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METHOD OF ANALYZING BINARY FLUID MIXTURES AND DEVICE THEREFOR

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FIG. 1

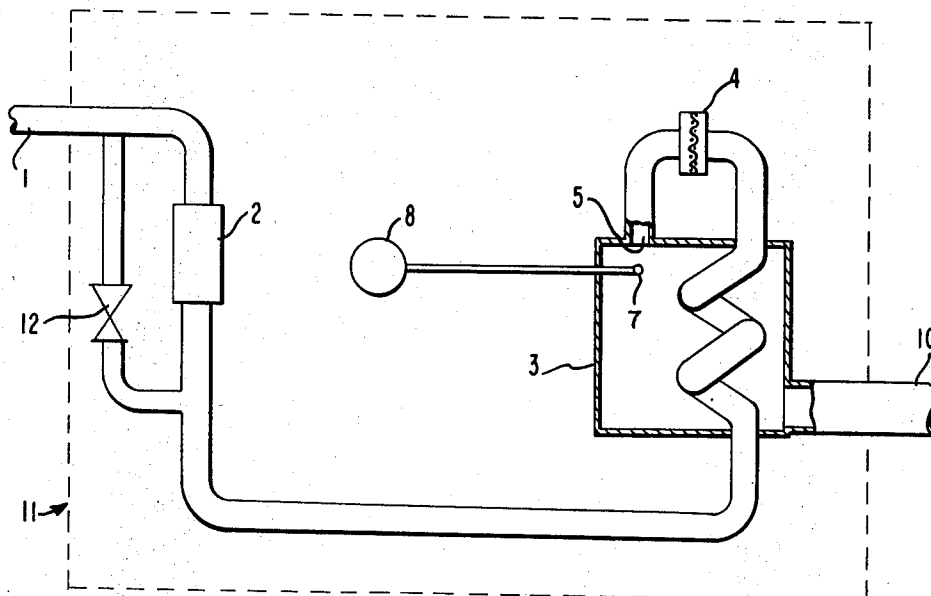
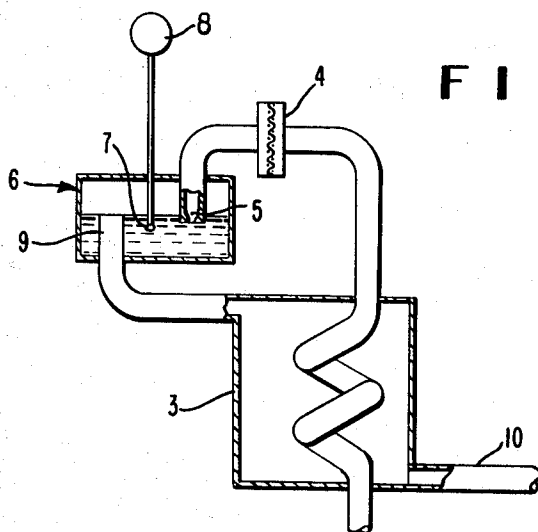


FIG. 2



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METHOD OF ANALYZING BINARY FLUID MIXTURES AND DEVICE THEREFOR

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6 Claims

ABSTRACT OF THE DISCLOSURE

Method of analyzing binary vaporizable fluid mixtures of known components to determine their percent composition by measuring the temperature of the mixture after a controlled expansion, and analyzing device containing a heat exchanger for carrying out such method.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to an improved method of analyzing vaporizable binary fluid mixtures of known components to determine their percent composition and to an improved analyzing device for use in such method. Throughout the specification and claims the term "binary fluid mixture" refers to a mixture which, except for trace amounts of impurities, consists of only two components, either or both of which is a gas, vapor or liquid at about 25° C. and atmospheric pressure. The term "vaporizable" means that the binary fluid mixture, and each component thereof, has a boiling point below about 250° C. at atmospheric pressure. Such fluid mixtures will at least partially evaporate upon passing through an orifice into an expansion chamber maintained at a pressure below the pressure before the orifice.

