

# Purification and Sealing "in Vacuum" of National Bureau of Standards Standard Samples of Hydrocarbons\*

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This report describes the procedure and apparatus used in the purification and sealing "in vacuum" of 19 National Bureau of Standards Standard Samples of hydrocarbons, including 9 paraffins, 3 cycloparaffins, and 7 alkylbenzenes.

## I. Introduction

Early in 1943, the Technical Advisory Committee of the Petroleum Industry War Council requested the National Bureau of Standards to include hydrocarbons of high purity in its Standard Samples program. On June 1, 1943, the Bureau announced that such work would be started and requested the laboratories of the petroleum, rubber, and chemical industries to submit suggestions as to the compounds most urgently needed, the sizes of the samples, etc. Work on the project was actually begun on July 1, 1943, in the Section of Thermochemistry and Hydrocarbons in the Bureau's Chemistry Division.

On January 10, 1944, announcement was made of the availability of 15 hydrocarbon compounds (*n*-pentane, isopentane, each of the five hexanes, cyclohexane, methylcyclopentane, benzene, toluene, ethylbenzene, and each of the three xylenes) National Bureau of Standards Standard Samples of hydrocarbons. On December 1, 1944, an additional four compounds (*n*-heptane, 2,2,4-trimethylpentane, methylcyclohexane, and isopropylbenzene), together with a second lot of one of the first 15 (toluene), was announced. Three of the latter compounds (2,2,4-trimethylpentane, methylcyclohexane, and toluene) were certified as to refractive index at seven wavelengths at 20°, 25°, and 30° C, by the Bureau's Optical Instruments Section, and as to density at 20°, 25°, and 30° C, by the Capacity and Density Section, for calibrat-

ing refractometers, spectrometers, picnometers, and density balances. One of the latter compounds (2,2,4-trimethylpentane) was certified as to calorimetric heat of combustion, by the Heat Measurements Section, for calibrating apparatus for determining the heating value of gasoline and other liquid fuels.

The present report describes the purification and sealing "in vacuum" of the above mentioned NBS Standard Samples of hydrocarbons.<sup>1</sup>

<sup>1</sup> Information concerning the certification of 2,2,4-trimethylpentane, methylcyclohexane, and toluene for refractive index (by the Bureau's Optical Instruments Section) and density (by the Capacity and Density Section), and of 2,2,4-trimethylpentane for calorimetric heat of combustion (by the Heat Measurements Section) is given in the certificates supplied with those Standard Samples.

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## II. Materials and Purification

The materials for the first lots of these 19 NBS Standard Samples of hydrocarbons were obtained as follows:

By gift, the following starting materials were obtained: 2,3-dimethylbutane, from the M. W. Kellogg Co., New York, N. Y., and the Standard Oil Co. (Indiana), Whiting, Ind.; methylcyclopentane, from the Houdry Process Corporation, Marcus Hook, Pa.; cyclohexane, from the Barrett Division of the Allied Chemical & Dye Corporation, New York, N. Y.; *o*-xylene, from the Standard Oil Development Co., Elizabeth, N. J.; isopropylbenzene, from the Atlantic Refining Co., Philadelphia, Pa., through the Technical Advisory Committee of the Petroleum Industry War Council and the Standard Oil Development Co.; *n*-hexane, 2-methylpentane, and 3-methylpentane, from the American Petroleum Institute Research Project 6 at the National Bureau of Standards.

By purchase, the following commercially available starting materials were obtained: *n*-Pentane, isopentane, and 2,2-dimethylbutane, from the Phillips Petroleum Co., Bartlesville, Okla.; *n*-heptane from the Westvaco Chlorine Products Co., New York, N. Y.; 2,2,4-trimethylpentane, from the Rohm & Hass Co., Philadelphia, Pa.; ethylbenzene, *m*-xylene, and *p*-xylene, from the Eastman Kodak Co., Rochester, N. Y.; benzene, from the Jones & Laughlin Steel Corporation, Pittsburgh, Pa.; toluene, from the J. T. Baker Chemical Co., Phillipsburg, N. J.

The starting materials for renewal lots of 15 of the above hydrocarbons were obtained as follows:

By gift, the following starting materials for renewal lots were obtained: Toluene, from the Humble Oil & Refining Co., Houston, Tex.; *o*-xylene, from the Standard Oil Development Co., Elizabeth, N. J.; 2,3-dimethylbutane, from the Phillips Petroleum Co., Bartlesville, Okla.

By purchase, the following starting materials for renewal lots were obtained: *n*-Pentane, isopentane, 2,2-dimethylbutane, *m*-xylene, *p*-xylene, and benzene, from the same sources as the first lots; *n*-hexane, 2-methylpentane, 3-methylpentane, and methylcyclopentane, from the Phillips Petroleum Co.; cyclohexane from the Barrett Division of the Allied Chemical & Dye Corporation; ethylbenzene, from the Dow Chemical Corporation.

The purification to which the above starting materials were subjected was similar to that de-

scribed in references [1, 2, 3], with regard to regular and azeotropic distillation. Benzene and *p*-xylene were subjected to crystallization also and *m*-xylene was purified by sulfonation and hydrolysis of the sulfonic acids prior to the final distillation. The following is a summary of the purification:

Regular distillation alone was used for *n*-pentane, isopentane, 2,2-dimethylbutane, *n*-heptane, 2,2,4-trimethylpentane,<sup>2</sup> and isopropylbenzene.

Both regular distillation and azeotropic distillation were used for *n*-hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, methylcyclopentane, cyclohexane, methylcyclohexane, toluene, ethylbenzene, and *o*-xylene.

Crystallization, followed by filtration through silica gel and by regular distillation, was used for the purification of the benzene. The crystallization was performed as follows: A volume of about 20 ml of benzene was mixed with 50 ml of ethanol in a cylindrical brass container (5 cm in diameter and 20 cm in length), which was placed in a cooling bath of ice and salt water (temperature near  $-10^{\circ}$  C). With vigorous hand stirring and scraping, a thick mush, or slurry, of hydrocarbon and alcohol was produced. This slurry was then transferred to the basket of a centrifuge<sup>3</sup> having a jacket cooled to near  $-10^{\circ}$  C with a mixture of ice and salt water. The centrifuge was operated for about 5 minutes, leaving in the basket about half of the benzene in crystalline form. The crystals were removed from the basket of the centrifuge and melted. The purified liquid benzene was washed three times with distilled water and then filtered through silica gel to remove any alcohol and water remaining dissolved in the hydrocarbon. The total quantity of benzene was purified in this way, in 200-ml portions.

