.64	226	1.71	T
Ethanol	0.16	3.71	0.05	-
C_4-alcohols	0.35	-	-	-
Phenol	-	27.3	0.06	-
Cresol	-	52.4	0.11	T
Dimethylphenols	-	0.40	-	-
Acetol	-	-	-	0.88

TABLE II-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF SELECTED FIBERS

Products	Nylon 6,6 mg/g x 10^2	Dacron[b] mg/g x 10^2	Dacron[c] mg/g	Rayon mg/g
Formaldehyde	-	487	0.42	0.32
Acetaldehyde	Tr[g]	405	37.0	0.13
Acrolein	-	-	0.26	T
C_3-aldehydes	-	2.02	0.07	0.06
Crotonaldehyde	-	0.80	0.04	0.03
C_4-aldehydes	0.11	0.03	0.06	T
C_5-aldehydes	0.35	-	-	-
Pyruvaldehyde	-	-	-	0.88
2-Methyl-2-butenal	-	-	-	0.01
Benzaldehyde	-	0.74	0.09	-
Furfural	-	-	-	7.11
5-Methyl-2-furfural	-	-	-	1.05
Acetone	0.03	3.17	0.01	0.37
Methyl ethyl ketone	-	5.28	-	1.13
Methyl vinyl ketone	-	-	0.01	-
2-Pentanone	-	0.86	-	-
3-Pentanone	-	-	0.01	-
3-Methyl-3-butene-2-one	-	-	-	0.48
2-Hexanone	0.13	-	-	-
3-Heptanone	1.46	0.71	0.03	-
1-Acetoxy-2-butanone	-	-	-	1.21
Cyclopentanone	47.5	1.23	0.03	0.04
3-Methylcyclopentanone	5.04	-	-	-
Cycloheptanone	1.81	-	-	-
Furyl methyl ketone	-	-	-	0.33
Acetophenone	-	0.83	0.01	-
1-Phenyl-1,2-propanedione	-	1.85	1.90	-
Methyl-but-1-enyl ether	-	0.09	-	-
Dimethoxymethane	0.11	11.4	T	-
1,1-Dimethoxyethane	-	0.20	T	-
p-Dioxane	1.78	0.54	0.05	-
1,3-Dioxolane	-	0.20	T	-
2-Methyl-1,3-dioxolane	0.62	Tr	0.04	-
Formic acid	-	0.74	-	-
Acetic acid	-	1.11	0.58	1.08

TABLE II-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF SELECTED FIBERS

Product	Nylon 6,6 mg/g x 10^2	Dacron[b] mg/g x 10^2	Dacron[c] mg/g	Rayon mg/g
Propionic acid	-	0.11	-	-
n-Butyric acid	-	1.06	-	-
Crotolactone	-	2.11	-	-
4-Hydroxy-2-pentenoic acid lactone	-	0.46	-	T
Methyl formate	-	68.4	0.01	-
Methyl acetate	-	24.6	0.02	-
Methyl propionate	-	1.08	-	-
Methyl-n-butyrate	-	0.11	-	-
Methyl-2-methylvalerate[h]	-	0.11	-	-
Isopropyl propionate[h]	-	0.06	-	-
Ethylene diformate	-	0.31	-	-
Methyl benzoate	-	1.83	0.34	-
Ethyl benzoate	-	1.43	0.23	-
Methyl-m-toluate	-	-	0.04	-
Acetoacetate (methyl ?)[h,i]	-	0.06	-	-
Furan	-	3.14	0.36	0.10
Methylfuran	-	-	-	0.23
2,3-Dihydrofuran	-	-	-	0.07
C_2-furans	-	-	-	0.30
C_3-furans	-	-	-	0.04
C_4-furans	-	-	-	0.02
Benzofuran	-	-	-	0.01
Methylbenzofurans	-	-	-	0.03
Dimethylbenzofurans	-	-	-	0.01
2-Pyrone[h]	-	0.14	-	-
Tetrahydropyran[h]	-	0.14	-	-
Ammonium carbamate ($NH_4CO_2NH_2$)	2620	-	-	-
Pyridine	7.28	-	-	-
2-Methylpyridine	1.62	-	-	-
Thiophene		-	-	0.04
Methylthiophene	-	-	-	T
2-Ethyl-5,7-dimethyl-thiophene	-	-	-	0.04

b) Degradation performed at 370°C. c) Degradation performed at 420°C. d) The value in the bracket includes both free carbon dioxide and that found combined in the form of $NH_4CO_2NH_2$. e) T = < 0.005 mg/g. f) The value in the bracket includes both free ammonia and that found combined in the form of $NH_4CO_2NH_2$. g) Tr = < 0.005 mg/g x 10^{-2}. h) Tentative identification only. i) Could include acetic anhydride.

TABLE III

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF REPRESENTATIVE PHOSPHATE ESTERS

Product	Tritolyl phosphate mg/g x 10^2	Tri-p-tolyl phosphate mg/g x 10^2	Tributyl phosphate mg/g	Tris(dichloropropyl) phosphate mg/g
CO	-	0.33	1.62	1.82
CH_4	2.25	-	0.08	0.24
H_2O	93.3	64.2	21.3	26.2
HCl	-	-	-	146
CO_2	27.6	12.5	2.16	5.10
C_2-species	0.07	0.01	0.37	0.40
C_3-species	0.03	0.01	1.08	0.54
C_4-species	29.6	0.02	540	0.04
C_5-species	0.05	Tr[b]	0.84	0.01
C_6-species	0.05	Tr	0.29	-
C_7-species	0.29	0.08	0.78	-
C_8-species	3.67	0.70	13.8	-
C_9-species	1.44	0.86	-	-
C_{10}-species	-	2.26	-	-
Benzene	0.95	0.02	-	-
Toluene	13.0	23.2	0.07	-
C_2-benzenes	11.3	0.58	0.06	-
C_3-benzenes	0.12	-	-	-
C_4-benzenes	-	-	0.01	-
C_5-benzenes	-	-	T[c]	-
C_6-benzenes	-	-	T	-
Dimethylindan	-	-	T	-
Trimethylindans	-	-	T	-
Tetramethylindans	-	-	T	-
Methyl chloride	-	-	-	0.07
Vinyl chloride	-	-	-	0.75
Ethyl chloride	-	-	-	0.16
Chloropropenes	-	-	-	3.06
1,2-Dichloroethane	-	-	-	8.32
1,2-Dichloropropene	-	-	-	2.45
1,3-Dichloropropene	-	-	-	3.01
2,3-Dichloropropene	-	-	-	8.85
1,2,3-Trichloropropane	-	-	-	116
Methanol	0.05	0.26	0.33	T
Ethanol	0.02	Tr	0.14	-

TABLE III-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF REPRESENTATIVE PHOSPHATE ESTERS

Products	Tritolyl phosphate mg/g x 10^2	Tri-p-tolyl phosphate mg/g x 10^2	Tributyl phosphate mg/g	Tris(dichloropropyl) phosphate mg/g
C_3-alcohols	-	-	0.09	-
C_4-alcohols	0.31	0.04	25.9[d]	-
3-Buten-2-ol	-	-	0.15	-
2-Chloroethanol	-	-	-	0.02
1,3-Dichloro-2-propanol	-	-	-	0.18
Phenol	39.3	Tr	-	-
Cresols	117	159	-	-
Acetaldehyde	0.02	0.06	0.19	1.92
Acrolein	-	-	-	22.7
C_3-aldehydes	-	-	0.32	3.96
Crotonaldehyde	-	-	0.24	-
n-Butyraldehyde	-	-	2.79	-
Isobutyraldehyde	0.02	-	0.02	-
Chloroacetaldehyde	-	-	-	T
Chloro-C_3-aldehydes	-	-	-	0.68
Acetone	0.17	0.06	0.21	0.10
Methyl vinyl ketone	-	-	0.04	-
Methyl ethyl ketone	0.10	Tr	-	-
2-Pentanone	-	-	T	-
Cyclopentanone	34.0	4.86	-	-
3,4,7-Trimethyl-1-indanone	0.38	-	-	-
Chloroacetone	-	-	-	8.15
sec-Butyl ether	-	-	0.08	-
di-n-Butyl ether	-	-	4.86	-
Methyl-p-cresyl ether	21.8	Tr	-	-
Dimethoxymethane	-	0.02	-	-
p-Dioxane	0.01	Tr	-	-
Acetic acid	-	Tr	-	-
n-Butyl formate	0.01	-	-	-
n-Butyl acetate	-	-	0.02	-
n-Butyl-n-butyrate	-	-	0.11	-
Dibutyl orthoformate	-	-	0.01	-
Furan	-	-	T	-
Tetrahydrofuran	-	-	0.25	-

b) Tr = < 0.005 mg/g x 10^{-2}. c) T = < 0.005 mg/g. d) These consisted of $> 99\%$ n-butanol.