DESCRIPTION OF THE PRIOR ART

Binary vaporizable fluid mixtures are well known and are widely used as propellants for expelling other materials such as insecticides, fungicides, deodorants, hair-treating compositions, foodstuffs, paints, and the like from pressurized containers in the form of aerosols, sprays and foams. These mixtures are also used as refrigerants, dielectrics, reactants in chemical processes and for other purposes.

In general, such binary fluid mixtures are produced by one of two methods. The most common method is by mixing the two components in the desired proportions, preferably in a continuous manner. The other is by producing the binary fluid mixture in a chemical process in which the proportions of the components of the mixture can be varied by changing the process conditions. In this manner, it is possible to produce mixtures containing components in the desired proportions. During either method of preparation, it is desirable to frequently analyze such binary fluid mixtures to determine the proportions of the components therein.

A number of devices are known which can be used to determine the composition of such mixtures. These devices include mass spectrometers, vapor phase chromatographic units, infrared spectrometers, and the like. However, each of these devices has a characteristic which renders it undesirable for many applications, such as being expensive, nontransportable, batchwise in operation which requires that samples of the binary fluid mixture be withdrawn periodically and placed in the device for analysis, or slow in operation which results in a time lapse from sample withdrawal to final analysis of from several minutes to an hour or more.

A device and method for continuously determining the composition of binary vaporizable fluid mixtures of known components has been described by Felton and Williams in U.S. Pat. 3,264,862. Their process involves flowing the mixture from a supply chamber at a predetermined temperature and pressure through an orifice, expanding the mixture adiabatically in an expansion chamber maintained at a predetermined pressure, and measuring the temperature of the expanded mixture. This temperature is characteristic of the composition of the mixture and varies regularly with variation in its composition. Thus, the composition of the mixture is determined by measuring the temperature of the expanded mixture under predetermined conditions, and comparing this temperature with the temperatures produced by a series of similarly expanded binary mixtures of the same components of known varying composition.

The process of the Felton and Williams patent requires that the binary mixture be available at the predetermined temperature and pressure for accurate analysis. Variations in temperature or pressure of the mixture entering the device cause errors in the determination of the composition of the mixture. Accordingly, it would be desirable to provide a method and device for analyzing binary vaporizable fluid mixtures which is not sensitive to the temperature and pressure of the mixture entering the device.

SUMMARY OF THE INVENTION

In accordance with this invention, an improved method and analyzing device for determining the composition of binary vaporizable fluid mixtures of known components has now been discovered which is not sensitive to the temperature and pressure of the mixture entering the analyzing device.

The improved method of this invention comprises:

- (a) Regulating the pressure of a stream of a binary vaporizable fluid mixture so that it flows at a constant pressure,
- (b) Passing the mixture at a constant pressure through the first side of a heat exchanger,
- (c) Rapidly reducing the pressure of the mixture thereby expanding and cooling the mixture,
- (d) Measuring the temperature of the mixture just after expansion,
- (e) Passing the expanded mixture through the second side of the heat exchanger,

Said steps being carried out continuously until the temperature just after expansion remains substantially constant, and

- (f) Comparing this temperature with the temperatures recorded for a series of similarly expanded binary fluid mixtures of the same components of known varying composition.

The improved analyzing device of this invention comprises:

- (a) An inlet for passing the binary vaporizable fluid mixture into the device,
- (b) A pressure regulator connected to said inlet which passes the mixture at a constant pressure,
- (c) A heat exchanger having the inlet to the first side connected to the pressure regulator,
- (d) A pressure reducing means connected to the outlet from said first side of the heat exchanger, said pressure reducing means causing a rapid pressure reduction as the binary fluid mixture passes therethrough,
- (e) Temperature sensing means positioned just after the pressure reducing means so as to measure the temperature of the mixture just after it passes through the pressure reducing means,
- (f) Means for connecting the pressure reducing means to the second side of the heat exchanger, and

(g) An outlet connected to said second side of the heat exchanger for removing the mixture from the device.

