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PURIFICATION OF HEXADECAFLUOROHEPTANE

S. Blumkin, N. C. Orrick, J. W. Grisard, and J. D. Gibson

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A B S T R A C T

The purification of hexadecafluoroheptane to a purity of 99.92 to 99.97 mole percent by fractional crystallization followed by selective adsorption with silica gel is reported. The details and use of a constant-low-temperature bath and centrifuge for fractional crystallization are given. A fifty-six foot silica gel adsorption column and its operation is described.

PURIFICATION OF HEXADECAFLUOROHEPTANE

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PURIFICATION OF HEXADECAFLUOROHEPTANE

One phase of the research program of this laboratory called for an accurate investigation of the physical properties of pure fluorocarbons. Minimum purity standards for this study were set at 99.9 mole percent. Finding that samples of required purity were unavailable, it was necessary to undertake the purification of the compounds to be investigated.

Of the fluorocarbons at hand in adequate quantities, hexadecafluoroheptane was selected as the compound likely to offer the least difficulty in purification, since it had the narrowest boiling range, and the least number of possible isomers. Earlier experience with fractional distillation of crude hexadecafluoroheptane at or near atmospheric pressure had shown that either more efficient fractionation or other purification methods would have to be investigated.

Selective adsorption by silica gel, recrystallization, and low pressure distillation[1] were tried and found to be effective. The operation of these methods are described here. The successful procedure finally adopted was fractional crystallization followed by silica gel adsorption.

METHODS USED TO DETERMINE PURITY

An essential to any purification program is a means of determining purity. Freezing curves, infra-red absorption spectra, and refractive indices were used to follow and compare the progress made with the different purification methods.

Freezing Curves

The time-temperature freezing curve of a sample afforded a quantitative measure, in mole percent, of the impurities present in a sample. The procedure, technique, and calculations are reported by Anderson[2] and by Glasgow[3]. This method, however, could yield no information as to the number, kind, and relative proportions of the impurities.

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1. Both low temperature-isothermal distillation and azeotropic distillation with a number of solvents such as ethyl ether, acetone, carbon tetrachloride, hexane, and benzotrifluoride were tried and found to be unsatisfactory.

2. Anderson, V. E., and G. D. Oliver, "Determination of Purity by Freezing Point Depression. Purity and Freezing Point of Hexadecafluoroheptane", Carbide and Carbon Chemicals Division, K-25 Plant, K-555, February 17, 1950.

3. Glasgow, A. R., Jr., A. J. Strieff, and F. D. Rossini, "Determination of the Purity of Hydrocarbons by Measurement of Freezing Points", J. Res. Natl. Bur. Standards, 35 355-373 (1945).

Infra-Red Absorption Spectra

In the absence of a background of spectral data on pure fluorocarbons, no absolutely quantitative data could be obtained from infra-red absorption spectra. If, however, the bands that remain unchanged in the spectra of a number of samples of widely variant purity are assumed to represent the characteristic absorption of the pure compound, then the number of impurities, and their approximate relative proportions may be deduced. Such semi-quantitative information proved very useful for comparison of the potentialities of the different purification methods.

Refractive Indices

Both freezing curve determinations and infra-red absorption scans are time consuming. The refractive indices served as a simple rapid check on the relative purities of a series of samples. A comparison of the refractive indices with the purities and infra-red scans of the first samples from the different purification methods made it evident that the impurities possessed higher refractive indices than hexadecafluoroheptane, and therefore in general a lower index sample represented a purer one. All refractive indices were measured at 25.0°C., with a precision of $\pm$ 0.00003, on a low range (n_D of 1.20 - 1.50) Precision Bausch and Lomb refractometer.

MATERIAL

Source and Purity

The hexadecafluoroheptane was available in a number of lots produced by the E. I. du Pont de Nemours and Company by fluorination of n-heptane with cobalt trifluoride[4]. These lots had an A.S.T.M. boiling range of about 6°C., and varied in refractive index from 1.2593 to 1.2595. A determination by the freezing point method of one lot having $n_D^{25} = 1.25933$ indicated a purity of 83.5 mole percent and freezing point of -58.4°C.

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4. Benner, R. G., et al., "Fluorocarbons by Fluorination of Hydrocarbons with Cobalt Trifluoride", Ind. Eng. Chem. 39, 329 (1947).

Earlier Experience with Rectification

Gabbard[5] reports the fractionation of hexadecafluoroheptane in a column equivalent to fifty plates at total reflux. The maximum purity obtainable by further fractionation of this sample at a 200 to 1 reflux ratio in a six-foot Podbielniak heligrid column rated at approximately 100 plates at total reflux is represented by a sample with a purity of 94.8 mole percent, freezing point of -54.0°C., and n_D^{25} of 1.25845.

PURIFICATION BY SILICA GEL ADSORPTION

Mair[6] has used silica gel adsorption in the purification of hydrocarbons. The procedure employed makes use of the experimentally determined relative adsorbabilities. The order of decreasing absorbabilities of hydrocarbons and therefore the order that they are obtained from a treatment of a mixture of hydrocarbon types by a silica gel column is paraffins, naphthenes, monoolefins, and aromatic hydrocarbons. The order of adsorbabilities of fluorocarbon types is not known, although the purification of hexadecafluoroheptane indicates the paraffin-type is less readily adsorbed than the naphthene-type.