TABLE IV

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER FLAME RETARDANTS

Product	Tris(2-chloroethyl) phosphate mg/g	Tris(2,3-dibromopropyl) phosphate mg/g
CO	19.3	7.85
CH_4	8.27	0.072
H_2O	15.1	15.3
HCl	25.3	3.61
HBr[b]	-	124.
CO_2	8.72	6.07
H_2S	-	T[c]
C_2-species	0.558	3.13
C_3-species	0.484	0.005
Benzene	3.71	0.164
Toluene	0.286	0.058
C_2-benzenes	0.191	-
C_3-benzenes	T	-
C_4-benzenes	0.085	-
C_5-benzenes	T	-
Methyl chloride	0.926	-
Vinyl chloride	135.	-
Ethyl chloride	0.441	-
1,2-Dichloroethane	305.	-
Chloropropenes	0.056	0.140
Chloropentane	0.097	-
Vinyl bromide	-	0.309
Ethyl bromide	-	0.449
Dibromoethylenes	-	1.49
1,2-Dibromoethane	-	0.069
Bromopropenes	-	26.9
Bromopropanes	-	6.19
Dibromopropenes[d]	-	219.
Dibromopropanes	-	22.3
Tribromopropenes	-	0.789
Tribromopropanes	-	152.
Bromochloropropenes	-	4.03
1-Chloro-2,3-dibromopropane	-	18.5

TABLE IV-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER FLAME RETARDANTS

Product	Tris(2-chloroethyl) phosphate mg/g	Tris(2,3-dibromopropyl) phosphate mg/g
Bromobenzene	-	?
Methanol	0.098	-
2-Chloroethanol	8.03	-
2,3-Dibromo-1-propanol	-	3.15
Acetaldehyde	12.1	-
Acrolein	-	0.084
Isobutyraldehyde	-	0.023
Chloroacetaldehyde	0.214	-
Bromopropionaldehyde	-	0.266
Acetone	0.068	1.25
Bromoacetone	-	4.96
1,3-Dibromopropanone	-	5.78
Bis(2-chloroethyl)ether	5.19	-
Bis(2-chloroethoxy)methane	2.49	-
$(ClCH_2CH_2O)_2CH(CH_2CH_2CO_2CH_3)^e$	0.776	-
Acetic acid	-	0.046
Propionic acid	-	0.043
Methyl formate	0.109	-
Methyl acetate	0.800	-
2-Chloroethyl acetate	1.24	-
Furan	0.001	-
p-Dioxane	0.002	-

b) This includes also the hydrogen bromide (1 mg/g) which was retained in the residue. c) < 0.005 mg/g. d) The value given for the dibromopropenes is too high due to the presence of bromobenzene which could not be separated from the dibromopropenes. e) Tentative identification only.

TABLE V

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF "PURE" COMPONENTS

Products	Dioctyl Phthalate mg/g	Carbon Black mg/g	Chlorinated Hydrocarbon mg/g	Nylon-6 mg/g
H_2	0.02	-	-	-
CO	4.11	3.80	7.38	-
CH_4	0.14	0.08	0.47	-
H_2O	1.37	19.4	9.21	18.4
HCl	-	-	499.7	-
CO_2	5.03	12.5	2.51	4.86
SO_2	-	0.59	-	-
COS	-	0.07	-	-
NH_3	-	-	-	0.17
C_2- and C_3-species	0.51	T[b]	1.67	0.01
C_4-species	1.20	-	-	-
C_5-species	1.01	-	-	T
C_6-species	0.08	T	0.30	
C_7-species	0.72	-	-	-
C_8-ene species (2-methyl-1-heptene)	119.4	-	-	-
Benzene	0.32	0.03	7.73	0.01
Toluene	0.04	0.08	1.01	T
Xylenes	-	-	0.06	-
Styrene	-	-	0.01	-
Methyl chloride	-	-	0.87	-
Vinyl chloride	-	-	0.76	-
Ethyl chloride	-	-	0.55	-
1,1-Dichloroethane	-	-	0.01	-
1,2-Dichloroethane	-	-	0.02	-
3-Chloropropane	-	-	0.51	-
Dichloropropenes	-	-	0.40	-
Chlorobutanes	-	-	0.14	-
Chlorobutenes	-	-	0.32	-
Dichlorobutenes	-	-	0.09	-
Chlorobenzene	-	-	9.69	-

TABLE V CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF "PURE" COMPONENTS

Products	Dioctyl Phthalate mg/g	Carbon Black mg/g	Chlorinated Hydrocarbon mg/g	Nylon 6 mg/g
Dichlorobenzenes	-	-	1.91	-
Chlorotoluenes	-	-	0.80	-
2-Propanol	-	-	-	0.22
Phenol	-	-	0.05	-
2-Chloroethanol	-	-	0.37	-
1-Chloro-2-propanol	-	-	0.27	-
Acetaldehyde	0.06	0.01	0.75	T
Acetone	4.78	0.01	0.61	-
Cyclopentanone	-	-	-	0.01
Phthalic anhydride	194	-	-	-

b) T = < 0.005 mg/g.

TABLE VI

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF MISCELLANEOUS ADDITIVES

Product	Diphenyl phthalate mg/g	Di-(2-ethylhexyl) sebacate mg/g	2-Mercapto-benzothiazole mg/g
CO	0.26	1.93	-
CH_4	-	0.16	0.04
H_2O	0.52	0.03	0.27
CO_2	1.32	6.85	0.44
SO_2	-	-	T[b]
COS	-	-	2.15
CS_2	-	-	7.30
H_2S	-	-	95.2
C_2-species	-	0.31	-
C_3-species	-	0.38	-
C_4-ene species	-	1.18	-
C_4-ane species	-	0.29	-
C_5-species	-	0.15	-
C_6-species	-	0.37	-
C_7-species	-	0.59	0.01
C_8-species	-	0.06	-
2-Ethyl-1-hexene	-	84.7	-
C_9-species	-	0.05	-
C_{10}-species	-	0.14	-
Benzene	0.03	-	0.01
Toluene	0.03	0.06	-
C_2-benzenes	T	-	0.01
C_4-alcohols	-	T	-
C_6-alcohols	-	T	-
2-Ethyl-1-hexanol	-	2.27	-
Phenol	4.38	-	-
Acetaldehyde	-	0.44	T
C_3-aldehydes	-	0.07	-
Crotonaldehyde	-	0.01	-
n-Butyraldehyde	-	0.20	-
n-Pentanal	-	0.04	-
2-Methylbutyraldehyde	-	T	-
n-Hexanal	-	T	-
C_6-dienal	-	T	-
2-Ethylhexanal	-	0.55	-
Acetone	0.01	0.04	-

TABLE VI-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF MISCELLANEOUS ADDITIVES

Product	Diphenyl phthalate mg/g	Di-(2-ethylhexyl) sebacate mg/g	2-Mercapto-benzothiazole mg/g
Methyl t-butyl ketone	-	-	T
3-Heptanone	-	0.18	-
γ-Butyrolactone	-	T	-
Methyl formate	-	T	-
Ethyl formate	-	T	-
2-Ethylhexyl acetate	-	1.33	-
C_8-acrylates	-	0.19	-
C_8-butyrates	-	0.02	-
Furan	-	0.01	-
C_3-furans	-	T	-
3-Methylthiophene	-	-	0.02
Benzothiazole	-	-	54.8

b) T = < 0.005 mg/g.