For the crystallization of the *p*-xylene, the same apparatus and procedure was used, except that the cooling bath was a mixture of water and ice at  $0^{\circ}$  C.

In the purification of the starting *m*-xylene which contained 5 to 10 percent of *p*-xylene

<sup>2</sup> The small amount of olefinic impurity in this material was removed by adsorption with silica gel.

<sup>3</sup> The centrifuge used in this work was a stock model (No. 418) of the International Centrifuge Co., Boston, Mass., altered by them to have a thermal insulated jacket suitable for containing a refrigerant. The rotating basket (5 in. in diameter and 2 1/2 in. in height) had a maximum speed of rotation 3,600 rpm. The wall of the basket was wire cloth, of 325 mesh, supported by perforated metal.

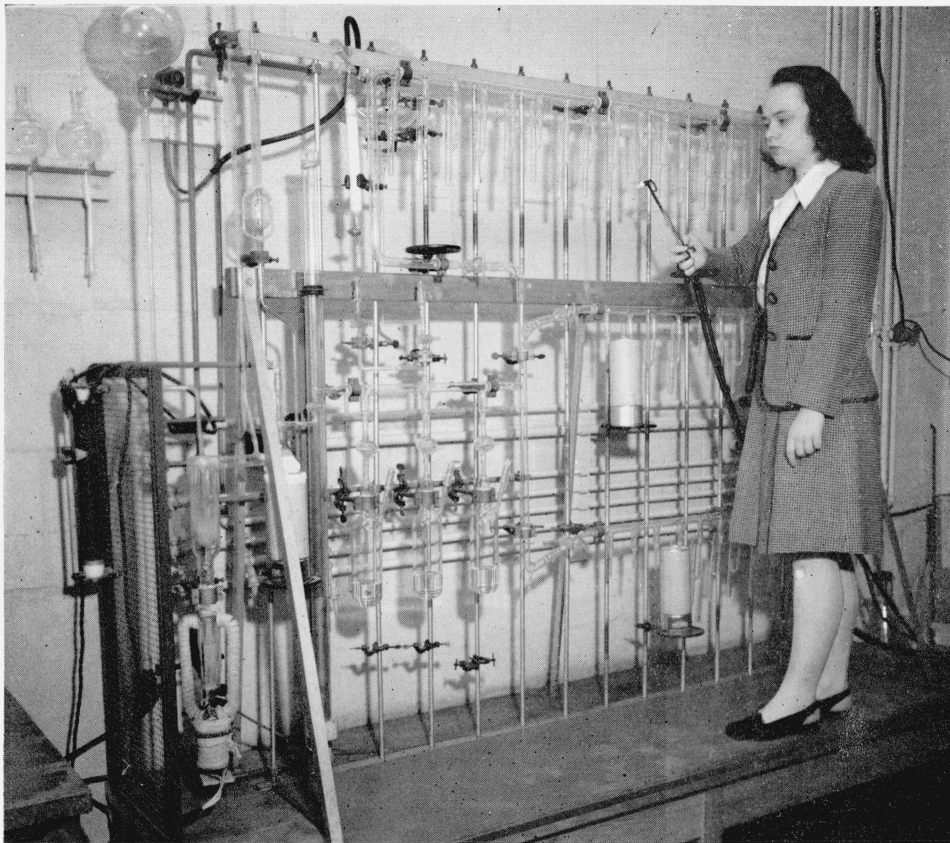


FIGURE 1.—Apparatus for sealing Standard Samples of hydrocarbons "in vacuum."

impurity, the bulk of the *p*-xylene was first removed by sulfonation and hydrolysis of the sulfonic acids, as follows (see reference 11): A 5-liter Pyrex glass flask with three necks, equipped with a stirrer, glass thermometer, and a 500-ml separatory funnel, was placed in a pail of cold water whose temperature was kept below that of the room. A volume of 1,200 ml of the *m*-xylene was placed in the flask, and 1,300 ml of concentrated (96 percent by weight) sulfuric acid was slowly added through the separatory funnel, while stirring, over a period of 3 hours. The temperature of the sulfonation reaction was kept between 35° and 45° C by regulating the rate of introduction of acid and by cooling the water surrounding the reaction flask. About 30 minutes after all the sulfuric acid had been added, 1,100 ml of distilled water was introduced slowly while stirring. Then the stirrer, separatory funnel, and surrounding water bath were removed. The 5-liter flask containing the reaction mixture was placed on a tripod and fitted with an inlet tube for steam and a condenser on the outlet leading to a receiver. Steam was introduced, and the reaction mixture was brought, with external heating, to a temperature of 125° C, when distillation began. Hydrolysis occurred slowly at 125° C, but rapidly at 130° to 132° C. The distillate of water plus hydrocarbon was collected in fractions of such volume as contained about 50 ml of hydrocarbon. The fractions were washed with water and filtered through silica gel. About 5 percent of the hydrocarbon material was lost in the process of sulfonation and hydrolysis. The purity of selected fractions was determined by measuring freezing points [4], in order to locate the purest material for blending for reprocessing or for the final product, if sufficiently pure. As required, the process of sulfonation and hydrolysis was repeated on selected blended fractions to improve the purity. Additional amounts of starting *m*-xylene<sup>4</sup> were processed as required. One lot of *m*-xylene purified by sulfonation and hydrolysis was further purified by crystallization, using the same apparatus and procedure as for the crystallization of benzene, except that the jacket of the centrifuge was cooled to near -80° C with carbon-dioxide slurry.