Apparatus

The Six-Foot Glass Adsorption Column. Preliminary investigation was made with the pyrex glass column shown in figure 1. It consisted of the column proper filled with silica gel[7], the feed reservoir at the top, and the sample receiver at the bottom.

The Fifty-Six Foot Metal Column. The fifty-six foot metal adsorption column[8], used in the actual purification of the fluorocarbon, is shown in figure 2. The column consisted of three basic parts: the head of the column, the fractionation section, and the sample receiver.

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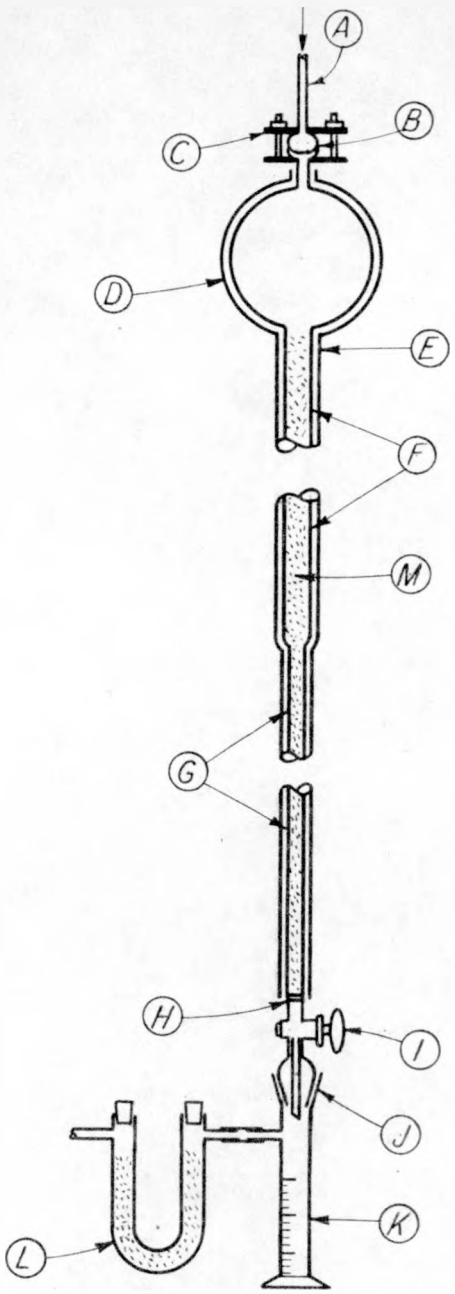
5. Gabbard, J. L., et al., "Physical Properties of Some Fluorocarbons and Related Compounds", Carbide and Carbon Chemicals Division, K-25 Plant, K-371, March 1949.

6. Mair, B. J., "Separation and Determination of Aromatic and Monoolefin Hydrocarbons in Mixtures with Paraffins and Naphthenes by Adsorption", J. Research Natl. Bur. Standards, 34, 435-51 (1945).

7. Prepared by the Davison Chemical Corporation, No. 22-08 through 200 mesh.

8. Mair, B. J., A. L. Gaboriault, and F. D. Rossini, "Assembly and Testing of 52-Foot Laboratory Adsorption Column", Ind. and Eng. Chem., 39, 1072-81 (1947).