TABLE VII

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF ADDITIVES AND FLAME RETARDANTS

Product	Chlorowax 70 mg/g	Decabromodiphenyl Oxide mg/g	Dimethyl Chlorendate mg/g	Methyl Pentachloro-stearate mg/g	Pentachloro-phenol mg/g
CO	6.25	-	25.5	-	-
CH_4	-	-	2.48	T[b]	-
H_2O	10.2	0.294	0.016	14.8	0.950
HCl	571.	-	141.	271.	28.7
HBr	12.1	-	-	-	-
CO_2	19.2	0.138	26.4	53.4	1.06
C_2-species	-	-	T	0.419	-
C_3-species	-	-	0.198	0.498	-
C_4-species	-	-	-	1.07	-
C_5-species	-	-	-	1.05	-
C_6-species	-	-	-	1.14	-
C_7-species	-	-	-	1.70	-
C_8-species	-	-	-	0.556	-
C_9-species	-	-	-	0.781	-
C_{10}-species	-	-	-	0.380	-
C_{11}-species	-	-	-	0.090	-
Benzene	1.68	T	0.024	3.20	0.353
Toluene	T	-	0.461	1.68	-
C_2-benzenes	-	-	-	1.36	-
C_3-benzenes	-	-	-	0.755	-
C_4-benzenes	-	-	-	0.438	-
Tetrahydronaphthalene	-	-	-	1.87	-
Methyltetrahydronaphthalenes	-	-	-	1.42	-
Methyl chloride	-	-	39.2	63.4	-
Methylene dichloride	-	-	0.222	-	-
Chloroform	0.014	-	-	-	-
Carbon tetrachloride	3.77	-	-	-	-
Vinyl chloride	0.502	-	-	-	-

TABLE VII-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF ADDITIVES AND FLAME RETARDANTS

Product	Chlorowax 70 mg/g	Decabromodiphenyl Oxide mg/g	Dimethyl Chlorendate mg/g	Methyl Pentachloro-stearate mg/g	Pentachloro-phenol mg/g
Dichloroethylenes	0.015	-	-	-	-
Trichloroethylene	-	-	0.071	-	-
Trichloroethane	0.011	0.015	0.234	-	0.010
Tetrachloroethane	0.190	-	-	-	-
Pentachloroethane	0.341	-	-	-	-
Hexachloroethane	0.051	-	-	-	-
Chloropropenes	0.002	-	-	-	-
Dichloropropenes	0.285	-	-	-	-
Trichloropropenes	0.214	-	-	-	-
Dichlorobutenes	0.192	-	-	-	-
Trichlorobutenes	0.053	-	-	-	-
Trichloropentenes	0.033	-	-	-	-
Hexachlorocyclo-pentadiene	-	-	189.	-	-
1,2-Dibromoethane	-	0.070	-	-	0.020
1-Bromo-2-chloro-ethane	-	0.002	-	-	-
Chlorobenzene	7.52	-	-	0.452	-
Dichlorobenzenes	8.92	-	-	-	-
Trichlorobenzenes	2.13	-	-	-	-
Tetrachlorobenzenes	0.175	-	-	-	-
Chlorotoluenes	0.242	-	-	-	-
Dichlorotoluenes	1.08	-	-	-	-
Chloronaphthalenes	1.17	-	-	-	-
Octachlorodibenzo-p-dioxin	-	-	-	-	171.[c]
Methanol	-	-	0.032	14.1	0.077
1,3-Dichloro-2-propanol	-	-	-	0.542	-
2,3-Dichloro-1-propanol	-	-	-	0.159	-

TABLE VII-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF ADDITIVES AND FLAME RETARDANTS

Product	Chlorowax 70 mg/g	Decabromodiphenyl Oxide mg/g	Dimethyl Chlorendate mg/g	Methyl Pentachlorostearate mg/g	Pentachlorophenol mg/g
Cresol	-	-	-	0.036	-
Formaldehyde	-	-	0.017	-	-
Acetaldehyde	-	-	0.033	-	-
Acetone	0.014	-	0.006	0.061	0.542
Methyl ethyl ketone	-	-	-	0.015	-
2-Pentanone	-	-	-	0.025	-
Cyclopentanone	-	-	-	0.325	-
Methyl ether	-	-	0.002	0.092	-
Dimethoxymethane	-	-	0.266	0.074	-
Fumaric acid	-	-	2.76	-	-
Methyl formate	-	-	0.132	-	0.008
Methyl acetate	-	-	-	1.42	0.009
Methyl acrylate	-	-	0.109	0.086	-
Methyl propionate	-	-	0.184	1.36	-
Methyl methacrylate	-	-	0.026	1.09	-
Methyl butyrate	-	-	-	1.84	-
Methyl crotonate	-	-	-	0.131	-
Methyl pentanoate	-	-	-	1.98	-
Methyl hexenoate	-	-	-	0.024	-
Methyl hexanoate	-	-	-	2.42	-
Methyl heptenoate	-	-	-	0.711	-
Methyl heptanoate	-	-	-	1.41	-
Methyl octenoate	-	-	-	1.19	-
Methyl octanoate	-	-	-	1.36	-
Methyl nonenoate	-	-	-	0.829	-
Methyl nonanoate	-	-	-	1.10	-
Methyl decanoate	-	-	-	0.751	-
Methyl benzoate	-	-	-	0.353	-
Dimethyl fumarate	-	-	155.	-	-

b) < 0.0005 mg/g. c) Found in the residue of the sealed tube.

TABLE VIII

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF NEOPRENE CONTAINING CONVEYOR BELTS

Products	Material E-1 mg/g	Material F-7 mg/g	Material F-10 mg/g
H_2	0.50	0.30	0.63
CO	9.12	6.68	5.06
CH_4	0.60	1.12	0.68
H_2O	31.4	58.0	110.8
HCl	116.8	80.7	68.0
CO_2	14.4	29.3	64.5
SO_2	0.20	0.61	0.28
COS	0.23	0.34	0.29
CS_2	1.02	0.45	0.34
H_2S	1.21	6.04	0.56
C_2- and C_3-species	4.45	2.11	5.35
C_4-species	2.46	1.96	0.81
C_5-species	0.32	1.53	0.66
Isoprene	-	1.19	-
C_6-species	?	2.12	2.32
C_7-species	0.13	0.78	0.57
C_8-species	5.87	0.31	0.11
Benzene	2.98	0.35	0.30
Toluene	0.70	0.11	0.11
Xylenes	0.50	0.15	0.10
Ethylbenzene	0.23	0.02	0.10
C_3-benzenes	0.54	0.22	0.13
C_4-benzenes	0.05	0.15	0.13
Phenylcyclohexane	-	T[b]	-
1-Phenylcyclohexene	-	-	T
Styrene	T	T	0.04
Methylstyrenes	-	-	0.02
Dimethylstyrenes	-	-	0.17
Methylnapthalenes	-	-	0.03
Methyltetrahydronapthalenes	-	-	0.01
Indene	-	-	0.41
Indan (2,3-dihydroindene)	0.17	0.17	0.54
Methylindans	-	0.18	0.23
Dimethylindans	-	0.03	0.09
γ-Terpinene	-	-	0.07

TABLE VIII-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF NEOPRENE CONTAINING CONVEYOR BELTS

Products	Material E-1 mg/g	Material F-7 mg/g	Material F-10 mg/g
Santene	-	0.04	-
Azulene	-	0.02	0.13
Methyl chloride	0.50	0.62	0.49
Vinyl chloride	-	-	T
Ethyl chloride	1.05	0.53	0.34
2-Chloropropene	T	T	0.04
3-Chloropropene	1.24	-	-
Chloroprene	1.80	0.70	0.93
2-Chloro-2-methylpropane	-	0.06	-
2-Chloro-2-butene	0.11	-	-
Chloroprene dimer	0.18[c]	0.09[c]	1.22
Chlorobenzene	0.22	0.02	0.06
Chlorotoluenes	0.52	0.13	0.26
Benzyl chloride	0.43[c]	-	-
Chloro-C_2-benzenes	0.09	0.20	0.13
3-Methylbenzyl chloride	-	-	T
Methanol	0.05	-	-
Ethanol	0.02	T	T
Butanols	0.04	0.29	0.04
3-Methyl-1-Pentynol	2.16	-	-
Furfuryl alcohol	-	-	0.04
Phenol	T	0.01	-
Cresols	0.43[c]	T	0.01
2,5-Dimethyl benzyl alcohol	0.15	-	-
2-Chloroethanol	0.13	2.15	0.04
Acetaldehyde	?	T	0.01
Butyraldehydes	-	T	T
2,4-Hexadienal	-	-	0.03
1-Methyl-3-cyclohexene-1-carboxaldehyde	-	0.08	-
Acetone	0.23	0.51	0.63
Methyl ethyl ketone	-	0.23	0.68
Methyl n-propyl ketone	-	0.02	0.11
Methyl isopropyl ketone	-	0.12	-
Cyclopentanone	0.72	0.82	1.12
Cyclohexanone	T	0.02	0.06

TABLE VIII-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF NEOPRENE CONTAINING CONVEYOR BELTS

Products	Material E-1 mg/g	Material F-7 mg/g	Material F-10 mg/g
p-Dioxane	-	-	T
Methyl-2-furyl ketone	-	0.04	0.05
Methyl-p-tolyl ketone	-	0.02	-
1-Indanone	-	-	0.08
4,7-Dimethyl-1-indanone	-	0.04	-
3,4,7-Trimethyl-1-indanone	-	0.01	-
Chloroacetone	-	0.21	0.06
Formic acid	T	0.30	0.60
Acetic acid	0.38	2.10	3.51
Propionic acid	?	12.0	0.38
Methyl acetate	T	0.03	0.01
Phenol ethers	-	T	-
Dimethylfurans	-	-	0.01
Benzofuran	-	-	T
1,2-Dimethylaminopyridine	-	-	0.10
Methyl mercaptan	-	T	-
Dimethylsulfide	-	T	-

b) T = < 0.005 mg/g.   c) Tentatively identified.

