United States Patent

[11] 3,578,757

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[45] Patented **May 18, 1971**

[54] **CHROMATOGRAPH FOR DETERMINATION OF ADMIXTURES IN GASES**
6 Claims, 8 Drawing Figs.

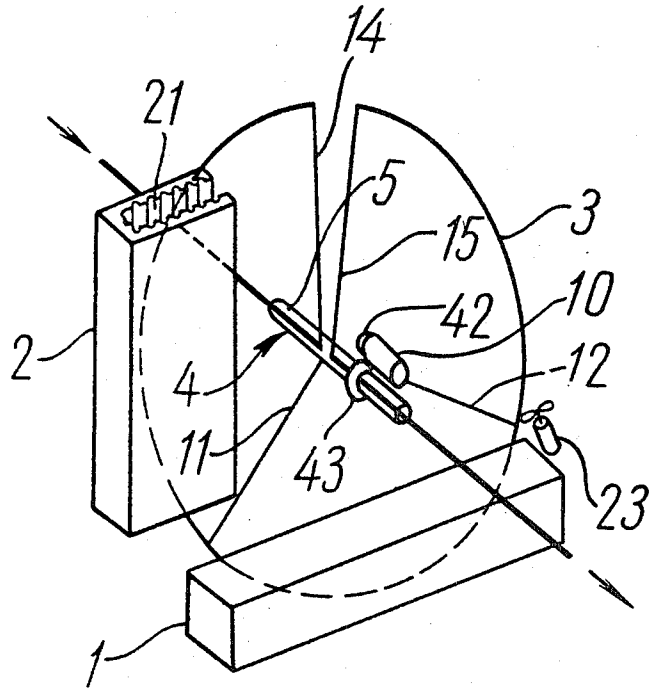
[52] **U.S. Cl.** **73/23.1,** 55/197, 23/255
[51] **Int. Cl.** **G01n 31/08,** B01d 15/08
[50] **Field of Search** ..... 73/23, 23.1, 53 (C); 55/53, 67, 78, 80, 197, 386, 390; 23/232 (C), 254 (C), (Inquired)

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Assistant Examiner—C. E. Snee, III
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ABSTRACT: A chromatograph for the determination of admixtures in gases, comprises a chromatographic column bent in the form of at least a single helix coil or an arc of circle and which is rigidly secured on the shaft of a drive device in a plane perpendicular to the axis of the shaft. The shaft is mounted in stationary supports so that at the same time one portion of the chromatographic column is immersed in a refrigerant bath and the other portion of the column is in a heater, and during the rotation of the shaft said portions of the column subsequently pass through the cooling and heating zones.