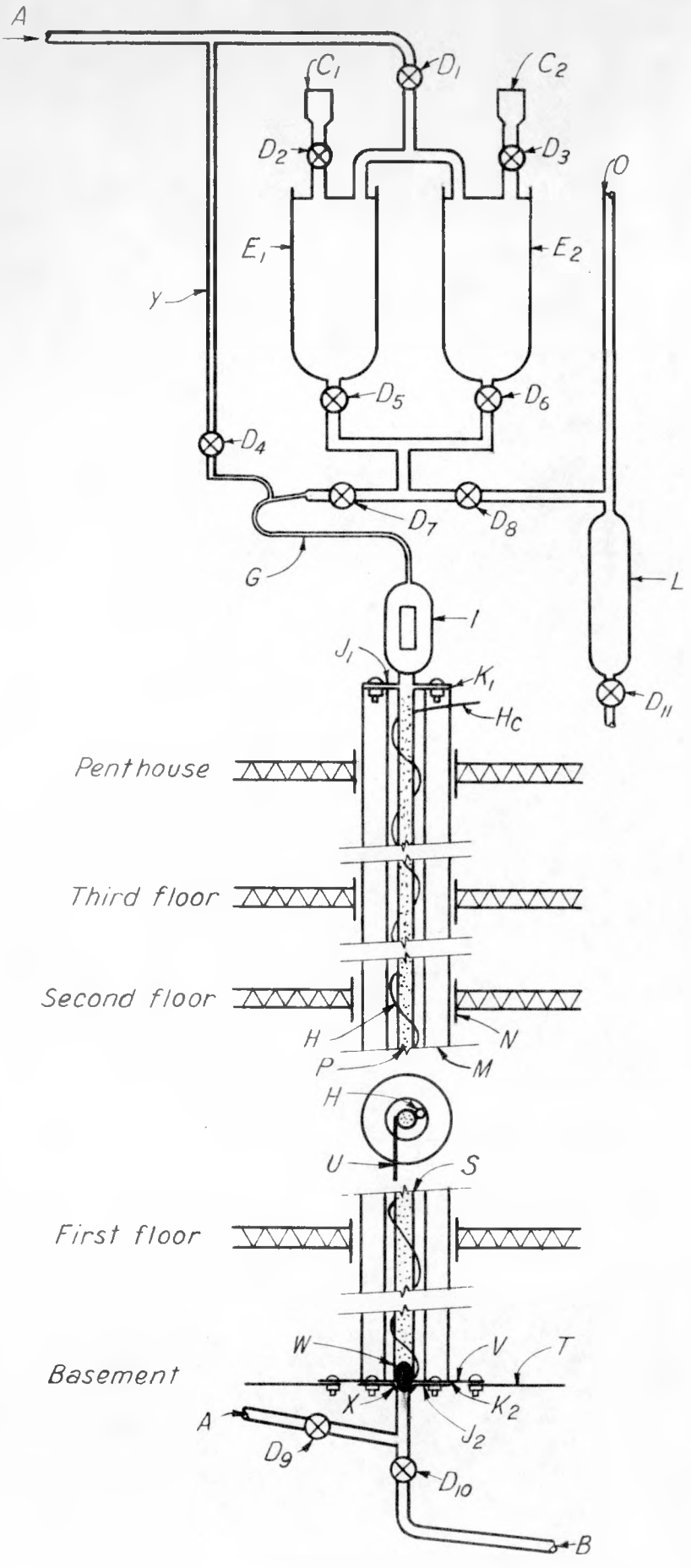


LEGEND:

A___ Connection to source of dry nitrogen pressure.
B___ Pyrex spherical glass joint (28/12).
C___ Metal joint clamp.
D___ Reservoir, 200 ml. capacity.
E___ Metal protecting screen.
F___ Upper section of column 15 mm. I.D. x 750 mm.
G___ Lower section of column 10 mm. I.D. x 100 mm.
H___ Sintered glass plug of medium porosity.
I___ Stopcock, 2 mm bore.
J___ Standard taper pyrex glass joint. (19/38)
K___ Product receiver 10 ml. capacity.
L___ Drying tube filled with silica gel.
M___ Silica gel adsorbent.

SIX - FOOT PYREX GLASS
ADSORPTION COLUMN

FIGURE 1



LEGEND:

A____Connection to source of dry air pressure.
B____Connection to sample collector.
C_1, C_2__Copper funnels for filling reservoirs.
D_1 - D_{11}__Packless diaphragm valves.
E_1, E_2__Reservoirs for feed and desorbing liquid.
G____Copper tubing $\frac{3}{16}$" O.D.
H, H_C___Calrod heaters
I____Sight glass.
J_1, J_2___Flanges at top and bottom of column.
K_1, K_2__Gaskets at top and bottom of column.
L____Receiver for desorbing liquid.
M___Magnesia insulation 1" thick.
N___Concentric side supports for column.
O___Vent to roof
P____Silica gel adsorbent
S____Stainless steel column - $\frac{3}{4}$" I.D. welded into one 56 ft. length.
T____Steel table on which column rests.
U____Copper constantan thermo-couple.
V____Steel plate, $\frac{3}{4}$" thick, bearing entire weight of column.
W___Glass wool plug.
X____Stainless steel screen.
Y____By-pass line.

56-FOOT METAL ADSORPTION COLUMN

FIGURE 2

HAMMER	N.C.O.
LD-A966	

The column head included the two reservoirs, E_1 and E_2, for holding the fluorocarbon mixture and the desorber, respectively; the sight glass, I, to observe when all the liquid had entered the column; the receiver, L, to collect desorbing liquid during reactivation of the silica gel adsorbent; and the necessary connecting tubing and control valves.

The fractionating section consisted of a 3/4-inch i.d. stainless steel tube, welded into a continuous 56-foot length, which contained the adsorbent. This tube was wrapped with five separate heating units each of which consisted of two 220 volt, 2000 watt Calrod heating elements connected in series. These heaters were controlled by variable voltage regulators and also Mercoid switches set to turn off automatically any sectional heater at 200°C. This was a precaution intended to prevent coalescence of the silica gel adsorbent. Surrounding the heating elements was a one-inch layer of magnesia insulation. Metal cylindrical sleeves, N, provided lateral support for the fractionation section, with sufficient clearance to allow for dimensional changes caused by wide temperature variations. A micromax recorded the temperatures of each of the five sections.

Valves used on the column were of the packless diaphragm type with soldered connections. The connecting lines consisted of 1/2-inch copper tubing with the exception of G and K which were made of more flexible 3/16-inch copper tubing.

The take-off tube, B, from the bottom of the column led into an air-tight box containing a device for automatic collection of samples. This consisted of a turntable rotated at the rate of one revolution in twenty-two hours by an electric motor through a train of reduction gears. In this way, bottles (125 ml.) arranged shoulder to shoulder around the track at the edge of the circular turntable passed beneath the sample take-off tube at a rate of one in 52.5 minutes. Glass funnels in the bottles, with thin copper gutters bent over the lips of adjacent funnels insured passage of the sample from the overhead take-off tube into the bottles without loss.