It is well known that most real gases, as contrasted with an ideal gas, cool when expanded rapidly, and that liquids also cool when expanded by a rapid reduction in pressure which causes partial vaporization. When starting up the device of this invention, a binary fluid mixture is passed through the first side of a heat exchanger and is rapidly expanded through a pressure reducing means thereby causing a reduction in the temperature of the mixture. The expanded fluid of reduced temperature is then heat exchanged with incoming mixture which has not passed through the pressure reducing means. This incoming mixture therefore enters the pressure reducing means at a temperature lower than the original mixture did and cools during expansion to a temperature lower than the original mixture. Accordingly, the temperatures before and after expansion get progressively lower until the equilibrium temperatures of the system are reached. These equilibrium temperatures will depend primarily upon the physical characteristics of the mixture, the magnitude of the pressure reduction experienced as the fluid passes through the pressure reducing means, and the heat exchange efficiency of the device.

When operating in accordance with this invention, it has been found that the temperature at which the sample enters the device has very little effect upon the temperature of the fluid after expansion. This process does not require that the initial temperature and pressure of the sample be predetermined or that they be the same as those of the series of similarly expanded binary fluid mixtures of the same components of known varying composition with which the sample is compared.

In accordance with this invention, the difficulties introduced by variations in the temperature and pressure of the sample when using the Felton and Williams device are overcome. Feed pressure variations are overcome by first passing the sample through a pressure regulator which adjusts the pressure to a predetermined level. Then, by heat exchanging the incoming and outgoing mixtures, an equilibrium or "self-cooling" temperature after expansion is established for the incoming sample which is substantially independent of the initial temperature of the sample. Accordingly, a greatly reduced sensitivity to initial sample temperature and pressure is accomplished in accordance with this invention.

DETAILED DESCRIPTION OF THE INVENTION

General description

Although the method and analyzing device of this invention is suitable for use with any binary fluid mixture of known components having a normal boiling point up to about 250° C., it is particularly useful with binary fluid mixtures which are gases or liquids having normal boiling points below about 50° C. Binary gas mixtures in which the components have normal boiling points of about -40° to 24° C. are readily liquefied at about room temperature by subjecting them to pressures equal to or above their vapor pressures, and frequently are maintained and handled as liquids under these conditions. This invention is particularly useful for the analysis of such binary liquid mixtures.

Typical examples of suitable binary fluid mixtures include mixtures containing about 40 to 70% by weight monofluorotrichloromethane (B.P. 23.8° C.) and about 60 to 30% by weight dichlorodifluoromethane (B.P. -29.8° C.), azeotropic mixtures containing dichlorodifluoromethane and dichlorotetrafluoroethane (B.P. 3.6° C.), mixtures containing monochlorodifluoromethane (B.P. -40.8° C.) and monochloropentafluoroethane (B.P. -38.7° C.), mixtures containing about 15 to 26% by weight isobutane (B.P. -10.2° C.) and about 85 to 74% by weight dichlorodifluoromethane, and mixtures containing octafluorocyclobutane (B.P. -6.1° C.) with nitrous oxide (B.P. -89.5° C.), propane (B.P. -42.5°

C.), cyclopropane (B.P. -34.4° C.), hexafluoroethane (B.P. -78.1° C.) or monochloropentafluoroethane. Other binary fluid mixtures which can be analyzed in accordance with the method of the present invention will be apparent to those skilled in the art.

In most cases, the initial temperature and the initial pressure of the binary fluid mixture will be that of the source of the mixture, such as that of the process stream, blending equipment or storage vessel. Usually the source of the binary fluid mixture will be a storage vessel or blending equipment, in which case the binary fluid mixture will be at about 25° C. When the binary fluid mixture is gaseous, it will usually be at a superatmospheric pressure of about 15 to 125 p.s.i.g. When the binary fluid mixture is a liquefied gas, the initial pressure will generally be the vapor pressure of the mixture which may be as high as about 2,000 p.s.i.g. Preferably, the initial pressure of the binary fluid mixture is at least about 8 p.s.i.g. since this allows the expansion chamber to be operated at substantially atmospheric pressure.