With the exception of 3-methylpentane, the

<sup>4</sup> Essentially the same process of sulfonation and hydrolysis has been used in this laboratory to purify 1-methyl-3-ethylbenzene which contained an appreciable amount of 1-methyl-4-ethylbenzene as impurity.

purity of the final selected standard sample lot of each compound was determined by measuring freezing points, with the apparatus and procedure described in reference [4]. The purity of the 3-methylpentane, which has not yet been crystallized, was estimated by analogy with 2-methylpentane, which was from the same source and similarly purified. The results are summarized in table 1.

TABLE 1—Summary of the purity of 19 NBS standard samples of hydrocarbons<sup>a</sup>

| Compound                                      | Standard Sample number | Calculated <sup>b</sup> amount of impurity in the sample |
|---|------------------------|--|
|   |                        | <i>Mole percent</i>                                      |
| <i>n</i> -Pentane.....                        | 201                    | 0.25 ± 0.10  |
|   | 201a                   | .15 ± 0.07   |
| 2-Methylbutane (isopentane).....              | 202                    | .13 ± 0.06   |
|   | 202a                   | .09 ± 0.06   |
|   | 203                    | .24 ± 0.09   |
| <i>n</i> -Hexane.....                         | 203a                   | .10 ± 0.05   |
| 2-Methylpentane.....                          | 204                    | .25 ± 0.10   |
|   | 204a                   | .16 ± 0.08   |
| 3-Methylpentane.....                          | 205                    | • (.25 ± 0.15)   |
|   | 205a                   | • (.20 ± 0.15)   |
| 2, 2-Dimethylbutane.....                      | 206                    | .12 ± 0.05   |
|   | 206a                   | .10 ± 0.04   |
| 2, 3-Dimethylbutane.....                      | 207                    | .06 ± 0.04   |
|   | 207a                   | .11 ± 0.06   |
| <i>n</i> -Heptane.....                        | 216                    | .10 ± 0.05   |
| 2, 2, 4-Trimethylpentane.....                 | (•, f, g) 217          | .12 ± 0.05   |
| Methylcyclopentane.....                       | 208                    | .25 ± 0.09   |
|   | 208a                   | .11 ± 0.06   |
| Cyclohexane.....                              | 209                    | .012 ± 0.007   |
|   | 209a                   | .010 ± 0.006   |
| Methylcyclohexane.....                        | •, f 218               | .36 ± 0.18   |
| Benzene.....                                  | 210                    | .05 ± 0.02   |
|   | 210a                   | (d)  |
| Toluene.....                                  | 211                    | .04 ± 0.02   |
|   | •, f 211 a             | .04 ± 0.02   |
| Ethylbenzene.....                             | 212                    | .20 ± 0.07   |
|   | 212a                   | (d)  |
| 1, 2-Dimethylbenzene ( <i>o</i> -xylene)..... | 213                    | .14 ± 0.05   |
|   | 213a                   | .010 ± 0.007   |
| 1, 3-Dimethylbenzene ( <i>m</i> -xylene)..... | 214                    | .17 ± 0.07   |
|   | 214a                   | .06 ± 0.04   |
| 1, 4-Dimethylbenzene ( <i>p</i> -xylene)..... | 215                    | .07 ± 0.03   |
|   | 215a                   | .06 ± 0.03   |
| Isopropylbenzene.....                         | 220                    | 0.07 ± 0.03  |

<sup>a</sup> Complete details as to prices, sizes of samples, and types of containers in which these Standard Samples are available may be obtained by writing to the National Bureau of Standards.

<sup>b</sup> Except for 3-methylpentane, the amount of impurity was calculated from the freezing point of the actual sample (determined as described in reference [4]) and the values of the freezing point for zero impurity and the cryoscopic constant given in the tables of the American Petroleum Institute Research Project 44 [5].

• Estimated by analogy with 2-methylpentane.

d In process of determination.

• This compound has been certified by the NBS Optical Instruments Section as to refractive index at 20°, 25°, and 30° C, at each of 7 wavelengths.

f This compound has been certified by the NBS Capacity and Density Section as to density at 20°, 25°, and 30° C.

g This compound has been certified by the NBS Heat Measurements Section as to calorimetric heat of combustion.

### III. Apparatus and Procedure for Sealing "In Vacuum"

#### I. Apparatus

The apparatus for sealing the Standard Samples "in vacuum" is shown in over-all view in figure 1 and consists of the following parts: (a) Vacuum pumps and gage, including a mercury diffusion pump, an oil pump, and a McLeod gage: (b) a

source of compressed air, with gage to regulate the pressure at about 2 lb/in.<sup>2</sup> above atmospheric pressure; (c) appropriate refrigerants, including water ice, carbon-dioxide slurry (consisting of a mush, or slurry, of solid carbon dioxide with equal volumes of carbon tetrachloride and chloroform), and liquid air (liquid nitrogen is preferable,