Operation

The Six-Foot Column. The 6-foot glass column was packed by pouring silica gel into the top while tapping the side of the column. The sample was then poured into the reservoir (D, figure 1) and forced into the adsorbent by pressurizing with dry nitrogen. As soon as all the sample had entered the adsorbent, the desorbing liquid was poured into the reservoir and forced into the adsorbent, pushing the sample ahead. Samples of one to five milliliters were collected as the fractionated material issued from the bottom of the column. This small column was used to predict action in the larger column and in particular to select the most effective desorbing agent.

The Fifty-Six Foot Column. The 56-foot column was operated in essentially the same manner as the smaller column. The column head was removed at flange J_2 (figure 2) and silica gel adsorbent was poured in while vibrating the column. The sample was introduced

into reservoir E_1 and the desorber into reservoir E_2. The hexadecafluoroheptane was then forced into the column under dry air pressure (0-2 psi.) and was immediately followed by the desorbing liquid. Selective adsorption of the sample occurred as it passed down the column, the fractions being collected in the bottles in the automatic sample collector.

The fact that adsorption of hexadecafluoroheptane by dry silica gel produces a rise in temperature permitted the progress of the sample to be followed down the column. Temperatures at intervals along the column wall were registered continually on a recording micromax. Control of the rate of flow of sample (1-2 ml. per minute) was achieved by adjusting the air pressure above it. The pressure required for fluorocarbons is less than that for hydrocarbons. After a sample was discharged from the column, the desorber remaining was removed by heating the column with the calrod heaters. With the silica-gel dried, flange J-2 was removed from the bottom, and the used adsorbent was caused to fall out by vibrating the column.

Experimental Results

Selection of Desorber. Forty chemicals were tested for miscibility with hexadecafluoroheptane. Seven of these, the most miscible, were selected for futher comparison by actual tests as the desorbing liquid in the six-foot column. Data from these tests are shown in table I.

Table I

Desorbing Liquids

Material	Recovery of hexadecafluoroheptane, volume percent	Remarks
Methanol	72.0	
Carbon tetrachloride	74.0	2-phases present
Acetone	78.0	2-phases present
p-Chlorobenzotrifluoride	84.0	
Benzotrifluoride	90.0	
Bis(trifluoromethyl) dichlorobenzene	90.0	Oily - very difficult to clean column
Freon-113	90.0	

The criteria for a good desorber are good recovery of sample and easy removal from silica gel. Of the compounds listed in table I, benzotrifluoride and Freon-113 were judged to be the best desorbers. Of the two the latter was selected for use in the fifty-six foot column, being both cheaper and more readily available.

The Fifty-six Foot Column. The first material issuing from the column in all runs had the lowest refractive index and the highest purity. A representative plot showing refractive index as a function of volume percent withdrawn is given in figure 3 for a crude feed and a feed partially purified by fractional crystallization. When crude feed was used, the first material obtained had a purity of about 97.5 mole percent and a refractive index of 1.25838; when the partially purified feed was used, the first sample had a purity of 99.8 mole percent purity and a refractive index of 1.25820. The difference in adsorbabilities of the hexadecafluoroheptane and its impurities was insufficient to give a sharp separation. Some impurity was present in the first sample and in increasing proportions in each succeeding one, the actual concentration being a function of the impurity content of the feed.

The purity of the first sample was also a function to some degree of the size of the charge fed to the column and the rate of flow of sample through the silica gel. Evidence indicated that the purification efficiency increased with decreasing size of charge and flow rate. Insufficient data was available to establish a quantitative relation between these conditions and efficiency. The most efficient run was made with a 1200 ml. charge and an average rate of flow through the adsorbent of 1.2 ml. per minute.