TABLE IX

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF CONVEYOR BELTS CONTAINING STYRENE-BUTADIENE RUBBER

Products	Material E-3 mg/g	Material E-5 mg/g	Material F-9 mg/g	Material E-4 mg/g
H_2	0.11	0.15	0.17	0.12
CO	12.0	3.67	?	2.53
CH_4	0.27	0.21	0.39	1.23
H_2O	71.4	33.9	20.2	42.8
HCl	2.8	14.1	39.4	15.9
CO_2	18.7	12.5	10.8	25.5
SO_2	0.17	0.09	-	T[b]
COS	0.56	1.34	0.36	0.45
CS_2	0.03	0.33	1.72	-
H_2S	0.02	0.74	7.63	0.25
HCN	-	0.50	T	-
C_2- and C_3 species	0.84	1.80	6.03	6.01
C_4-species	0.56	0.62	2.91	0.95
C_5-species	0.23	0.60	5.32	0.88
C_6-species	1.06	1.59	2.81	0.71
C_7-species	0.34	0.12	0.99	0.56
C_8-species	6.87	0.90	2.49	0.05
C_9-species	-	-	0.03	-
1-Methyl-4-isopropenyl-1-cyclohexene	-	-	-	8.21
C_{11}-species	-	-	0.01	-
C_{12}-species	-	-	0.07	-
C_{13}-species	-	-	0.02	-
Benzene	0.50	0.32	1.98	0.35
Toluene	1.03	0.17	0.16	0.79
Xylenes	0.33	0.60	0.18	0.96
Ethylbenzene	0.28	0.50	0.16	0.83
C_3-benzenes	0.27	0.03	0.15	0.05
C_4-benzenes	0.02	0.02	0.04	0.05
o-Allyltoluene	-	-	0.02	-
C_5-benzenes	-	-	0.02	-
Styrene	0.95	0.27	0.56	1.12
Methylstyrenes	0.08	0.03	0.12	0.11
C_2-Styrenes	0.06	0.02[c]	0.19	T
Tetrahydronapthalenes	0.01[c]	0.02[c]	0.02	0.02[c]

TABLE IX-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF CONVEYOR BELTS CONTAINING STYRENE-BUTADIENE RUBBER

Products	Material E-3 mg/g	Material E-5 mg/g	Material F-9 mg/g	Material E-4 mg/g
Methylnapthalenes	0.01^{c}	0.03^{c}	T	?
Methyltetrahydronapthalenes	0.01^{c}	0.02^{c}	0.01	0.01^{c}
Indene	0.02^{c}	0.02^{c}	0.10	0.06^{c}
Indan (2,3-dihydroindene)	0.02^{c}	0.03^{c}	0.10	0.06^{c}
Methylindans	0.01^{c}	0.02^{c}	0.01	0.01^{c}
Dimethylindans	T	0.03^{c}	0.01	0.01^{c}
Azulene	?	?	0.10	?
Methyl chloride	T	0.39	10.39	0.01
Vinyl chloride	-	-	0.34	T
Ethyl chloride	-	0.12	2.77	0.13
2-Chloropropene	-	-	0.26	-
Chloroprene	-	-	0.27	-
2-Chloro-2-butene	-	-	0.63	-
3-Chloro-2-methylpropane	-	-	0.06	-
Chlorobenzene	0.01	0.01	0.09	T
Chlorotoluenes	0.02	?	0.12	-
Chloro-C_2-benzenes			0.01	-
Dichlorobenzene	-	0.01	0.03	-
Methanol	0.23	T	2.74	0.04
Ethanol	0.04	T	T	0.11
Allyl alcohol	-	-	-	0.02
C_3-alcohols	-	-	-	T
C_4-alcohols	0.08	0.05	0.01	T
C_5-alcohols	-	-	T	-
Phenol	0.02	0.67	0.03	0.06
Cresols	?	?	1.77	?
4-Methyl-2-ethylphenol	-	-	0.02	-
2-Chloroethanol	0.01	T	0.03	0.04
Acetaldehyde			0.46	0.71
Acetone	0.02	0.09	0.06	0.21
Methyl ethyl ketone	0.03	0.02	0.06	0.10
Methyl n-propyl ketone	-	-	T	-
Methyl isopropenyl ketone	-	-	-	0.07
4-Methyl-2-pentanone	-	-	-	0.07
Methyl-2-furyl ketone	-	-	T	-
p-Dioxane	-	0.04	0.01	-
Cyclopentanone	2.46	1.78	0.02	0.02

TABLE IX-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF CONVEYOR BELTS CONTAINING STYRENE-BUTADIENE RUBBER

Products	Material E-3 mg/g	Material E-5 mg/g	Material F-9 mg/g	Material E-4 mg/g
Methylcyclopentanone	-	-	0.06	-
Cyclohexanone	-	0.10	0.02	0.02
Dimethylindanones	?	?	0.01	?
Trimethylindanones	?	?	0.03	?
Formic acid	-	-	2.91	-
Acetic acid	T	0.14	0.71	0.23
Methoxyacetic acid	-	1.73	-	-
Methyl acetate	0.12	-	0.02	T
Vinyl acetate	-	-	-	0.07
Ethyl formate	0.01	-	T	-
Ethyl acetate	0.08	-	-	?
2-Methylfuran	-	0.01	-	0.28
Dimethylfurans	-	0.12	-	?
Ethylmethylfurans	-	-	0.02	-
Methyl mercaptan	?	?	0.01	?
Dimethyl sulfide	T	T	0.02	?
Dimethyl disulfide	?	?	0.21	?
Methylthiophenes	?	?	0.08	?
Thiacyclopentane	?	?	0.01	?
Acetonitrile	-	0.22	-	-
5-Cyanohexene	-	-	0.25	-

b) T = < 0.005 mg/g. c) Tentatively identified.

TABLE X

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PVC CONTAINING CONVEYOR BELTS

Products	Material E-2 mg/g	Material F-3 mg/g	Material F-6 mg/g
H_2	0.02	T^b	0.01
CO	3.01	?	?
CH_4	0.01	0.07	-
H_2O	60.6	7.14	140.1
HCl	89.6	155.5	95.0
CO_2	33.9	4.54	40.0
COS	-	?	0.05
CS_2	0.01	-	-
H_2S	?	0.15	0.34
C_2- and C_3-species	19.5	0.87	0.24
C_4-species	T	0.04	0.32
C_5-species	?	?	0.64
Isoprene	-	-	1.03
C_6-species	T	?	1.21
C_7-species	0.10	1.05	0.07
C_8-ene species	19.6	81.5	24.8
C_9-ene species	-	7.00	-
1-Undecene	-	3.38	-
Benzene	2.62	13.9	4.56
Toluene	3.73	2.90	0.21
Xylenes	0.23	T	0.11
Ethylbenzene	T	T	0.06
Methylstyrenes	T	T	0.06
Divinylbenzene	-	0.18	-
Methyl chloride	0.16	0.29	0.45
Vinyl chloride	0.34	2.36	T
Ethyl chloride	3.46	0.76	T
1,2-Dichloroethane	5.87	2.33	0.01
2-Chloropropene	-	-	0.03
1-Chlorohexane	-	-	0.43
1-Chloroheptane	-	1.72	-
1-Chloro-2-ethylhexane	-	-	12.8
1-Chlorodecane	-	1.00	-
Myristyl(C_{14}) chloride	-	0.02	-
Benzyl chloride	16.0	-	-

TABLE X-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PVC CONTAINING CONVEYOR BELTS

Products	Material E-2 mg/g	Material F-3 mg/g	Material F-6 mg/g
Chlorotoluenes	1.51	0.50	-
Methanol	0.02	-	-
Ethanol	0.50	T	T
C_3-alcohols	0.04	-	-
C_4-alcohols	5.09	?	T
C_5-alcohols	0.93	-	0.03
Cyclic C_6-alcohol	-	4.43	-
C_8-alcohols	0.11	0.52	0.05
C_9-alcohols	-	0.29	-
Dodecanols	-	0.53	-
Phenol	-	-	17.5
2-Chloroethanol	6.66	0.35	0.04
Acetaldehyde	0.98	1.10	T
C_4-aldehyde	?	0.13	?
C_5-aldehyde	-	5.54	-
Acetone	0.10	0.02	0.31
Methyl ethyl ketone	T	0.02	0.82
Methyl n-propyl ketone	-	-	0.01
Methyl 2-furyl ketone	-	-	0.01
Cyclopentanone	6.51	0.07	4.00
Chloroacetone	T	-	0.27
p-Dioxane	-	0.27	0.01
bis(2-Chloroethoxy) methane	-	2.77	-
Acetic acid	0.13	0.01	1.19
Methyl acetate	0.02	0.23	0.03
Ethyl formate	0.01	0.01	0.01
Ethyl acetate	0.03	?	0.01
n-Butyl formate	0.33	0.03	0.06
n-Butyl acetate	0.10	?	0.08
Chloroethyl acetate	0.40	T	0.01
Methyl mercaptan	-	-	T
Dimethyl disulfide	-	-	T
1-Hexanethiol	-	-	0.48
2-Methylpyridine	-	-	0.14
Benzonitrile	0.15	-	-

b) T = < 0.005 mg/g.