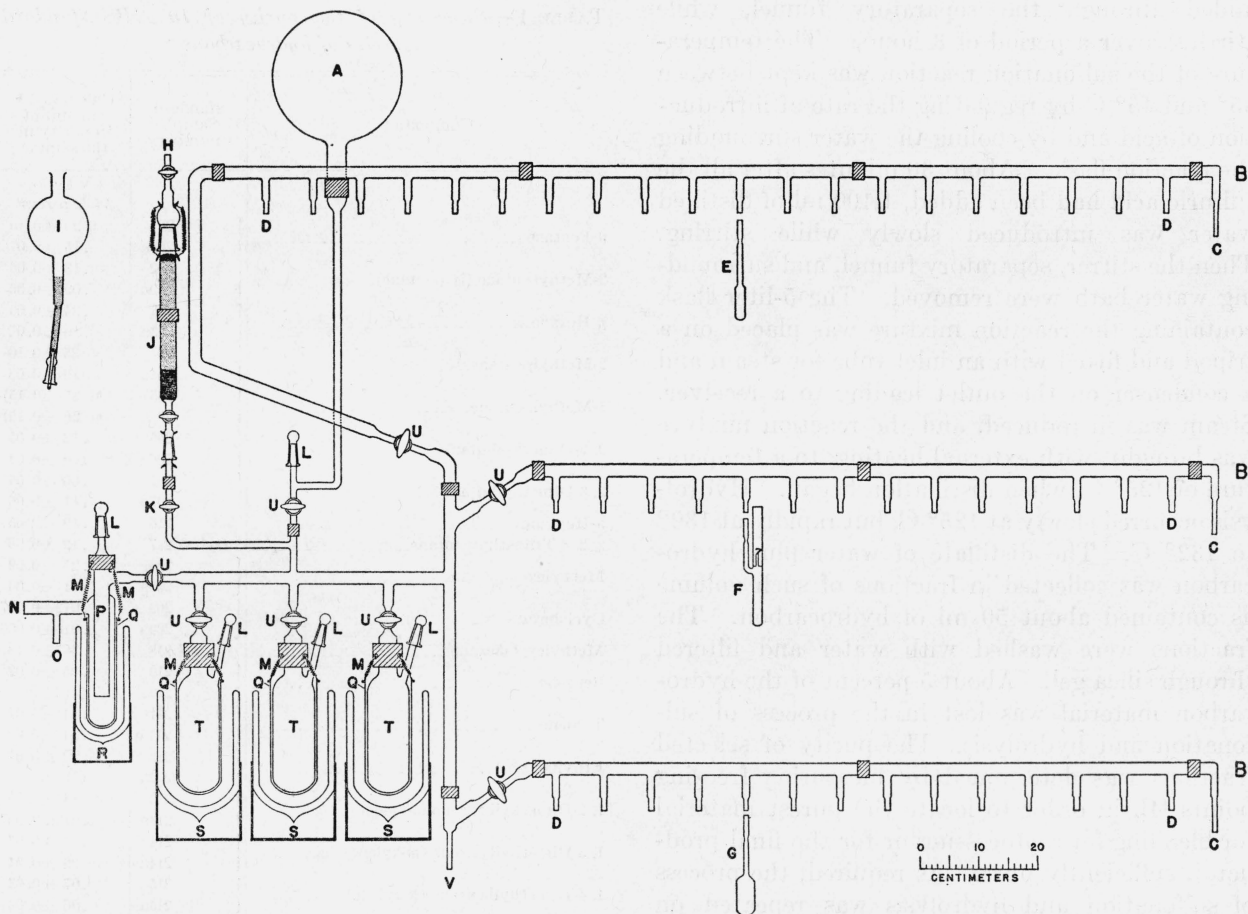


FIGURE 2.—Manifold system and accessory parts for sealing hydrocarbons "in vacuum."

A, gas reservoir, with capacity of 5 liters.

B, three branches of the manifold system.

C, outlets, sealed when hydrocarbon is in the system, but opened for use of the glass blower when empty ampoules are being sealed to the manifold.

D, connections to which empty ampoules are sealed.

E, ampoule (plain, with capacity of 5 ml), before being sealed in position.

F, ampoule (with internal vacuum break-off tip, with capacity of 8 ml), before being sealed in position.

G, ampoule (plain, with capacity of 25 ml), before being sealed in position.

H, connection to source of compressed air at a pressure of about 2 lb/in.<sup>2</sup> above atmospheric pressure.

I, one of three filling tubes (containing silica gel in the shaded portion), which fit on reservoirs T at L at the time of introducing the hydrocarbon into the reservoirs.

J, tube containing (in order from the outer end) anhydrous magnesium perchlorate and phosphorus pentoxide, separated by layers of dry asbestos, for removing water vapor from the air introduced into the system.

K, stopcock, with oblique bore 3½ mm in diameter, ground for high vacuum.

L, standard ground joints, 14/35, with closed caps.

M, expansion springs, made of bronze wire.

N, connection to the mercury diffusion pump.

O, connection to the McLeod gage.

P, trap, refrigerated with liquid air.

Q, shields on each of the three reservoirs, T, and on the trap, P, made of thin brass, for protection from the refrigerant.

R, vacuum-jacketed vessel, Pyrex glass, with capacity of 1 pint, for containing liquid air.

S, vacuum-jacketed vessels, Pyrex glass, with capacity of 1/2 gallon, for containing the appropriate refrigerant.

T, reservoirs for the purified hydrocarbon material, with capacity of 500 ml.

U, stopcocks, with oblique bore 7 mm in diameter, ground for high vacuum.

V, outlet for drainage, sealed closed when hydrocarbon is in the system.

if available); (d) manifold system and accessory parts, the details of which are shown in figure 2.

Details of the several glass ampoules used in this work are shown in figure 3.

## 2. Procedure

### (a) Preparing the apparatus

The apparatus is prepared as shown in figure 2, but with the vessels, *R* and *S*, the shields, *Q*, and the drying tube, *J*, not yet in position. The

ground joints, *L* (including both male and female parts), and the stopcocks, *K* and *U* (including plug and barrel), and the tubing adjacent to it, are cleaned with a cotton swab and with a pipe cleaner, using three fresh portions of carbon tetrachloride as washing solvent. Carbon tetrachloride is introduced into the reservoirs, *T*, glass-insulated electric heaters<sup>5</sup> are placed in position on the lower part of the reservoirs, and the solvent is boiled at atmospheric pressure. By proper

<sup>5</sup> Glascol Apparatus Co., Terre Haute, Ind.