In accordance with this invention, the binary fluid mixture undergoes a pressure reduction during determination of its composition. This pressure reduction need only be sufficient to cause the binary fluid mixture to flow through the pressure reducing means. The minimum pressure reduction necessary to accomplish this end will vary depending upon the particular binary fluid mixture being analyzed. Minimum pressure reductions of about 1 to 5 p.s.i. are typical. Preferably the pressure after the pressure reducing means is substantially atmospheric, and the pressure before the pressure reducing means is regulated slightly above atmospheric, thereby providing the necessary pressure reduction. Since it is difficult to accurately regulate superatmospheric pressures of less than about 8 p.s.i.g., the pressure before the pressure reducing means is preferably regulated to a constant pressure of about 8 to 12 p.s.i.g.

When using the analyzing device of this invention to determine the composition of a binary fluid mixture of known components in unknown proportions, the analyzer is first calibrated with a series of known binary fluid mixtures of these components. More specifically, a series of mixtures of the two components in varying known proportions is passed through the analyzer and a constant equilibrium temperature is established for each in the expansion chamber. A calibration curve is prepared by plotting the recorded temperature or equivalent measurements, such as thermistor bridge imbalances, against the composition of the known mixtures. The binary fluid mixture to be analyzed is then passed through the analyzer and its composition is determined by comparing its equilibrium temperature or equivalent measurement with those recorded for the known mixtures, that is, the observed measurement is used to read the composition of the analyzed binary fluid mixture from the calibration curve.

Since the equilibrium temperatures of expanded binary fluid mixtures vary regularly with variations in the proportions of the components, it is not necessary to employ a large number of known mixtures with small variations in proportions in preparing the calibration curve. Differences in concentration of about 4 to 6% between adjacent members of the series of known mixtures are usually sufficient. The analyzer is most commonly used in controlling a process for blending the two component of the binary fluid mixture, in which case variations in the composition of the mixture are within a narrow range. Accordingly, it is sufficient if the series employed in the calibration contains only a few mixtures of known composition in which the proportions are varied over a range which approximates the range of expected variations in the mixtures to be analyzed.

By the use of the process and the analyzer of this invention, a binary vaporizable fluid mixture can be analyzed to determine its composition quickly, simply and

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inexpensively. The analyzing device of this invention may be operated batchwise, intermittently, periodically or continuously as desired. It is portable and easily assembled and calibrated. The accuracy of the analysis will depend primarily upon the sensitivity and accuracy of the temperature sensing means. By the use of a temperature sensing means which is accurate to within 0.01°C ., it is usually possible to obtain analyses which are accurate to within 1%, which is sufficient for most purposes in commercial operations.

A preferred embodiment of the improved method of this invention comprises:

(a) Passing a stream of the binary fluid mixture through a pressure regulator which passes the mixture at a constant pressure of at least about 8 p.s.i.g.,

(b) Passing the mixture from the pressure regulator through the first side of a heat exchanger wherein the temperature of the fluid is reduced,

(c) Passing the mixture from the heat exchanger through a constricting orifice into an expansion chamber containing a body of liquid binary fluid mixture, thereby rapidly reducing the pressure of the mixture at least about 8 p.s.i. under substantially adiabatic conditions with a resulting expansion and cooling of the mixture, said expanding mixture discharging from the orifice below the surface of the body of liquid,

(d) Measuring the temperature of the body of liquid,

(e) Passing the expanded mixture through the second side of said heat exchanger, whereby the incoming mixture is cooled to approximately its boiling point at the pressure after the orifice, and

(f) Comparing the measured temperature of the body of liquid with the temperature recorded for a series of similarly expanded binary fluid mixtures of the same components of known varying composition.