PURIFICATION BY LOW PRESSURE DISTILLATION

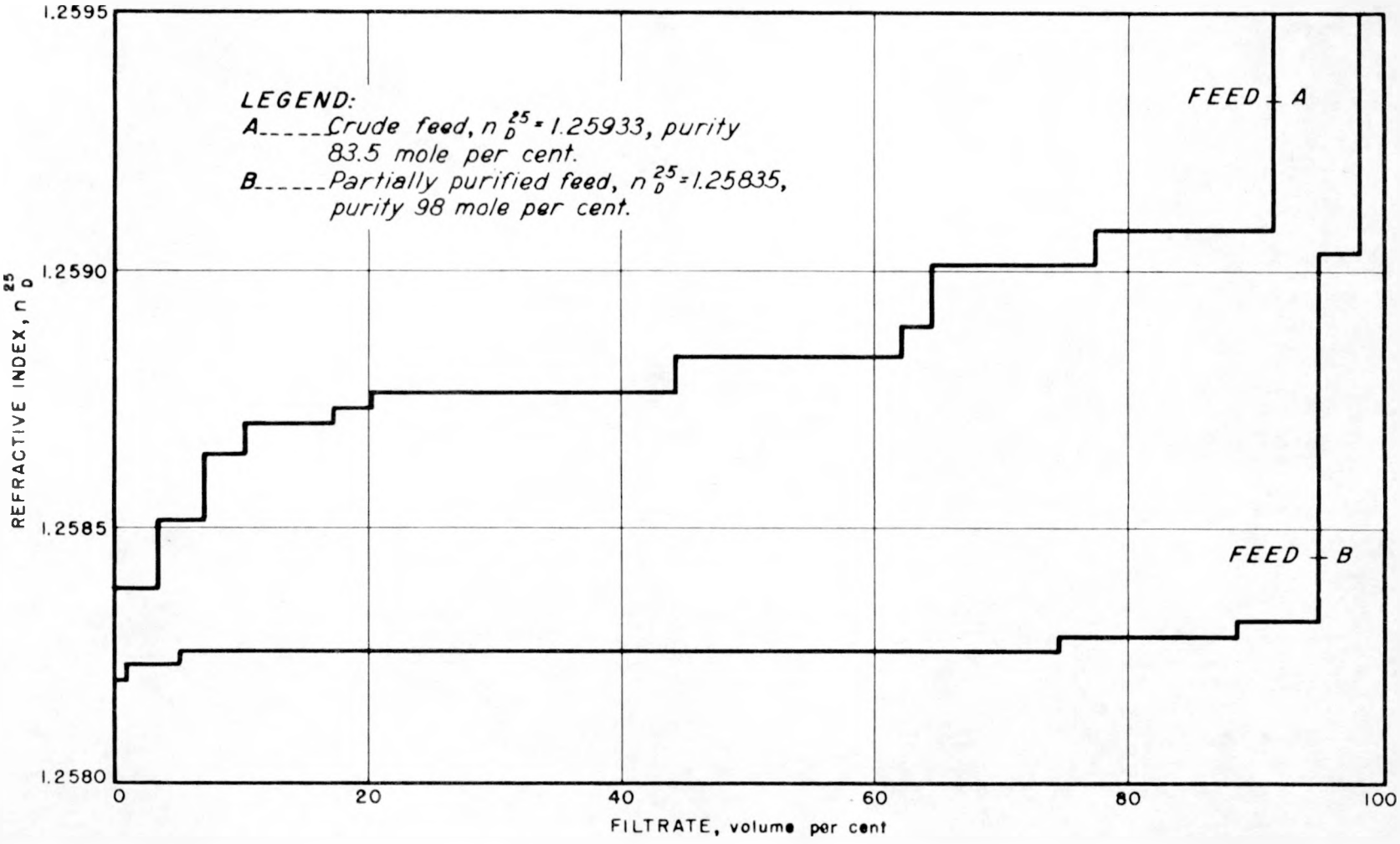
Hexadecafluoroheptane was fractionated in a six foot, 25 mm. i.d. Podbielniak heligrid column, rated at approximately 100 theoretical plates at total reflux. The head of the column consisted of a total reflux condenser and an intermittent take-off valve operated by an adjustable timer. The distillation was carried out at a pressure of 100 mm. Hg, and a reflux ratio of 200 to 1.

The feed for this fractionation was a sample partially purified by fractional crystallization, to a purity of about 95 mole percent and n_D^{25} 1.25865. The center cut fraction from the temperature plateau had a refractive index of 1.25832 and a purity of 99.55 mole percent.

A distillation at 725 mm. of mercury of a somewhat more impure sample in the same column had yielded a center cut of n_D^{25} 1.25848 and a purity of 94.8 mole percent.

PURIFICATION BY FRACTIONAL DISTILLATION

Equilibrium melting with separation of the melt from the crystals by decantation was found to improve the purity of crude readily from less than 84 mole percent to about 96.3 - 96.7 mole percent. Though the yield of best material was small (1 to 2%) and the number of recrystallizations required were many (about nine), this represented an improvement over distillation at a pressure of 725 mm. of mercury. To better the purification efficiency of recrystallization a constant low-temperature bath was built and a low temperature centrifuge was adapted for use.



TYPICAL RESULTS FROM THE 56-FOOT ADSORPTION COLUMN

FIGURE 3

Apparatus

Low-Temperature Bath. This bath consisted of two chambers, one about twice the size of the other. The smaller contained the coolant, a slush of dry-ice and trichloroethylene, and the larger contained acetone, which was maintained at constant temperature by the intermittent operation of a centrifugal pump which circulated the acetone through a coil of copper tubing submerged in the slush chamber. Agitation and thereby minimization of temperature gradients was attained by the location of the intake to the pump at the middle of the bath floor and the arrangement of three widely separated outlets at the surface level along the periphery of the bath. Temperature regulation was effected by thermohm control of a thyratron relay which operated the pump. A housing and covers of cork and plywood provided thermal insulation for the two chambers, both from each other and the room. This bath could be maintained within 0.5°C. of any desired temperature in the range -72 to -40°C.[9]

Low-Temperature Centrifuge. A jacketed clinical centrifuge[10], was used to fractionate melting crystals of hexadecafluoroheptane. A sketch of this centrifuge with certain modifications adapting it for use with a circulating coolant is given in figure 4. A centrifugal pump was used for circulation of the acetone from the constant temperature bath through the centrifuge jacket and back to the bath. The entire system, centrifuge, pump impeller housing, and circulation lines were enclosed in a box of plywood and cork to reduce heat gain from the atmosphere. Ports in appropriate locations on the box provided access to the centrifuge for charging and take-off of sample.