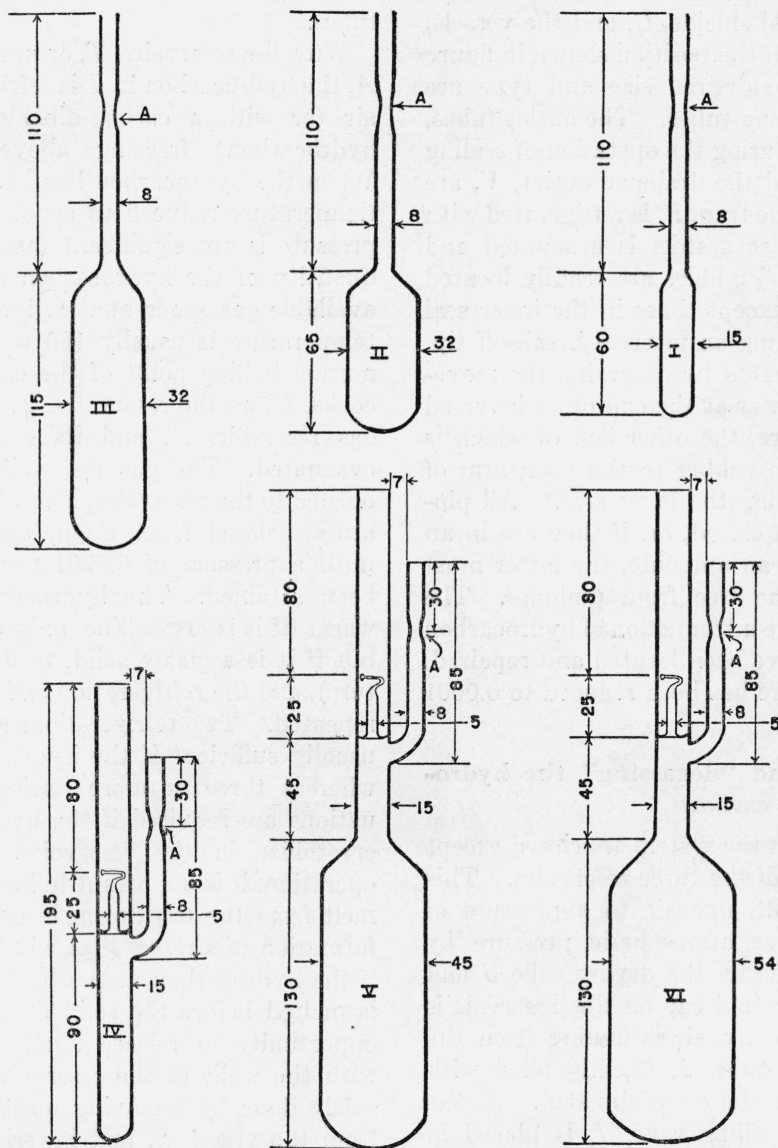


FIGURE 3.—Glass ampoules used for containing hydrocarbons.

The ampoules are all made of Pyrex glass. I, Plain ampoule, with capacity of 5 ml; II, plain ampoule, with capacity of 25 ml; III, plain ampoule, with capacity of 50 ml; IV, ampoule with internal vacuum break-off tip, with capacity of 8 ml (taken from drawing A-1626 of the Consolidated Engineering

Corporation, Pasadena, Calif.); V, similar to IV, but with a capacity of 135 ml; VI, similar to IV, but with a capacity of 200 ml. *A* indicates a thickened wall at the constriction, to facilitate sealing off "in vacuum."

manipulation of the various stopcocks, solvent is caused to distill and reflux through all parts of the manifold system. After the solvent is cooled it is removed through outlet *V* and syphoned out of the trap and reservoirs. The above cleaning process is repeated, with fresh solvent, three times. After liquid solvent from the last refluxing has been withdrawn, all parts of the system are thoroughly flushed with air to remove solvent vapors. The ground joints and stopcocks are lubricated, using the minimum amount of grease (Apiezon *L* in winter and Apiezon *N* in summer). The drying tube, *J*, the metal shields, *Q*, and the vessels, *R* and *S*, are placed in the position shown in figure 2. Ampoules of the desired size and type are sealed to the connecting tubes. The outlet tubes, *C*, used for blowing during the operation of sealing on the ampoules, and the drainage outlet, *V*, are closed by fusing. The trap, *P*, is refrigerated with liquid air. The entire system is evacuated and tested for pinholes. Pinholes are readily located with a spark tester except those in the inner seal of the ampoules having an internal break-off tip. Pinholes here are located by observing the movement of a drop of water at the end of an inverted U-tube, of 2-mm bore, the other end of which is connected with clean rubber to the open arm of the ampoule containing the inner seal.<sup>6</sup> All pinholes must be sealed closed, or, if they are in an inaccessible place in an ampoule, the latter must be replaced with one free from pinholes. The system is ready for the introduction of hydrocarbon when all pinholes have been located and repaired, and when the pressure has been reduced to 0.0001 mm Hg or lower.

#### (b) Introducing and "degassing" the hydrocarbon

All the stopcocks in the system are closed except the stopcock to one of the three reservoirs. This reservoir is filled with dry air to a pressure of about 2 lb/in.<sup>2</sup> above atmospheric pressure by opening the stopcocks on the drying tube *J* and stopcock *K*. The ground cap on this reservoir is removed, and, while dry air is issuing from the reservoir, the filling tube, *I*, (freshly filled with silica gel) is placed on the reservoirs at *L*. At the same time that the filling tube, *I*, is placed in position, the stopcock to the reservoir is closed. In a similar manner, the other reservoirs are fitted with filling tubes. The drying tube, *J*, is closed

off from the system, and the portion of glass tubing bounded by the stopcock, *K*, and the eight stopcocks, *U*, is evacuated. Hydrocarbon (preferably cooled to 0°C) is introduced into the filling tubes, the stopcocks, *U*, to the reservoirs are opened, and the liquid drawn into them by partially and momentarily opening the stopcock, *U*, to the evacuated reservoir, *A*. After all the hydrocarbon has been introduced into the reservoirs, the filling tubes are removed and replaced with caps, *L*, using the same procedure described for the original substitution of the caps with the filling tubes.

With the reservoirs, *T*, open to the gas reservoir, *A*, the hydrocarbon in *T* is refrigerated with liquid air (or with a carbon-dioxide slurry for those hydrocarbons freezing above about -60°C). When the hydrocarbon has become solid, and its temperature reduced to a point where the vapor pressure is not significant (as determined by the quantity of the hydrocarbon required to fill the available gas space at the given pressure), which temperature is usually 160 to 200° C below the normal boiling point of the compound, the stopcocks, *U*, on the reservoirs, *T*, are closed, and the gas reservoir, *A*, and its connecting lines, are evacuated. The gas reservoir, *A*, is repeatedly opened to the reservoirs, *T* (still at the low temperature), closed from them, and then evacuated, until a pressure of 0.0001 mm Hg or lower has been attained. The hydrocarbon is allowed to warm (if it is crystalline, only until it has melted, but if it is a glassy solid, to near room temperature), and the refrigeration and evacuation process repeated. Two refrigerations and evacuations are usually sufficient if the hydrocarbon crystallizes, whereas three or more refrigerations and evacuations are required if the hydrocarbon does not crystallize in the reservoirs. In the warming operation, it is important to have the hydrocarbon melt from the top down, in order to prevent the formation of stresses that will break the reservoir if the hydrocarbon at the bottom of the reservoir is melted before the solid at the top has had an opportunity to release itself from solid contact with the walls of the reservoir. This melting is safely done by removing most of the refrigerant from the vessel, *S*, and lowering the vessel until the level of hydrocarbon in *T* is 2 or 3 cm above the top of the vessel, *S*. When about half of the hydrocarbon has been melted, downward from the top, vessel *S* is withdrawn, and the reservoirs are

<sup>6</sup> This simple test was suggested by A. F. Forziati, of this laboratory.

surrounded with water at room temperature to expedite the melting.