TABLE XI

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PVC CONTAINING CONVEYOR BELTS

	F-A mg/g	Scandura mg/g
CO	?	?
CH_4	0.090	0.229
H_2O	66.9	19.0
HCl	130.[b]	178.[c]
CO_2	24.7	4.38
C_2-species	1.27	4.44
C_3-species	0.290	0.622
C_4-species	0.064	0.854
C_5-species	0.364	0.450
C_6-species	0.675	-
C_7-species	0.224	0.696
C_8-species	11.1	10.1
C_9-species	0.068	1.59
C_{10}-species	2.79	0.080
C_{11}-species	-	0.049
C_{12}-species	-	0.506
C_{14}-species	-	0.915
Benzene	6.81	8.87
Toluene	0.399	1.01
C_2-benzenes	0.034	0.516
C_3-benzenes	-	0.698
C_4-benzenes	-	0.224
C_5-benzenes	-	0.236
C_7-benzenes	-	0.023
C_8-benzenes	-	0.381
C_9-benzenes	-	0.429
Methylstyrenes	0.023	0.196
Dimethylstyrenes	-	0.066
Naphthalene	-	0.544
Methylnaphthalenes	-	0.194
Methyltetrahydronaphthalenes	-	0.103
Methyl chloride	0.739	-
Ethyl chloride	0.670	-
Vinyl chloride	-	5.28
1,2-Dichloroethane	0.946	3.70
1-Chlorohexane	10.3	-
Chlorooctanes	22.3	0.911
Chlorononanes	7.81	0.816
Chlorodecanes	10.0	0.414
Chloroundecanes	-	0.654
Chlorododecanes	-	0.752
Methanol	-	0.002
Ethanol	-	0.037
1-Hexanol	0.123	-
2-Ethylhexanol	3.03	-
C_{12}-alcohols	-	1.46
C_{14}-alcohols	-	0.760
Phenol	4.28	-
2-Chloroethanol	0.168	1.28
Acetaldehyde	-	0.794
Acetone	0.218	0.018
Methyl ethyl ketone	0.387	0.020
Cyclopentanone	2.64	-
Methylcyclopentanone	0.032	-
Furan	-	T[d]
p-Dioxane	1.28	0.163
Bis(2-chloroethyl)ether	0.423	-
Acetic acid	-	0.042
2-Ethylhexyl acetate	0.478	-
2-Chloroethyl acetate	-	0.006

b) This includes 27 mg/g found in the residue. c) This includes 1 mg/g found in the residue. d) <0.0005 mg/g.

TABLE XII

PRODUCTS OF NEOPRENE COMPOSITIONS (SEALED TUBE STUDIES)

Products	"Uncured" mg/g	"Cured" mg/g	4A mg/g	3A mg/g
CO	13.2	6.19	19.1	7.35
CH_4	2.15	1.04	0.72	1.16
HCl	311.9	200.0	109.8	64.7
CO_2	16.1	104.4	137.5	26.6
SO_2	-	0.54	0.32	0.69
COS	-	-	-	0.03
CS_2	-	0.84	0.50	2.12
H_2S	-	0.11	0.22	0.31
C_xH_y[b]	3.52	3.38	4.35	2.27
C_6H_6	1.41	0.25	0.11	0.63
$C_6H_5CH_3$	0.69	T	T	0.04
CH_3Cl	0.39	0.22	1.08	0.57
C_2H_3Cl	0.36	-	0.07	1.98
C_2H_5Cl	1.13	0.79	0.54	1.28
$(CH_2Cl)_2$	0.54	-	-	3.08
C_4H_5Cl	6.30	2.27	1.73	0.71
C_4H_7Cl	0.62	-	-	-
CH_3OH	-	-	0.04	0.19
C_2H_5OH	-	-	-	0.30
$i\text{-}C_3H_7OH$	-	-	-	0.06
$n\text{-}C_3H_7OH$	0.27	?	-	-
CH_3CHO	-	0.04	0.04	2.61
$(CH_3)_2CO$	0.07	0.07	0.04	0.49
$HCOOH$	-	-	0.07	0.08
CH_3COOH	2.39	-	-	-

[b] C_xH_y denotes hydrocarbons C_2 through C_4.

TABLE XIII

PRODUCTS OF NEOPRENE COMPOSITIONS (STAGNATION BURNER STUDIES)

Products	"Uncured" mg/g	"Cured" mg/g	4A mg/g	3A mg/g
HCl	300.3	181.1	99.4	44.9
CO_2	48.0	1160	1050	32.7
SO_2	0.95	6.36	5.74	0.55
COS	-	0.04	0.03	0.17
CS_2	-	0.01	0.01	0.54
H_2S	0.05	0.20	0.06	0.65
C_xH_y [b]	3.53	7.44	4.60	1.91
C_6H_6	1.42	0.02	0.10	0.29
CH_3Cl	0.51	0.43	0.37	0.28
C_2H_3Cl	0.38	-	0.78	-
C_2H_5Cl	0.55	0.75	0.78	0.48
$(CH_2Cl)_2$	0.31	-	0.04	3.32
C_4H_5Cl	4.14	0.26	0.16	0.83
C_4H_7Cl	4.07	-	-	-
CH_3OH	-	0.26	-	0.42
C_2H_5OH	-	-	1.50	-
i-C_3H_7OH	-	0.05	-	-
n-C_3H_7OH	-	T	0.17	0.04
CH_3CHO	-	-	0.08	5.29
$(CH_3)_2CO$	0.06	0.01	0.39	0.99
HCOOH	-	-	T	-
CH_3COOH	0.02	0.01	0.16	0.80

[b] C_xH_y denotes hydrocarbons C_2 through C_4.

TABLE XIV

PRODUCTS OF PVC COMPOSITIONS
(SEALED TUBE STUDIES)

Products	PVC mg/g	6A mg/g	13A mg/g	7A mg/g	9B mg/g	10B mg/g
CO	19.7	4.84	5.02	5.65	8.91	5.83
CH_4	0.80	0.20	0.54	0.55	0.85	1.94
HCl	550.6	174.2	253.7	263.5	205.8	300.0
CO_2	12.1	29.1	18.1	19.0	32.4	33.7
SO_2	0.38	0.25	0.37	-	-	0.22
COS	-	0.16	-	-	-	-
CS_2	-	-	-	0.36	-	-
C_xH_y[b]	1.51	1.71	6.14	2.87	2.18	4.52
Isoprene	-	-	-	-	0.66	-
C_6H_6	47.5	5.12	26.7	25.4	35.8	19.5
C_6H_{12}	-	1.05	-	-	-	-
$C_6H_5CH_3$	0.61	0.57	1.51	0.84	0.42	0.58
$C_6H_4(CH_3)_2$	0.08	0.03	0.08	0.11	0.02	0.02
CH_3Cl	0.44	3.75	3.19	T	0.72	0.48
C_2H_3Cl	0.05	-	-	0.05	-	-
C_2H_5Cl	0.03	1.10	20.7	T	0.34	0.33
$(CH_2Cl)_2$	0.10	-	0.81	-	-	-
C_4H_5Cl	0.56	0.02	0.19	-	-	0.31
$C_6H_{13}Cl$	0.10	0.16	-	0.11	0.35	-
$C_6H_5CH_2Cl$	0.03	-	-	T	-	-
CH_3OH	0.03	0.03	0.05	0.06	0.05	0.06
C_2H_5OH	0.02	T	1.10	0.28	4.88	0.66
$n-C_3H_7OH$	0.03	0.23	0.43	0.02	1.18	1.11
$i-C_3H_7OH$	0.07	-	T	0.08	0.40	0.16
HCHO	?	?	?	?	?	0.06
CH_3CHO	0.13	T	0.02	0.09	-	0.02
$(CH_3)_2CO$	0.07	0.64	0.03	1.44	2.82	1.36
HCOOH	-	T	-	-	0.16	0.13
CH_3COOH	0.06	0.23	0.30	0.03	0.72	0.50

[b] C_xH_y denotes hydrocarbons C_2 through C_4

TABLE XV

PRODUCTS OF PVC COMPOSITIONS
(STAGNATION BURNER STUDIES)