Temperatures to the nearest 0.5°C. of the bath and the air in the centrifuge basket were measured with copper-constantan thermocouples and a Leeds and Northrup portable potentiometer.

Operation

The important feature of the jacketed centrifuge is that one can make very effective separation of melt and crystals under controlled temperature conditions. The manner in which the centrifuge was used in the purification of hexadecafluoroheptane is one of several possible techniques.

The constant temperature bath was set at a temperature several degrees below that required to freeze a given sample solid, and

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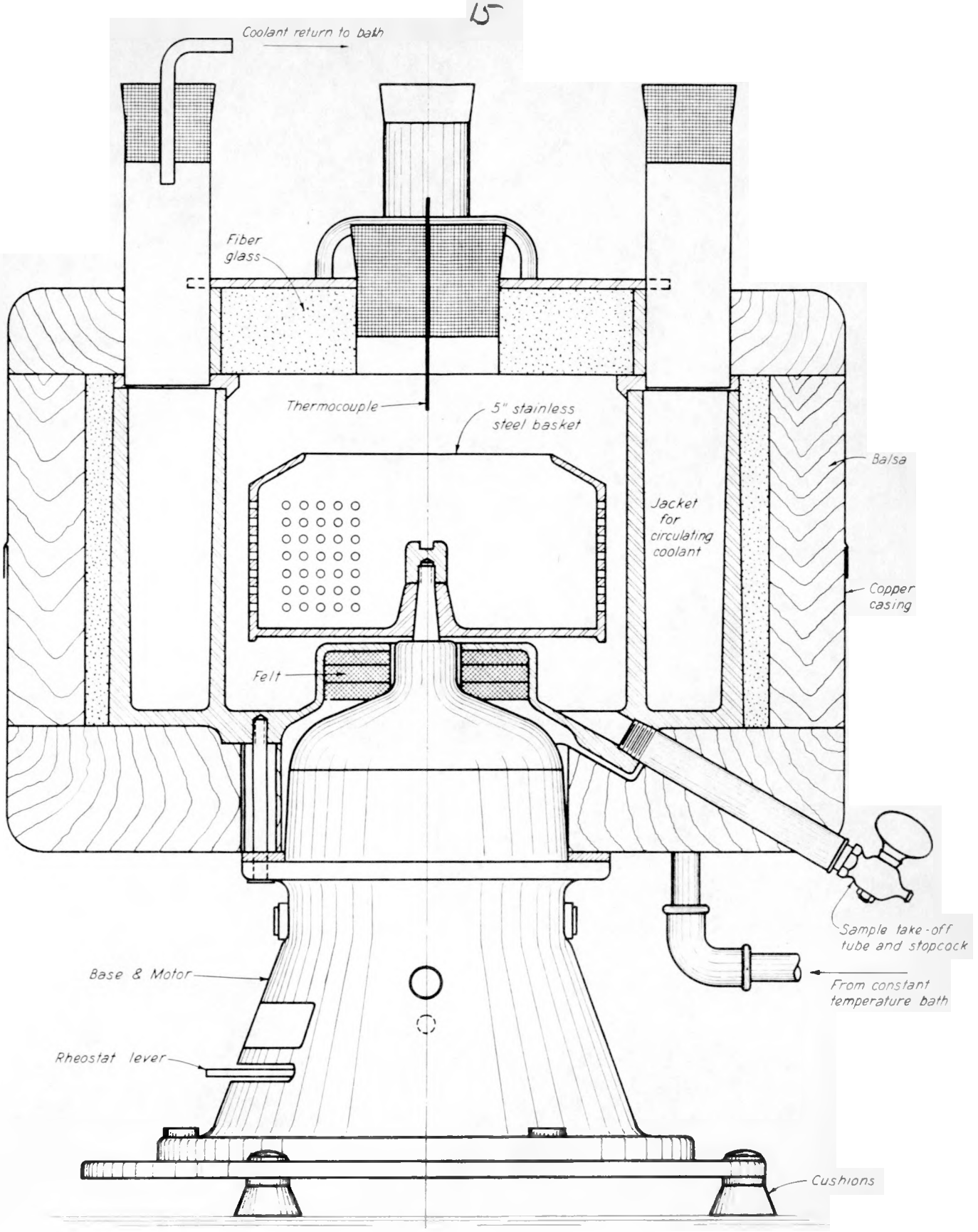
9. The upper end of this range is not a limit since no attempt was made to operate the bath above this temperature. The lower end was the actual limit found experimentally.

10. Manufactured by the International Equipment Company of Boston, Massachusetts, Model No. A5270, 5" Low-Temperature Modified Clinical Centrifuge.