### (c) Filling and sealing the ampoules

The hydrocarbon is transferred from the reservoirs, *T*, through the vapor phase at room temperature to the individual ampoules. During this operation, the stopcocks to the trap, *P*, the drying tube, *J*, and the gas reservoir, *A*, are closed, and the stopcocks on the reservoirs, *T*, and those leading to the branches of the manifold, *B*, are open. The reservoir, *T*, is surrounded with water at room temperature, the first ampoule in one of the branches of the manifold is cooled with an appropriate refrigerant (usually carbon-dioxide slurry, but see below), and the hydrocarbon passes as vapor through the line at room temperature from the reservoir to the ampoule. Occasionally, the transfer of hydrocarbon is blocked by the accumulation in the connecting lines of a small amount of air that was not completely removed from the hydrocarbon during the degassing operation. To remove this air, the stopcocks on the reservoirs are closed, the hydrocarbon in the ampoule is cooled to the temperature of liquid air (or to the temperature of carbon-dioxide slurry if the hydrocarbon has a sufficiently low vapor pressure), and the manifold lines are connected to the source of high vacuum. This secondary degassing operation may be repeated as necessary. When the desired quantity of hydrocarbon has been collected in the given ampoule, the stopcock on the given branch of the manifold is closed, and the hydrocarbon vapor remaining in that branch of the manifold is condensed into the ampoule. This ampoule, protected with a close-fitting metal shield, is refrigerated with liquid air (if available, liquid nitrogen is preferable), and is sealed off at the constriction. If the hydrocarbon has a

sufficiently low vapor pressure, carbon-dioxide slurry may be used as the refrigerant in the last-named operation. With the apparatus described, it is possible to have three ampoules, one on each of the three branches of the manifold, being filled simultaneously.

When all the ampoules on the manifold have been sealed off and hydrocarbon still remains in the reservoirs to be transferred, the stopcocks to the reservoirs and to the branches of the manifold are closed, the connecting tubes are cut off as shown at *D* in figure 2, and clean empty ampoules of the desired type and size are sealed on. The manifold system and the ampoules are evacuated, all pinholes are repaired or removed, and the operation of filling and sealing of the individual ampoules is performed as before.

For hydrocarbons such as benzene, *p*-xylene, cyclohexane, and *o*-xylene, which freeze at temperatures above that of the carbon-dioxide slurry, some modification is necessary in the procedure of transferring hydrocarbon from the reservoirs to the ampoules, in order to control the quantity delivered to each ampoule. If carbon-dioxide slurry is used as the refrigerant the hydrocarbon will condense as solid in the ampoule, and it is necessary at appropriate intervals to melt the hydrocarbon to ascertain its quantity, in terms of a measured volume at a given temperature. Three or more such meltings may be required to adjust the quantity in the ampoule within the desired limits. An alternate procedure is to let the refrigerant around the ampoule be one whose temperature is above the freezing point of the given hydrocarbon, so that the latter is condensed as liquid in the ampoule. For the latter procedure, appropriate refrigerants would be ice and water at 0° C for *o*-xylene, water at 7° C for benzene and cyclohexane, and water at 14° C for *p*-xylene.

## IV. Discussion

The foregoing apparatus and procedure for sealing "in vacuum" is satisfactory for hydrocarbons having normal boiling points below about 170° C and freezing points below room temperature. The rate of transfer through the vapor phase at room temperature of hydrocarbons normally boiling very much above 170° C becomes almost impracticably slow, however, and a different apparatus has been designed and is being assembled to handle hydrocarbons having normal

boiling points above about 170° C, with freezing points either below or above room temperature [6].

For olefin hydrocarbons, the final drying of the hydrocarbon by filtration through silica gel may be used only if such contact with silica gel can be done in such a short time and at a sufficiently low temperature as not to affect the purity of the material. Normally, for olefin hydrocarbons, the filtration through silica gel should be omitted and a different method used to remove the minute



amount of water and oxidation products from the purified material before its introduction into the reservoirs of the apparatus.

The apparatus and procedure described in section III of this report have also been used, since September 1, 1944, to seal <sup>7</sup> "in vacuum" approximately 200 ampoules, each of over 70 hydrocarbons prepared as Standard Samples of hydrocarbons in the cooperative program of the American Petroleum Institute and the National Bureau of Standards on hydrocarbons for spectrometer calibration. Details of this work are given in references [7, 8, 9, 10]. This cooperative program was organized by the API Research

<sup>7</sup> Thomas E. Eble, now with the United States Food and Drug Administration, assisted in this work. The operations of sealing "in vacuum" are currently being performed by Beryl A. Gaffney and Audrey H. Hull, of this laboratory.

Project 46 Committee on Hydrocarbons for Spectrometer Calibration (W. J. Sweeney, chairman).

For the benefit of those laboratories that do not already have an established procedure for transferring Standard Samples of hydrocarbons "in vacuum," there is attached an appendix to this report, which gives a description of the apparatus and procedure used for this purpose for  $C_5$  and higher hydrocarbons by the Hydrocarbon Standard Samples Laboratory at the National Bureau of Standards.

Grateful acknowledgment is made to the organizations and individuals listed in section II of this report for their contributions of materials for use in this work.