Products	PVC mg/g	6A mg/g	13A mg/g	7A mg/g	9B mg/g
HCl	421.4	168.6	184.4	146.9	155.4
CO_2	49.2	23.2	22.6	31.6	24.0
SO_2	0.23	0.12	0.40	-	-
COS	-	0.11	-	-	-
C_xH_y[b]	1.92	0.65	3.03	0.90	0.33
C_6H_6	39.4	16.0	33.3	17.6	32.0
C_6H_{12}	-	0.73	-	-	-
$C_6H_5CH_3$	0.40	0.48	0.02	0.09	0.50
$C_6H_4(CH_3)_2$	0.20	0.02	T	T	T
CH_3Cl	0.36	3.31	2.49	0.51	0.13
C_2H_3Cl	-	0.16	0.15	-	-
C_2H_5Cl	T	0.50	12.4	0.24	0.03
$C_6H_{13}Cl$	-	-	0.05	-	2.11
$C_6H_5CH_2Cl$	-	0.01	-	-	-
CH_3OH	0.01	0.03	0.04	0.03	0.04
C_2H_5OH	-	T	7.22	0.38	0.05
n-C_3H_7OH	T	0.04	0.48	T	T
i-C_3H_7OH	0.01	0.02	0.06	0.01	T
HCHO	?	?	?	?	?
CH_3CHO	0.16	-	0.77	-	-
$(CH_3)_2CO$	0.01	0.15	0.59	1.26	0.02
HCOOH	0.10	-	-	-	-
CH_3COOH	0.01	0.04	0.47	0.38	0.14
$HCOOC_2H_5$	-	-	0.56	0.02	-
4-Methylcyclohexanone	-	-	-	-	2.08

[b] C_xH_y denotes hydrocarbons C_2 through C_4.

TABLE XVI

PRODUCTS OF URETHANE RIGID FOAMS
(SEALED TUBE STUDIES)

Products	Material 1B mg/g	Material 2B mg/g	Material 16A mg/g
CO	-	-	34.5
CH_4	1.60	0.96	2.36
HCl	23.2	5.85	17.3
NH_3	3.17	10.7	-
HCN	T	T	T
CO_2	144.2	148.7	191.5
C_xH_y [b]	1.81	3.90	2.18
C_6H_6	2.92	0.77	0.18
$C_6H_5CH_3$	0.21	0.18	0.30
CH_3Cl	1.08	1.03	0.22
C_2H_3Cl	0.28	0.22	0.22
C_2H_5Cl	11.70	7.43	0.07
$CH_2Cl\text{-}CH_2Cl$	40.0	52.0	17.7
$CH_2Cl\text{-}CH{=}CH_2$	0.87	0.51	0.23
C_6H_5Cl	0.14	0.04	-
$CH_2Cl\text{-}CH_2Br$	-	-	26.0
CH_3Br	-	-	1.85
C_2H_3Br	-	-	0.51
C_2H_5Br	-	-	3.12
$CH_2Br\text{-}CH_2Br$	-	-	12.5
$CFCl_3$	89.2	56.0	9.25
$CHFCl_2$	1.63	0.92	-
CH_3OH	0.02	0.07	0.44
C_2H_5OH	0.42	0.77	-
$i\text{-}C_3H_7OH$	0.07	0.07	T
$n\text{-}C_3H_7OH$	0.03	-	T
$CH_2Cl\text{-}CH_2OH$	1.29	1.10	0.03
$CH_2Cl\text{-}CHOH\text{-}CH_3$	0.94	2.91	3.41
CH_3CHO	-	-	0.15
Sorbaldehyde	-	-	1.04
$(CH_3)_2CO$	2.37	1.54	14.4
$CH_3COC_2H_5$	0.50	0.74	0.16
1,4-Dioxane	0.14	0.18	1.67
HCOOH	-	0.06	0.04
CH_3COOH	0.02	0.39	1.52
$C_6H_5NH_2$	58.6	66.9	-
p-Toluidine	10.3	7.4	-
p-Phenylenediamine	?	Yes	-
2,4-Toluenediamine	?	Yes	-

[b] C_xH_y denotes hydrocarbons C_2 through C_4

TABLE XVII

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF SOLVENTS AND FIRE EXTINGUISHANTS

Product	ClH_2CCHCl_2 mg/g	$Cl_2C{=}CHCl$ mg/g	$Cl_2C{=}CCl_2$ mg/g
CO	314.	57.8	-
H_2O	44.7	-	-
HCl	696.	243.	1.43
CO_2	61.8	8.23	0.97
$COCl_2$	39.6	116.	-
C_6-species	0.008	-	-
C_7-species	0.004	-	-
Benzene	0.008	-	-
Chloroform	0.012	-	-
Methylene dichloride	0.793	-	-
Dichloroethylenes	2.52	34.9	-
Trichloroethylene	421.	11.0	-
Tetrachloroethylene	35.8	2.59	4.85
Hexachloroethane	14.3	-	-
Tetrachloropropene	0.126	-	-
Pentachloropropene	16.9	-	-
Trichlorobutenes	15.6	-	-
Tetrachlorobutene	6.68	-	-
Pentachlorobutadienes	0.224	-	-
Hexachlorobutadiene	5.92	-	-
Hexachlorobutane	6.61	-	-
Heptachlorobutene	2.12	-	-
Tetrachloropentadiene	0.021	-	-
Pentachlorocyclopentadiene	0.102	-	-
Hexachlorocyclopentadiene	0.128	-	-
Hexachlorobenzene	21.4[b]	-	-
Chloroacetaldehyde	-	T[c]	-
Acetone	-	0.008	-

[b] Found in residue of sealed ampoule. [c] <0.005 mg/g.

TABLE XVIII

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF MISCELLANEOUS HYDRAULIC FLUIDS

Products	Ucon Hydrolube 275 CP mg/g	Citgo Glycol FR-20 XD mg/g	SNFH mg/g	Duro FR-HD mg/g	Quintolubric 822-300	
					370°C mg/g	"420°C" mg/g
CO	1.51	1.89	-	3.50	1.36	1.87
CH_4	T[a]	-	-	-	0.511	0.797
H_2O	347	212	200	400	8.39	8.32
CO_2	3.26	4.15	1.50	1.79	1.39	2.95
COS	-	-	-	0.032	0.016	0.106
N_2O	0.344	0.295	-	-	-	-
C_2-species	0.071	0.901	0.011	0.650	0.187	0.867
C_3-species	0.056	0.045	0.011	0.392	0.410	2.23
C_4-species	0.002	0.004	0.009	1.34	0.958	4.64
C_5-species	-	-	0.005	0.409	0.761	5.21
C_6-species	-	-	0.008	0.519	1.20	5.88
C_7-species	-	-	0.017	0.628	1.15	8.32
C_8-species	-	-	0.025	0.262	1.27	7.22
C_9-species	-	-	0.037	1.11	0.890	6.34
C_{10}-species	-	-	-	0.61	0.464	5.48
C_{11}-species	-	-	-	0.277	1.52	9.74
C_{12}-species	-	-	-	0.232	0.383	3.36
C_{13}-species	-	-	-	-	0.253	0.525
C_{14}-species	-	-	-	-	0.026	-
Benzene	T	0.002	0.002	0.008	0.098	0.205
Toluene	0.003	0.007	0.009	0.088	0.157	0.332
C_2-benzenes	-	-	0.028	0.012	0.122	0.663
C_3-benzenes	-	-	0.007	0.013	0.056	0.063
C_4-benzenes	-	-	-	0.003	0.074	0.121
C_5-benzenes	-	-	-	-	0.118	0.447
C_6-benzenes	-	-	-	-	0.016	-
C_7-benzenes	-	-	-	-	0.033	-
Styrene	-	-	-	-	T	0.694
Tetrahydronapthalenes	-	-	-	0.006	-	-
Dimethylindans	-	-	-	-	0.056	1.19
3,4,7-Trimethyl-1-indanone	-	-	-	-	0.138	0.357
Chloroform	-	-	0.005	-	-	-