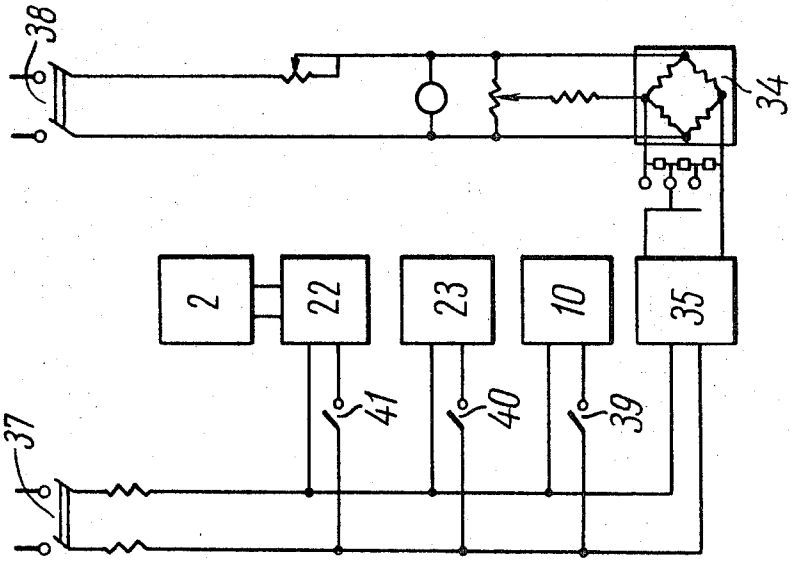


FIG. 7

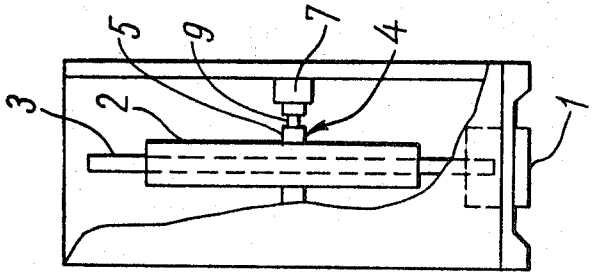


FIG. 1

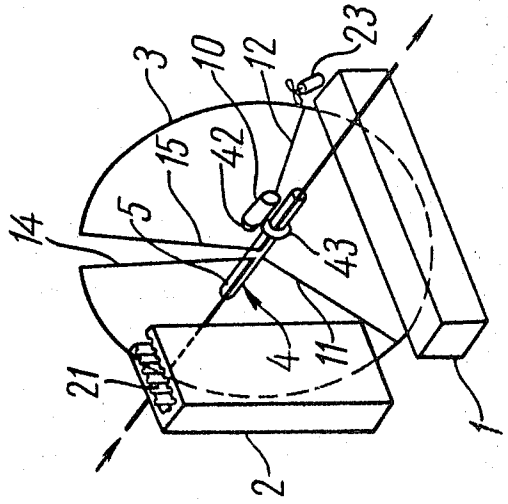


FIG. 2

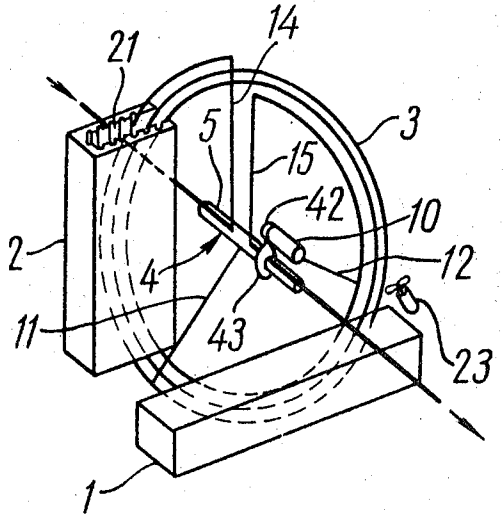


FIG. 3

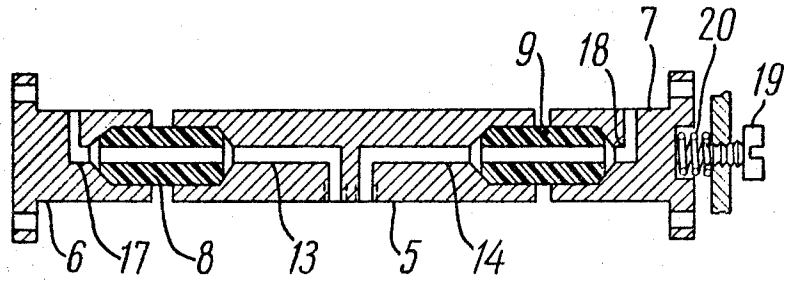


FIG. 4

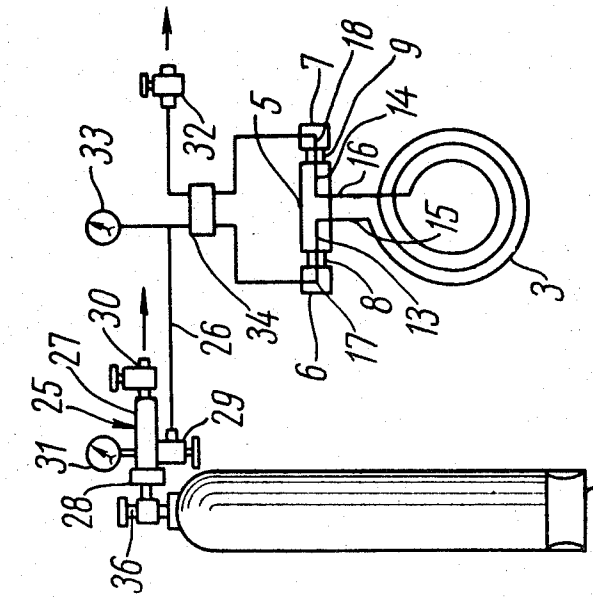

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FIG. 6

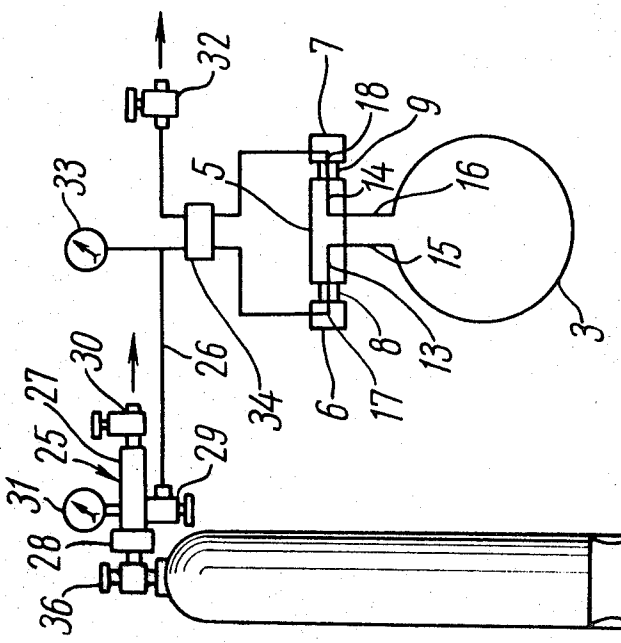

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FIG. 5

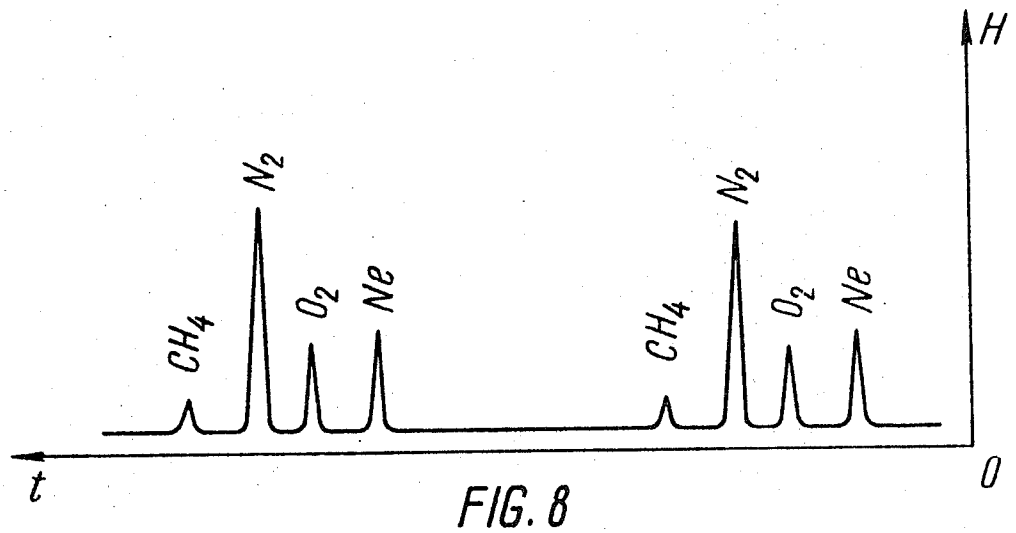


FIG. 8

CHROMATOGRAPH FOR DETERMINATION OF ADMIXTURES IN GASES

This invention relates to chromatographs for determination of gas admixtures, and can particularly be used to advantage for determination of admixtures in gases, boiling at low temperatures, such as helium and neon.

Known in the art are chromatographs for determination of gas admixtures, comprising a bath filled with a refrigerant, a heater, a chromatographic column in the form of a coil, and a drive unit which moves the chromatographic column in the cooling and the heating zones. In chromatographs of this type the entire chromatographic column is first placed into the refrigerant bath and then into the heater.

Disadvantages of the prior art chromatographs consist in their complicated construction and in the requirement for a preliminary cooling of the entire chromatographic column which considerably prolongs analytic procedure.