THE LOW TEMPERATURE CENTRIFUGE

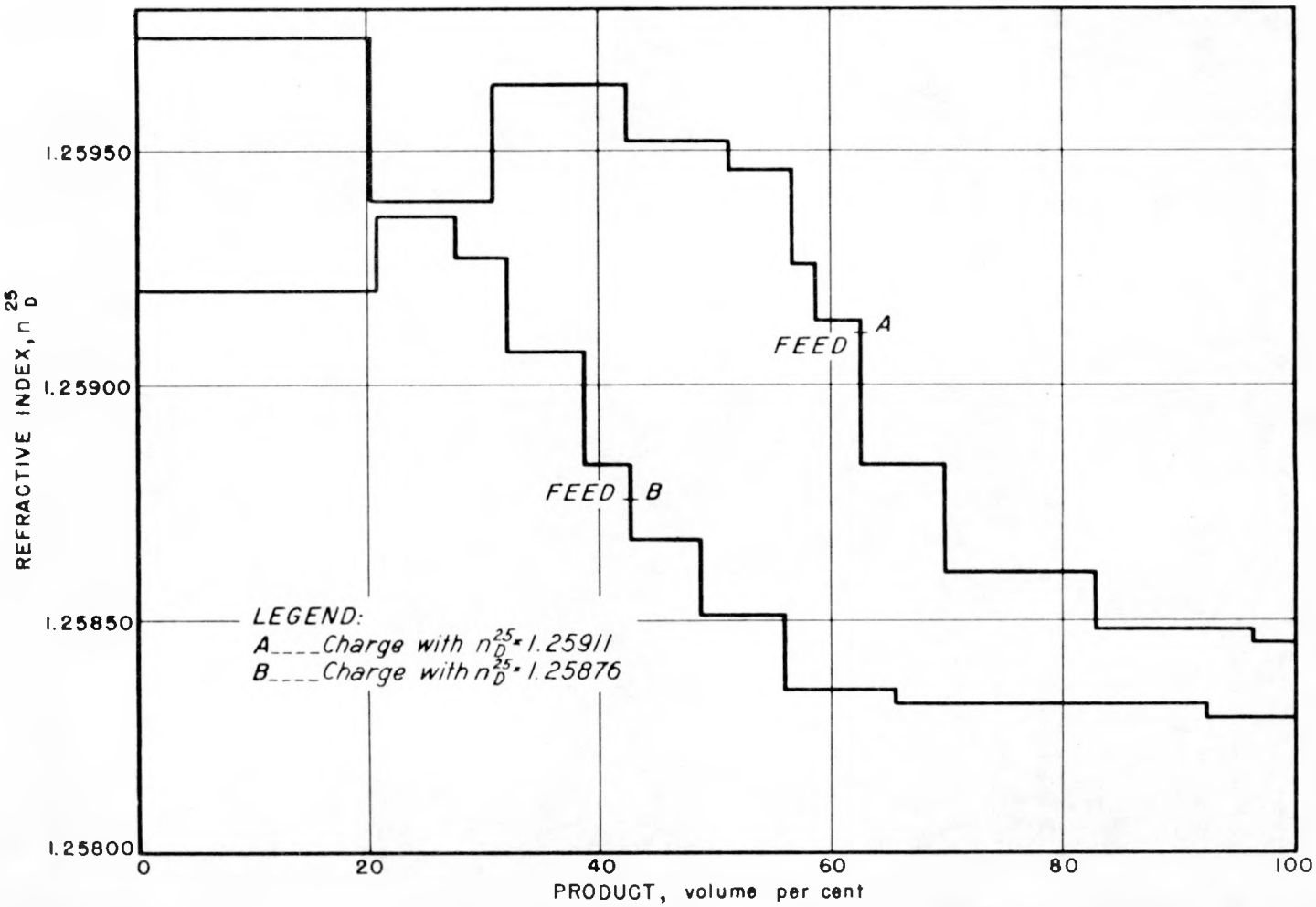
FIGURE 4

the bath fluid was circulated through the centrifuge jacket until the temperature of the air in the centrifuge basket reached a minimum. This generally called for a bath temperature of -62 to -57°C. and resulted in a basket air temperature of -45 to -40°C. The sample to be fractionated was frozen solid in a stainless steel tube and was introduced into the basket. Centrifuging was then begun. The metal stopcock in the drain from the basket compartment floor was then opened to allow take-off of the first melt. In a typical run the flow of melt was rapid at first, then slower and slower, till it ceased about the time one-third to one-half the charge had been taken off. This was due to the refreezing of part of the melt on the basket compartment wall, which was at a temperature between the initial and final freezing points of the sample. When the take-off rate became extremely slow or had ceased altogether, the pumping of coolant through the centrifuge jacket was stopped to permit the wall of the basket compartment to warm slowly. The flow of melt from the centrifuge resumed as the thin layer of crystals thawed on the slowly warming wall under nearly equilibrium conditions. Take-off continued at a drop rate till the entire charge was removed.

In some runs the warming of the basket compartment wall was effected at a slower rate by adjusting the bath temperature upward to to 10° rather than stopping the pump. This was not the regular procedure, since during most centrifuge runs other samples were in the bath, and it was necessary to maintain a constant temperature. These latter samples were ones which were kept in the bath for a period of 4 to 16 hours at a constant temperature at which about half the sample would freeze. Then without removing the sample from the bath the melt was drawn off through a tube with the use of the suction of a water aspirator.