TABLE XVIII-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF MISCELLANEOUS HYDRAULIC FLUIDS

Products	Ucon Hydrolube 275 CP mg/g	Citgo Glycol FR-20XD mg/g	SNFH mg/g	Duro FR-HD mg/g	Quintolubric 822-300	
					370°C mg/g	"420°C" mg/g
Tetrachloroethylene	-	-	0.007	-	-	-
Methanol	0.052	0.066	0.009	0.068	0.215	0.045
Ethanol	0.239	0.167	-	0.027	0.019	0.003
C_3-alcohols	0.025	0.029	T	-	0.011	0.002
C_4-alcohols	0.009	-	-	-	-	0.003
C_5-alcohols	-	-	-	-	-	0.001
C_6-alcohols	-	-	-	-	0.447	0.964
Ethylene glycol	9.83	10.3	2.70	-	-	-
1,2-Propanediol	-	-	3.59	-	-	-
Acetaldehyde	0.330	0.297	0.007	1.58	0.397	0.003
Propionaldehyde	0.004	0.017	0.168	0.284	0.084	0.029
Acrolein	-	-	T	0.006	0.017	T
C_4-aldehydes	-	0.005	0.001	0.315	0.830	1.54
C_5-aldehydes	0.015	0.028	0.001	0.262	0.337	1.24
C_6-aldehydes	0.009	-	0.050	0.186	0.321	-
C_7-aldehydes	-	-	-	-	0.046	-
Acetone	0.058	0.086	0.010	0.500	0.130	0.078
Methyl ethyl ketone	0.081	0.051	T	0.266	0.137	0.002
C_5-ketones	0.005	0.015	0.001	0.117	-	0.008
C_6-ketones	0.002	0.007	-	0.033	-	-
C_7-ketones	-	-	-	0.064	-	-
C_8-ketones	-	-	-	0.025	-	-
C_{10}-ketones	-	-	-	-	0.052	-
C_{11}-ketones	-	-	-	-	0.015	-
C_{12}-ketones	-	-	-	-	0.028	-
Cyclopentanone	0.004	0.005	-	-	0.013	0.004
Cyclohexanone	-	0.009	-	0.034	0.004	0.003
Methyl ether	0.004	0.003	T	-	-	-
Methyl ethyl ether	0.011	0.007	0.001	-	-	-
Methyl propyl ether	0.003	0.005	-	-	0.003	-
Methyl butyl ether	0.024	0.003	-	-	-	-
Ethyl butyl ether	0.001	0.005	-	-	-	-

TABLE XVIII-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF MISCELLANEOUS HYDRAULIC FLUIDS

Products	Ucon Hydrolube 275 CP mg/g	Citgo Glycol FR-20XD mg/g	SNFH mg/g	Duro FR-HD mg/g	Quintolubric 822-300	
					370°C mg/g	"420°C" mg/g
Diphenyl ether	-	-	-	-	0.013	-
Ethylene oxide	0.693	1.04	-	-	-	-
Furan	-	0.008	-	T	T	-
2-Methyltetrahydrofuran	-	-	-	0.062	-	-
2-Methyl-1,3-dioxolane	0.028	0.049	-	-	-	-
C_2-1,3-Dioxolanes	0.004	-	-	-	-	-
p-Dioxane	0.013	0.125	-	0.034	-	-
Formic acid	0.004	-	-	-	-	0.001
Acetic acid	0.018	-	-	-	-	0.061
Propionic acid	-	-	-	-	-	0.026
Long chain aliphatic acids	-	-	-	-	0.147	1.07
Methyl formate	-	-	-	-	T	-
Methyl acetate	-	-	-	-	0.003	0.016
Aliphatic diesters	-	-	-	-	0.062	0.308
Thiacyclopropane	0.015	0.056	-	0.804	-	-
Thiophene	-	-	-	0.010	-	-
Divinyl sulfide	0.004	0.008	-	-	-	-
Acetonitrile	0.022	0.006	-	-	-	-
Propionitrile	0.020	0.009	-	-	-	-
1-Cyano-1-butene	0.001	-	-	-	-	-

a) < 0.0005 mg/g

TABLE XIX

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

Products	Fyrquel 220		Pydraul 50E		Pydraul MC		Dasco FR 300		$(\Phi O)_3PO + C_{28}H_{58}$
	370°C mg/g	420°C mg/g	370°C mg/g	420°C mg/g	370°C mg/g	"420°C" mg/g	370°C mg/g	"420°C" mg/g	"420°C" mg/g
CO	-	T[a]	0.596	T	0.694	T	1.25	2.19	1.72
CH_4	0.125	0.169	-	0.296	T	0.097	0.104	0.197	0.147
H_2O	1.16	1.04	0.979	0.004	0.324	-	8.92	10.5	7.72
CO_2	0.116	0.085	0.494	0.197	0.060	0.076	0.850	1.43	0.480
COS	0.001	T	-	-	T	-	0.214	0.299	-
CS_2	-	-	-	-	-	-	0.022	T	-
SO_2	0.001	T	-	-	0.069	T	-	-	-
H_2S	0.003	T	-	-	-	-	0.113	T	-
PH_3	-	-	-	-	-	2.78	-	0.141	T
C_2-species	0.024	0.067	0.068	1.47	0.042	0.413	0.351	1.64	0.697
C_3-species	0.008	0.038	0.131	3.03	0.032	0.301	1.54	5.61	1.04
C_4-species	0.004	0.017	2.55	6.33	0.131	0.788	1.58	3.93	1.19
C_5-species	0.003	0.007	0.351	4.93	0.092	1.33	0.683	2.80	1.18
C_6-species	0.008	0.014	0.435	6.99	0.435	21.8	1.72	2.29	1.45
C_7-species	0.015	0.007	0.166	0.519	5.22	5.07	1.09	1.91	1.55
C_8-species	0.147	0.015	0.158	0.685	25.0	24.7	1.26	2.28	1.75
C_9-species	0.053	T	1.93	5.68	4.65	23.4	0.056	1.16	1.88
C_{10}-species	-	-	T	0.203	T	0.996	0.048	0.915	1.99

TABLE XIX-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

Products	Fryquel 220		Pydraul 50E		Pydraul MC		Dasco FR 300		$(\Phi O)_3PO$ $+C_{28}H_{58}$
	370°C mg/g	420°C mg/g	370°C mg/g	420°C mg/g	370°C mg/g	"420°C" mg/g	370°C mg/g	"420°C" mg/g	" 420°C " mg/g
C_{11}-species	-	-	T	0.149	1.14	1.91	0.052	0.527	2.36
C_{12}-species	-	-	T	0.062	0.002	T	0.029	0.278	2.48
C_{13}-species	-	-	-	0.003	-	-	0.028	0.191	1.39
C_{14}-species	-	-	-	-	-	-	0.004	0.065	1.12
C_{15}-species	-	-	-	-	-	-	0.006	T	0.025
Benzene	0.001	0.004	0.022	0.192	0.084	1.61	0.004	0.165	0.034
Toluene	0.014	0.014	0.011	0.856	0.011	0.471	0.372	0.432	0.060
C_2-benzenes	0.166	0.180	0.045	0.412	T	0.235	0.376	2.64	0.068
C_3-benzenes	0.063	0.293	0.280	1.21	0.527	7.52	0.032	1.63	0.047
C_4-benzenes	0.001	0.136	-	0.184	-	-	0.050	0.219	0.085
C_5-benzenes	-	-	0.011	0.191	-	-	0.005	-	0.048
C_6-benzenes	-	-	-	0.022	-	-	-	-	-
Styrene	-	-	0.001	-	-	-	-	-	-
α-Methylstyrene	-	-	1.52	1.65	-	1.32	-	0.006	-
C_2-styrenes	-	0.019	0.002	-	-	-	0.012	0.073	-
Biphenyl	0.026	0.009	-	-	-	-	-	-	-
Napthalene	0.001	-	-	-	-	-	0.006	-	-
Methylnapthalene	0.021	0.013	-	-	-	-	-	-	-

TABLE XIX-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

Products	Fyrquel 220		Pydraul 50E		Pydraul MC		Dasco FR 300		$(\Phi O)_3PO$ $+C_{28}H_{58}$
	370°C mg/g	420°C mg/g	370°C mg/g	420°C mg/g	370°C mg/g	"420°C" mg/g	370°C mg/g	"420°C" mg/g	"420°C" mg/g
Tetrahydronapthalenes	-	-	-	-	-	-	0.011	0.112	-
Methyltetrahydronapthalenes	-	-	-	0.006	-	-	0.031	T	-
Dimethyltetrahydronapthalenes	-	-	-	-	-	-	0.004	-	-
Indan	-	-	-	0.006	-	-	0.141	T	-
Trimethylindans	-	-	-	-	-	-	0.003	-	-
Methanol	0.054	0.001	0.008	-	-	-	0.036	0.008	0.112
Ethanol	T	-	T	-	-	-	T	0.001	0.026
C_3-alcohols	-	-	-	-	-	-	-	-	0.002
C_4-alcohols	-	-	0.001	-	-	-	0.025	0.008	0.001
C_6-alcohols	-	-	0.003	-	-	-	-	-	-
Phenol	0.394	0.439	7.12	34.1	10.3	66.3	10.6	5.14	21.6
Cresols	0.758	1.02	-	-	-	-	0.214	1.33	-
Xylenols	2.04	4.11	-	-	-	-	0.149	1.10	-
C_3-phenols	0.069	0.116	-	-	-	-	-	0.033	-
Formaldehyde	-	-	-	-	-	-	-	-	0.002
Acetaldehyde	0.106	0.072	0.105	0.001	0.014	-	0.180	0.120	0.368
Propionaldehyde	0.003	0.002	0.022	0.001	0.003	-	12.2	5.88	0.346
Acrolein	-	-	0.003	-	-	-	0.433	0.107	0.034