An object of this invention is to provide a chromatograph capable of operating in the continuous process stream without changing over gas streams or electrical circuits while in operation. Another object of the invention is to provide a chromatograph for determination of admixtures in gases which would be convenient in use and simple in construction.

With these and other objects in view, the chromatograph for determination of admixtures in gases comprises, according to the present invention, a chromatographic column which is a helical tube of at least one coil fixedly attached to a shaft of a drive unit, said shaft being borne in stationary supports so that one part of the column is immersed in the refrigerant in the cold bath, while the other part of the column is in the heater zone, and during rotation of the shaft the column passes in turn to and from the cold and the heater zones, the shaft and stationary supports being provided with interconnected communicating channels for gas delivery into and discharge from the chromatographic column.

The shorter time of the analysis with the present chromatograph has been achieved due to the use of a temperature field which shifts along the sorbent bed without preliminary cooling of the entire sorbent bed.

These and other objects and advantages of the invention will be better understood from the description of specific embodiments thereof and the appended drawings, in which:

FIG. 1 is a general view of the chromatograph provided by the invention, with partial cutaway;

FIG. 2 is a schematic axonometric view of the chromatograph according to the invention;

FIG. 3 is a schematic axonometric view of an alternative modification of the chromatograph;

FIG. 4 is a section taken along the axis of the shaft of the drive unit of the chromatograph according to the invention;

FIG. 5 illustrates a diagram of gas flow in the chromatograph shown in FIG. 2;

FIG. 6 illustrates a gas flow diagram for the chromatograph shown in FIG. 3; and

FIG. 7 is an electrical circuit diagram of the chromatograph according to the invention;

FIG. 8 is a typical detector trace according to the invention.

The chromatograph according to the invention comprises a refrigerant bath 1 (FIGS. 1—3) and a heater 2, which ensure refrigeration and heating of the chromatographic column respectively, and a chromatographic column 3, manufactured from stainless steel.

In one embodiment of the invention the chromatographic column 3 is an open coil and is a helical tube in the other embodiment of the chromatograph as shown in FIGS. 2 and 3, respectively.

The column 3 is filled with a suitable sorbent and is intended to concentrate and separate gas admixtures. The said column 3 is rotatably supported due to a drive unit 4 comprising a shaft 5 borne in stationary supports 6 and 7 (FIG. 4) packed with special bushes 8 and 9, and operatively associated with an electric motor 10 (FIGS. 2 and 3).

The chromatographic column 3 is fixedly attached to the shaft 5 with the aid of pins 11 and 12 perpendicularly to the

shaft 5, so that one part of the chromatographic column is immersed into the refrigerant bath 1, while its other part is in the heater 2. As the shaft 5 rotates the column parts pass in turn through the cold and warm zones. Channels 13 and 14 in the shaft 5 (FIG. 4), intended to pass the analyzed gas, are connected with the chromatographic column inlet and outlet openings by means of metal capillary tubes 15 and 16 (FIGS. 5, 6).

The stationary supports 6 and 7 also have channels 17 and 18 (FIG. 4) which communicate with channels 13 and 14, respectively.

The packing bushes 8 and 9 manufactured of flaro-plast (fluorinated plastic material) perform the functions of both packing glands and bearings. The packing bushes 8 and 9 are made in the form of cylinders with conical bases.

The shaft 5 and stationary supports 6 and 7 also have cones which accept the cones of the bushes 8 and 9. The surfaces of the cones of the packing bushes and their matching surfaces of the shaft 5 and of the stationary supports 6 and 7 are polished.

In order to prevent gas leakage, one stationary support 7 can be shifted in the direction of the shaft 5 by manipulating an adjusting screw 19 and a spring 20. The low coefficient of friction between metal and flaro-plast ensures rather free rotation of the shaft 5 mounting in the chromatographic column 3.

The heater 2 is a U-shaped rectangular ceramic housing. The inner surface of the housing has grooves 21 (FIGS. 2, 3) parallel to the housing axis into which a heating element (not seen in the drawing) is placed. An autotransformer 22 (FIG. 7) serves to control the operation of the heater.

An electric fan 23 cools a portion of the chromatographic column 3 (FIG. 2) or several portions of the chromatographic column (FIG. 3) prior to their being immersed into the refrigerant bath 1.