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## VI. Appendix.—Apparatus and Procedure for Transferring Standard Samples of Hydrocarbons "In Vacuum"

### I. Introduction

For the benefit of those laboratories that do not already have an established procedure for transferring "in vacuum" Standard Samples of hydrocarbons, there is presented here a description of the apparatus and procedure used for this purpose for  $C_5$  and higher compounds in the Hydrocarbon Standard Samples Laboratory at the National Bureau of Standards.

### 2. Method

The main glass ampoule containing the hydrocarbon, "sealed in vacuum" back of an internal vacuum "break-off" tip, is sealed to a glass manifold to which are also sealed the required number of empty auxiliary ampoules to which the hydrocarbon is to be transferred. The entire

system is evacuated. The "break-off" tip is broken by means of an electromagnetic hammer previously installed above the main glass ampoule containing the hydrocarbon. The appropriate amount of hydrocarbon is transferred to the first auxiliary ampoule by refrigerating the latter and permitting the transfer to take place through the vapor phase at room temperature. The main ampoule is refrigerated, and the first auxiliary ampoule is sealed off. The operations are repeated for each auxiliary ampoule.

### 3. Apparatus

#### (a) Vacuum system

This system must be capable of producing and measuring pressure of 0.0001 mm Hg and lower. (A suitable system may consist of a mercury or oil vapor diffusion

pump backed by an appropriate mechanical oil pump, for producing the required low pressure, and a McLeod gage for measuring the low pressure.) For lubricating the ground joints and stopcocks in the high-vacuum system, Apiezon grease *L* may be used in winter and Apiezon grease *N* in summer.

### (b) Refrigerant

For hydrocarbons normally boiling below about 80° C, liquid air or liquid nitrogen may be used as the refrigerant. (If liquid air is used, each ampoule so refrigerated should be provided with a closely fitting thin-metal cylinder for protection in case of breakage.) For hydrocarbons normally boiling above about 80° C, the refrigerant may consist of a slush, or slurry, of solid carbon dioxide in a 50-50 mixture of chloroform and carbon tetrachloride. For the ampoules, the refrigerants may be contained in cylindrical vacuum-jacketed vessels of about 1-pint capacity.

### (c) Manifold system

This assembly is shown in figure 4, as follows: *A*, connection to the high-vacuum system; *B*, standard ground joint and cap, 14/35; *C*, liquid-air or liquid-nitrogen trap, with closely fitting thin-metal protecting tube if liquid

air is used; *D*, stopcock, with 3 1/2-mm oblique bore, ground for high vacuum; *E*, main horizontal tube of manifold; *F*, solenoid, about 1,200 ampere turns (a solenoid for this purpose suitable for use directly on 110-volt alternating current, may be made by winding No. 30 AWG copper wire, enameled and single silk covered, in a layer 1.5 cm in thickness on a Bakelite tube 5 cm in length and about 1.8 cm in inside and 2.3 cm in outside diameter.); *G*, connection to main ampoule containing the standard sample (see note (a) below); *H*, iron (mild annealed steel) rod incased in glass (a suitable rod may be 5/16 in. in diameter and 1 1/2 in. long, with rounded ends, fitting inside glass tubing 10 mm in outside diameter with standard wall thickness). The ends of the glass case should be heavily thickened; *I*, main glass ampoule containing Standard Sample; thin-metal protecting tube should be provided if liquid air is to be used; *J*<sub>1</sub>, *J*<sub>2</sub>, *J*<sub>3</sub>, . . . , *J*<sub>n</sub>, connections to auxiliary ampoules; *K*<sub>1</sub>, *K*<sub>2</sub>, *K*<sub>3</sub>, . . . , *K*<sub>n</sub>, auxiliary ampoules; these may be plain or have an internal vacuum break-off tip, as shown; thin metal protecting tubes should be provided if liquid air is to be used; *L*<sub>1</sub>, *L*<sub>2</sub>, *L*<sub>3</sub>, . . . , *L*<sub>n</sub>, place where the auxiliary ampoules are sealed off after filling; *M*, outlet for attaching rubber tubing for blowing glass; outlet is sealed off after all auxiliary ampoules are attached.