TABLE XIX-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

Products	Fyrquel 220		Pydraul 50E		Pydraul MC		Dasco FR 300		$(\Phi O)_3PO + C_{28}H_{58}$
	370°C mg/g	420°C mg/g	370°C mg/g	420°C mg/g	370°C mg/g	"420°C" mg/g	370°C mg/g	"420°C" mg/g	"420°C" mg/g
2-Methyl propenal	-	-	0.001	-	-	-	-	0.002	-
C_4-aldehydes	-	T	0.005	0.001	-	-	0.085	0.001	0.254
C_5-aldehydes	T	T	0.007	-	-	-	-	-	0.252
C_6-aldehydes	-	-	-	-	-	-	-	-	0.043
Cinnamaldehyde	-	-	0.014	-	-	-	-	-	-
2-Phenyl-2-butenal	-	-	-	-	-	-	0.001	-	-
Propionaldehyde trimer, $(C_3H_6O)_3$	-	-	-	-	-	-	6.90	2.51	-
Acetone	0.049	0.005	0.066	0.001	0.018	0.039	0.007	0.762	T
Methyl ethyl ketone	0.016	T	0.024	0.002	0.018	0.071	-	0.034	0.024
C_5-ketone	0.008	-	0.003	-	-	-	0.013	-	-
Cyclopentanone	T	-	-	-	-	-	0.014	0.005	-
Cyclohexanone	-	-	-	-	-	-	0.004	0.024	-
Methyl phenyl ether	-	-	0.009	-	-	-	-	-	-
Diphenyl ether	-	0.020	-	-	-	-	-	-	-
Methyl p-cresyl ether	-	-	-	-	-	-	0.027	-	-
Furan	0.001	-	-	-	0.001	-	-	-	-
Dimethylfurans	-	-	0.010	-	-	-	0.013	-	-
2-Methyltetrahydrofuran	-	-	-	-	-	-	-	-	0.141

TABLE XIX-CONTD.

VOLATILE PRODUCTS OBTAINED ON THERMAL OXIDATIVE DEGRADATION OF PHOSPHATE ESTER BASED HYDRAULIC FLUIDS

Products	Fyrquel 220		Pydraul 50E		Pydraul MC		Dasco FR 300		$(\Phi O)_3PO + C_{28}H_{58}$
	370°C mg/g	420°C mg/g	370°C mg/g	420°C mg/g	370°C mg/g	"420°C" mg/g	370°C mg/g	"420°C" mg/g	"420°C" mg/g
1,3-Dioxolane	T	-	T	-	-	-	-	-	-
2-Ethyl-4-methyl-1,3-dioxolane	-	-	-	-	-	-	-	0.970	-
p-Dioxane	T	-	T	-	-	-	-	-	-
Dimethyl dioxanes	-	-	-	-	-	-	1.41	0.259	-
s-Trioxane	-	-	-	-	-	-	-	-	0.002
Acetic acid	T	-	-	-	-	-	-	-	0.004
Methyl formate	0.002	-	-	-	-	-	-	-	0.022
Ethyl formate	-	-	-	-	-	-	-	-	0.028
n-Propyl formate	-	-	-	-	-	-	-	-	0.001
Methyl acetate	T	-	-	-	-	-	T	-	-

a) < 0.0005 mg/g

TABLE XX

PRODUCTS OF PINE SAMPLES
(SEALED TUBE STUDIES)

Products	Untreated Pine-1D mg/g	Untreated Pine-6D mg/g	Treated Pine-2D mg/g	Treated Pine-3D mg/g	Treated Pine-4D mg/g	Treated Pine-5D mg/g
H_2	0.09	0.07	0.13	0.01	0.01	0.13
CO	48.1	48.3	45.1	20.7	58.1	43.4
CH_4	2.21	0.78	1.18	2.79	0.98	2.30
H_2O	324.8	276.6	268.1	243.1	306.3	320.2
HCl	19.3	-	0.51	-	-	-
HCN	?	?	?	?	0.51	?
CO_2	112.1	115.8	73.8	77.7	88.7	135.4
SO_2	-	-	-	-	15.0	-
COS	-	-	-	-	0.08	-
C_xH_y [b]	0.39	0.85	1.22	1.03	1.04	0.36
C_6H_6	0.57	0.28	0.82	0.92	1.43	0.50
$C_6H_5CH_3$	0.11	0.54	5.64	17.7	0.29	0.25
Xylenes	0.05	0.02	0.18	0.04	-	T
CH_3Cl	-	-	3.41	0.11	-	0.05
C_2H_5Cl	-	-	-	0.03	-	-
CH_3OH	13.8	7.74	5.15	6.48	9.42	7.97
HCHO	1.85	2.38	1.84	1.68	3.64	2.40
CH_3CHO	1.22	1.54	3.57	0.43	0.07	1.21
Furfural	1.56	2.18	3.04	4.32	1.39	4.28
5-Methyl-2-furaldehyde	0.07	0.03	0.01	0.02	-	0.02
Acrolein	0.67	0.62	1.21	0.43	?	0.47
$(CH_3)_2CO$	1.38	3.15	1.77	2.72	2.01	1.49
$CH_3COC_2H_5$	0.44	1.34	0.36	1.19	1.24	0.86
$CH_3COC_3H_5$	2.70	1.83	0.56	2.75	0.02	0.35
2,3-Pentanedione	0.11	0.10	0.29	0.30	-	-
HCOOH	?	?	?	?	0.23	?
CH_3COOH	7.74	7.27	7.68	10.9	-	4.57
Methyl formate	4.24	2.78	5.44	2.32	0.93	0.84
Methyl acetate	2.63	1.84	2.08	1.95	3.96	0.88
Vinyl acetate	2.11	2.28	2.02	1.37	0.08	0.18
Furan	1.15	1.46	2.83	1.13	0.36	1.60
2-Methylfuran	1.19	2.13	1.23	0.32	0.35	2.13
2,5-Dimethylfuran	0.60	0.40	0.27	3.38	0.13	0.84

[b] C_xH_y denotes hydrocarbons C_2 through C_4.

TABLE XXI

PRODUCTS OF PINE SAMPLES
(STAGNATION BURNER STUDIES)

Products	Untreated Pine-1D mg/g	Treated Pine-2D mg/g	Treated Pine-3D mg/g	Treated Pine-4D mg/g	Treated Pine-5D mg/g
H_2O	486.2	334.3	224.3	468.5	410.3
HCl	1.46	8.57	-	-	-
CO_2	199.6	226.8	171.8	274.0	590.9
SO_2	-	-	-	22.3	-
COS	-	-	-	0.12	-
HCN	?	?	?	1.32	?
C_xH_y[b]	0.85	1.37	0.59	0.87	1.53
C_6H_6	0.86	0.85	1.61	1.08	0.19
$C_6H_5CH_3$	0.07	20.0	22.0	0.03	0.19
Xylenes	T	T	-	0.03	0.01
CH_3Cl	0.22	0.46	0.30	-	-
CH_3OH	2.78	4.15	3.68	8.81	5.17
HCHO	2.09	0.37	0.71	0.50	9.97
CH_3CHO	2.53	0.84	0.81	0.76	1.12
Furfural	1.09	1.15	2.23	4.85	3.18
5-Methyl-2-furaldehyde	T	T	-	T	-
Acrolein	0.21	0.70	0.59	0.22	0.68
$(CH_3)_2CO$	2.81	2.02	1.80	0.45	1.45
$CH_3COC_2H_5$	0.69	0.15	0.62	0.48	0.70
$CH_3COC_3H_5$	0.71	1.74	1.55	-	0.52
2,3-Pentanedione	T	T	-	-	0.04
HCOOH	?	?	?	0.13	?
CH_3COOH	0.01	0.62	3.04	0.30	2.83
Methyl formate	0.28	1.23	1.12	0.04	0.23
Methyl acetate	0.76	0.96	0.85	0.45	0.18
Vinyl acetate	1.48	1.76	1.90	0.06	0.16
Furan	1.41	0.88	1.26	0.37	0.79
2-Methylfuran	1.05	1.77	1.06	0.06	0.76
2,5-Dimethylfuran	0.79	1.62	0.96	0.03	0.18

[b] C_xH_y denotes hydrocarbons C_2 through C_4.