The chromatograph has a special inlet device 25 for connection to the cylinder 24 (FIGS. 5 and 6) containing the analyzed gas, which allows a quick flush required during the change of cylinders. The inlet device 25 is connected with the chromatographic column through a flexible metal capillary tube 26 and comprises a housing 27 with a coupling nut 28, a control valve 29, a valve 30 and a pressure gauge 31. The control valve 29 maintains the preset flow rate of the gas to be analyzed, the valve 30 serves for flushing the system, and the pressure gauge 31 measures the pressure within the gas cylinder 24.

All connections in the chromatograph are made with metal capillary tubes.

During the period between analyses, the control valves 29 and an outlet valve 32 are closed, while the system confined therebetween remains under the pressure of the analyzed gas. The residual pressure is controlled by the pressure gauge 33.

For the detection of admixtures separated from the chromatographic column use is made of a detector 34 (for example, a katharometer) adapted to deliver signals of certain value (depending upon the amount of each component of the admixtures) to a recorder 35 serving to record said signals on plotting paper.

The inlet unit 25 is connected by the coupling nut 28 to the cylinder 24 containing helium to be analyzed and a valve 36 (FIGS. 5, 6) of the cylinder 24 and the valve 30 are opened. After the system has been given the required flush, the valve 30 is closed and the control valve 29 and the outlet valve 32 are opened one after another.

From the cylinder 24, through the control valve 29 and a flexible metal tube 26, the gas is continually delivered into the comparator chamber of the detector 34. Further, the gas passes through the channel 17, packing bush 8, channel 13 and metal capillary tube 15, and finally enters the chromatographic column 3. From the chromatographic column 3 the gas passes through the metal capillary tube 16, channel 14, packing bush 9 and channel 18, and finally enters the working chamber of the detector 34. Through the outlet valve 32 the gas is discharged from the detector 34 to atmosphere. Now the following electrical connections are made: a tumbler switch

37 (FIG. 7) cuts in the mains voltage, a tumbler switch **38** makes the circuit of the bridge, a tumbler switch **39** starts the electric motor **10**, a tumbler switch **40** cuts in the fan **23** and a tumbler switch **41** makes the circuit of the heater **2**. The rotary motion of the electric motor **10** is transmitted through a reducing gear **42** (FIGS. **2**, **3**) to a driven gear **43** fixed on the shaft **5**. By selecting a proper gear in the reducer **42**, the required speed of rotation of the chromatographic column **3** is obtained. The sense of rotation is opposite to the direction of the gas flow through the chromatographic column **3**. Further, the bath **1** is primed with the refrigerant—liquid nitrogen—and the flow rate of the analyzed gas is adjusted with the aid of the control valve **29** and a soap film flowmeter (not shown in the drawing) which is installed at the chromatograph outlet.

As the chromatographic column **3** rotates (FIGS. **2** and **5**) the temperature field, having the gradient with an interval of from the temperature of the refrigerant to the sorbent regeneration temperature, moves in the direction of the gas flow. The temperature field helps to separate and concentrate the admixtures which separately pass to the working chamber of the detector **34**, as the chromatographic column **3** outlet enters the heater **2** zone.

As the chromatographic column **3** (FIGS. **3** and **6**), made in the form of a helical tube rotates, a number of temperature fields, each having the temperature gradient with an interval of temperatures from that of the refrigerant to the sorbent regeneration temperature, move along the sorbent bed in the direction of the gas flow. These temperature fields follow one after another, their number being equal to the number of the helix coils.

In accordance with the number of the temperature fields, the same number of zones move along the chromatographic column **3** in which the admixtures are separated and concentrated. The amount of admixtures accumulated in each zone, corresponds to the number of admixtures contained in that part of the gas which enters the chromatographic column **3** during one complete revolution.

Considering a specific case of analysis, let a gas, for example, helium containing microadmixture of neon, oxygen, nitrogen and methane be continuously passed through the chromatographic column **3** in a direction opposite to that of the column rotation.

The chromatographic column **3** rotates continuously within the cooling and heating zones. At the same time, along the bed of sorbent, there is moved a temperature field with a temperature gradient ranging from minus 196° C. to 350° C. (when using liquid nitrogen as refrigerant).