Experimental Results

The combination of constant low-temperature bath and centrifuge proved very effective in removing the greater part of the impurities in commercial hexadecafluoroheptane. A plot of the refractive indices of the fractions obtained from the centrifuge against the volume percent of the product is given in figure 5 for two runs with charges of different purities. This figure shows that the first, lower melting and therefore more impure, sample coming from the centrifuge differed widely in refractive index from the last, purer fraction, thereby indicating a significant change in the concentration of impurities. The cruder procedure of separating melt from crystals by decanting with no control over the melting rate could not compare with centrifugation under controlled temperature conditions. Whereas the former procedure required seven or eight recrystallizations to go from a sample of n_D = 1.25911 to one of n_D = 1.25848 with a yield of less than 2%, the latter method could do the same in one step with a yield of 15 to 25% (17% in the case shown in figure 5). In addition the sample of n_D^{25} = 1.25848 of a purity of 96.3 - 96.7 mole percent represented the limit of purity obtainable with the decantation procedure. Centrifugation also had a limit but a higher one represented by a best sample of n_D^{25} = 1.25829 and a purity of 98.4 mole percent. When a sample of this purity was charged to the centrifuge, all fractions taken off



TYPICAL FRACTIONAL MELTING OF HEXADECAFLUOROHEPTANE IN CENTRIFUGE

FIGURE 5

had practically the same refractive index. Refinement of temperature control undoubtedly would have enabled further progress, but the availability of the silica gel column made this unnecessary.

DISCUSSION

Comparison of Methods Based on Infra-Red Analysis

The information supplied by infra-red analysis proved invaluable for comparison of the different purification methods. The absorption spectra of the products of these methods yielded evidence of the presence of four impurities, identity unknown, in crude hexadecafluoroheptane. Comparison of the spectral data showed that fractional distillation at 725 mm. of mercury in a column equivalent to 100 theoretical plates removed two of these unknowns completely but did not appear to affect the concentration of the remaining two appreciably. Both silica gel adsorption and recrystallization removed the same unknowns as fractional distillation did and in addition reduced the concentration of the remaining two impurities preferentially. Recrystallization removed one of these latter two impurities to a point where its absorption bands were nearly absent, and the other to some small extent. The silica gel adsorption column removed both of these almost completely.

Purification Procedure Adopted

In view of the data supplied by infra-red analysis and the practical considerations involved in each method, a combination of recrystallization and silica gel adsorption was used to prepare a sizeable volume of pure hexadecafluoroheptane.

Recrystallization as the First Step. Recrystallization was adopted as the preliminary step since the method permitted the rapid processing of large quantities. The first purification of crude was made by separating the crystals from melt by suction in batches of crude that had been standing in the bath at constant temperature for eight to sixteen hours. Depending upon the particular temperature at which the samples had stood, this step resulted in a 30-40% yield of material of n_D^{25} 1.2589 - 1.2591. Further purification was then made by centrifugation. Fractions from different centrifuge runs with the same refractive indices were mixed and reprocessed. All fractions with refractive index greater than 1.2590 were treated as rejects, being either mixed into the crude if the refractive index were lower or rejected entirely if higher than that of crude. In this manner a large volume of sample of n_D^{25} = 1.25832 and estimated purity of 98 mole percent was obtained from the commercial grade hexadecafluoroheptane of purity less than 83 mole percent.

Final Purification by Silica Gel Column. This 98 mole percent sample was then divided into feed batches for the silica gel column. The first 5% of sample by volume taken off the column had a purity of 99.7 to 99.8 mole percent and the next 70% a purity of 99.2 to 99.6 mole percent. This larger batch was then repassed through the column to

obtain more sample of purity of 99.7 to 99.8 mole percent. The combined batches of the latter were then repassed through the silica gel column, with first fractions coming off the final run with a purity of 99.92 to 99.97 mole percent, $n_D^{25} = 1.25820$, and freezing point of -51.4°C. It is noteworthy that the pure compound is odorless.

CONCLUSION

The selective adsorption property of silica gel provides a method for purifying commercial hexadecafluoroheptane of purity less than 83 mole percent to a final product purity of at least 99.92 mole percent.

Recrystallization using centrifugation under controlled temperature conditions is another effective method for improving the purity of hexadecafluoroheptane. Final product purity attained by this technique was 98.4 mole percent. This procedure would yield a still purer sample with refinement of temperature control.

Fractional distillation at 100 mm. Hg of a recrystallized sample of 95% purity in a 100 plate column will make a separation yielding a fraction with a purity of 99.5 mole percent.

Since recrystallization of large volumes can be carried out more rapidly than silica gel adsorption, the most practical procedure for purification is recrystallization to the limit of purity readily attainable as a first step, followed by the minimum number of passes through the silica gel column.

ACKNOWLEDGEMENT

The authors wish to acknowledge the contributions of Patricia J. H. Woltz in making the infra-red analyses and Verner E. Anderson in determining the purities by the freezing point method.

NOTEBOOK REFERENCES

Number	Issued to
965	Charles W. Rhoades
1058	N. C. Orrick
1099	Charles W. Rhoades
1144	S. Blumkin
1461	N. C. Orrick

This work was completed November 1949.