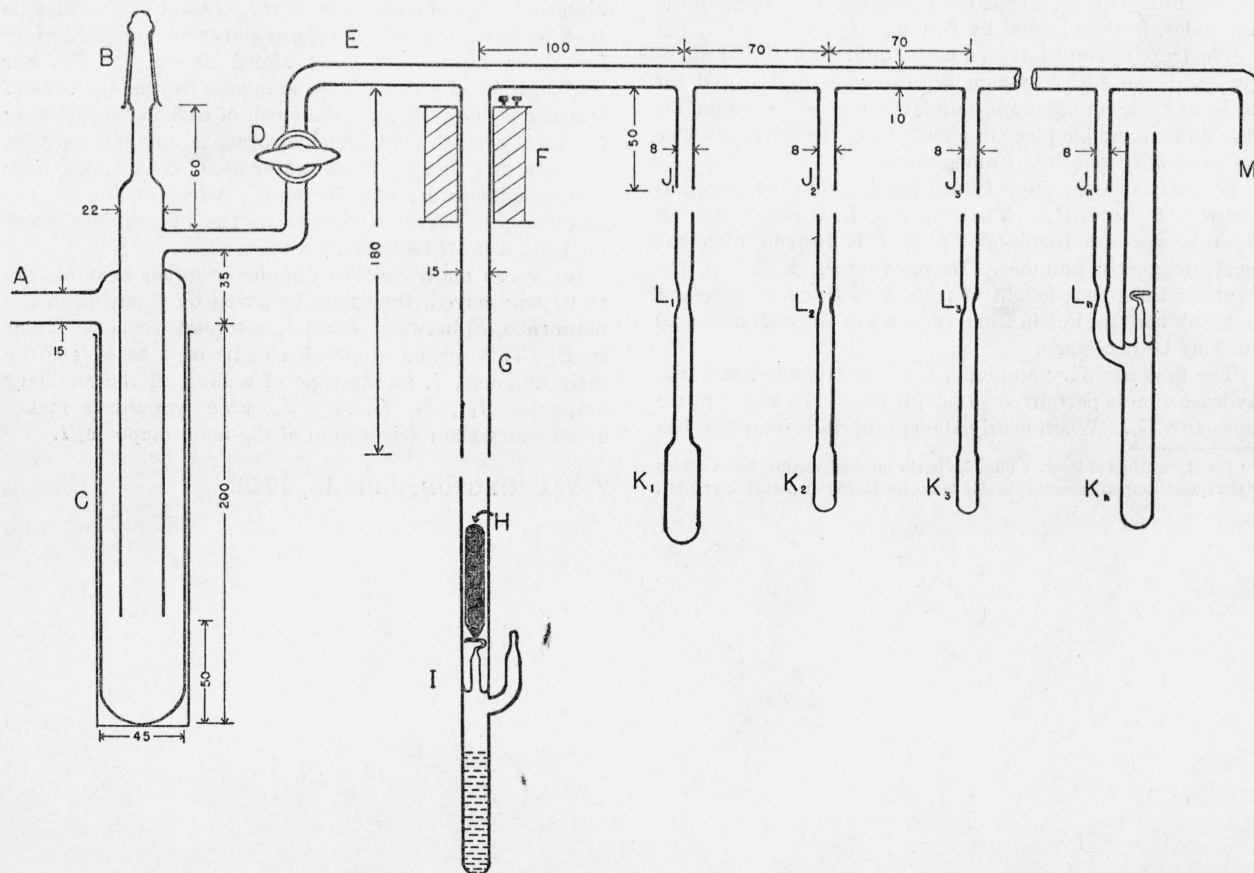


FIGURE 4.—Apparatus for transferring Standard Samples of hydrocarbons "in vacuum".

See text in appendix for details. All dimensions in millimeters. Glass is Pyrex.

## 4. Procedure

The manifold system is prepared as shown in figure 4. The connecting tubes,  $G$  (see footnote "a"),  $J_1, J_2, J_3, \dots, J_n$ , are cut off to the lengths indicated. The ground joint,  $A$ , (including both male and female parts), and the stopcock,  $D$ , (including plug and barrel and the tubing adjacent to it), are cleaned with carbon tetrachloride, using a pipe cleaner with cotton swab and three fresh portions of solvent. To remove traces of stopcock lubricant that may be in the tubing near the stopcock, the unlubricated plug of the stopcock is placed in the open position, suction is applied at  $A$ , and fresh liquid solvent is drawn into the trap,  $C$ , from a beaker of the solvent held around connecting tube  $G$ , with the other connecting tubes being temporarily stoppered with clean corks. The solvent is then withdrawn from the trap,  $C$ , and vapors of the solvent are removed from the system by flushing with air. The ground joint,  $A$ , and the stopcock,  $D$ , are then lubricated, using the minimum amount of Apiezon grease  $L$  or  $N$ .

The glass incased iron rod,  $H$ , is placed inside the main ampoule,  $I$ , as shown in the illustration. Ampoule  $I$  is sealed to connecting tube  $G$ . The auxiliary ampoules,  $K_1, K_2, K_3, \dots, K_n$ , are sealed to the connecting tubes,  $J_1, J_2, J_3, \dots, J_n$ , respectively. The outlet,  $M$ , used for blowing during the operations of sealing on the ampoules, is then closed by fusing.

The trap,  $C$ , is refrigerated with liquid air or liquid nitrogen, and the entire system is evacuated and tested for pinholes.<sup>8</sup> If pinholes are found, these must be sealed, or, if in an inaccessible place in an ampoule, the latter must be replaced with one free from pinholes.

Evacuation is continued until the pressure is reduced to below 0.0001 mm Hg. The stopcock,  $D$ , is closed and the internal vacuum break-off tip in  $I$  is broken with the electromagnetic hammer. In most cases, a fall of the hammer through a height of from 5 to 10 cm is sufficient to break the tip, but in some cases a fall through about 20 cm may be necessary.

The first auxiliary ampoule,  $K_1$ , is refrigerated and the hydrocarbon is permitted to pass through the vapor phase from  $I$  to  $K_1$ . When nearly the appropriate quantity has

<sup>8</sup> For the method of locating pinholes in the internal vacuum break-off tip of the special ampoules, see section III-2-a of the preceding part of this report.

been transferred to  $K_1$ , the passage of hydrocarbon to  $K_1$  is halted by refrigerating the main ampoule,  $I$ , and the ampoule  $K_1$  is sealed off at  $L_1$ . See note (b).

The remaining auxiliary ampoules,  $K_2, K_3, \dots, K_n$ , are then sealed off in order.

## 5. Discussion

For a modification of the apparatus and procedure when many volatile samples are to be transferred, see note (c).

## 6. Notes

(a) If the main ampoule,  $I$ , containing the Standard Sample, is made of Pyrex red glass (No. 2,280), a short length of tubing of 15-mm outside diameter, consisting of 50 mm of ordinary Pyrex clear glass (No. 774) joined to 10 mm of Pyrex uranium glass (No. 332) joined to 50 mm Pyrex red glass (No. 2,280) (which piece of tubing is obtainable on request from the National Bureau of Standards), is first sealed to connecting tube  $G$ , with the Pyrex red glass end of the added tube being free to receive the Pyrex red-glass ampoule. The same connecting tube may be used over and over again.

(b) For refrigeration at the time of sealing off the ampoules, liquid air or liquid nitrogen is recommended to be used for those hydrocarbons normally boiling below about 80° C, and a slush, or slurry, of solid carbon dioxide (in a 50-50 mixture of chloroform and carbon tetrachloride) for those normally boiling above about 80° C. For refrigeration of the auxiliary ampoules during the time of transfer of hydrocarbon, the slush of carbon dioxide may be used, except when the hydrocarbon solidifies at that temperature, in which case water at 0° C or appropriate higher temperature may be used. Before sealing off, the ampoules, however, a change to the appropriate lower refrigerant must be made.

(c) When many volatile samples in larger amounts are to be transferred, time may be saved by inserting in the main tube,  $E$ , between  $G$  and  $J_1$ , a second stopcock similar to  $D$ . This second stopcock can be used to isolate the main ampoule,  $I$ , at the time of sealing off the auxiliary ampoules,  $J_1, J_2, J_3, \dots, J_n$ , which procedure makes unnecessary the refrigeration of the main ampoule,  $I$ .

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