The direction of motion of the temperature field and the decrease of temperature inside the latter (from plus 350° to minus 196° C.) coincides with the direction of flow of gas under analysis, however, the rate of the gas flow is in all cases higher than that of the temperature field displacement and depends upon the desired sensitivity of the instrument.

With an appropriate type of sorbent, rate of gas flow and rate of the column rotation, the bulk of the gas being analyzed, in this particular case, helium, will freely pass through the bed of sorbent in the temperature field, while admixtures will be entrapped by the sorbent at their characteristic temperatures and will concentrate in certain zones corresponding to various components of the admixture.

Those zones occupy certain portions of the temperature field (depending upon the admixture properties), are immovable with respect to the refrigerant bath **1** and the heater **2** and move on the bed of sorbent during rotation of the column **3**.

Thus, during the whole period of one complete revolution of the column **3**, there will be taking place the concentration of the admixture components in said zones and, at the moment the outlet of the column **3** passes through said zones, all the components will separately pass to the recording instrument **34**, that is, the full cycle of analyzing all the admixtures takes place during one revolution of the column **3**. The chromatogram of an analysis of admixtures in helium is merely an example presented for clarifying the mode of the chromatograph operation.

The above is equally true both for chromatographs with a column in the form of an arc of a circle or a single helix coil, and for chromatographs with a column made as several helix coils.

The coils following the first one serve to make up for a possible passage of admixture components through the bed of sorbent in the temperature field, for when a component passes through the bed of sorbent in the first temperature field, it get to the bed of sorbent in the second temperature field.

The first results of the analysis may be read from the instrument after the chromatographic column **3** completes the number of revolutions equal to that of the helix coils. Then the readings can be obtained after each revolution, as the chromatographic column **3** outlet enters the heater **2** zone.

Before the chromatograph is taken out of operation, the refrigerant is discharged from the bath **1**, then the outlet valve **32**, control valve **29**, and valve **36** of the cylinder **24** are closed one after another. Finally, tumbler switches **37**, **38**, **39**, **40** and **41** are turned off.

The present chromatograph automatically determines admixtures in low-boiling gases, for example in helium. No pure carrier gas is required for the analysis. The chromatograph is free from disadvantages inherent in the prior art instruments of the same kind, in which gas sampling is employed. The chromatograph may operate in the continuous process stream without changing over gas streams or electrical circuits. Results of the analyses are recorded on a paper chart at 6 minute intervals.

While a specific embodiment of the chromatograph has been disclosed in the description, it will be understood that various modifications and changes within the spirit of the invention may occur to those skilled in the art. Those modifications and changes are considered to be falling within the scope of the invention as set forth in the appended claims.

We claim:

1. A chromatograph for the determination of admixtures in gases, said chromatograph comprising a chromatographic column for receiving a gas to be analyzed, refrigerant means and heater means spaced proximate one another for constituting cooling and heating zones respectively, said chromatographic column being rotatably supported and interposed between said cooling and heating zones such that one portion of said chromatographic column is within said cooling zone and a further portion thereof is within said heating zone, drive means connected to said chromatographic column for imparting rotation thereto to thereby pass successive portions of said chromatographic column between said zones, said chromatographic column including at least a single coil having an inlet for receiving said gas to be analyzed and an outlet for discharging said gas, support means for rotatably supporting said coil, said support means being provided with an inlet channel and an outlet channel communicating with said inlet and outlet of said coil respectively, detector means connected to said outlet of said support means, and recorder means connected to said detector means for receiving signals therefrom, said signals indicating the amount of admixtures in said gas being analyzed.

2. A chromatograph as claimed in claim **1**, wherein said coil is substantially circular.

3. A chromatograph as claimed in claim **1**, wherein said coil is helical.

4. A chromatograph as claimed in claim **1**, wherein said support means includes a shaft to which said chromatographic column is fixedly connected, and stationary end supports, said shaft including opposite end portions rotatably supported one in one of each of said end supports, said inlet and outlet channels of said support means extending respectively from a respective one of said end supports to said shaft.

5. A chromatograph as claimed in claim **1**, wherein said heater means includes a substantially U-shaped member embracing said coil.

6. A chromatograph as claimed in claim **1**, wherein said refrigerant means includes a liquid refrigerant bath wherein said coil is immersed.