A preferred embodiment of the improved analyzing device of this invention comprises:

(a) An inlet for passing the binary vaporizable fluid mixture into the device,

(b) A pressure regulator connected to said inlet which passes the mixture at a constant pressure,

(c) A heat exchanger having the inlet to the first side connected to the pressure regulator,

(d) A constricting orifice connected to the outlet from said first side of the heat exchanger, said orifice causing a rapid pressure reduction of at least about 8 p.s.i.,

(e) An expansion chamber connected to said orifice having an overflow outlet for retaining a body of liquid mixture, said orifice discharging binary fluid mixture in the expansion chamber below the level of the overflow outlet,

(f) Temperature sensing means positioned in said expansion chamber below the level of the overflow outlet, including means extending outside the expansion chamber for indicating the temperature,

(g) Means for passing the mixture from the overflow outlet through the second side of the heat exchanger and removing the mixture from the device.

Description of the drawing

In order that the invention may be more readily understood, it will be further described in connection with the accompanying drawing. FIG. 1 is a vertical cross-sectional view of one embodiment of the analyzing device of this invention. FIG. 2 is a vertical cross-sectional view of a preferred embodiment of a portion of the analyzing device of FIG. 1.

Referring now to FIG. 1, a stream of the binary fluid mixture to be analyzed is introduced at sample inlet 1, at the temperature and pressure of the source of the mixture. The sample proceeds continuously through pressure regulator 2 which is set to pass the sample at a predetermined constant pressure. Preferably, the pressure regulator passes the incoming sample at a constant pressure of about 8 to 12 p.s.i.g. which allows substan-

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tially atmospheric pressure to be used in the expansion chamber.

When the binary fluid mixture to be analyzed is gaseous or a liquefied gas, the initial pressure is generally greater than necessary, in which case pressure regulator 2 reduces the pressure to the preferred range of about 8 to 12 p.s.i.g. When the binary fluid mixture to be analyzed is a liquid having a normal boiling point of about 25° to 50°C ., the mixture is generally passed through pressure regulator 2 at atmospheric pressure and the expansion chamber is maintained at reduced (subatmospheric) pressure by the application of a vacuum at the exit end of the analyzing device. The amount of vacuum necessary will depend upon the volatility and boiling point of the binary liquid mixture, and the amount of pressure drop through the orifice.

The sample from pressure regulator 2 passes through the first side of heat exchanger 3. A screen or other filtering means 4, positioned before the pressure reducing orifice, is optional and is provided when necessary to remove solid particles entrained in the binary fluid mixture thereby preventing such particles from clogging the pressure reducing orifice. The mixture is expanded through pressure reducing orifice 5 into a suitable expansion chamber which is maintained at a pressure of at least about 8 p.s.i. below the pressure before the orifice. The expansion chamber may be a separate chamber or it may be the chamber side of heat exchanger 3 as illustrated in FIG. 1. On passing through orifice 5 the binary fluid mixture expands, resulting in partial evaporation if either of the components of the mixture approaches the orifice as a liquid, whereby the temperature of the mixture is lowered. Orifice 5 may be a constricting orifice, thereby providing the necessary pressure reduction, or it may be of the non-constricting type as illustrated in FIG. 1. In the latter case, the required pressure reduction results from the difference in size between orifice 5 and exit tube 10.

Temperature sensing means 7 is positioned just after orifice 5 so that it measures the temperature of the gaseous mixture just after it passes through the orifice. The temperature sensing means must be spaced sufficiently distant from the orifice that it does not obstruct the orifice or prevent the binary fluid mixture from expanding on passing through the orifice, but sufficiently close to the orifice that the expanded mixture immediately impinges on the temperature sensing means so that it can measure the reduced temperature caused by the expansion. Since expansion of the binary fluid mixture as it passes through the orifice is substantially instantaneous, the temperature sensing means is usually spaced about $\frac{1}{32}$ to about $\frac{1}{4}$ inch from the orifice, and preferably about $\frac{1}{8}$ inch.

Temperature sensing means 7 is connected to a means 8 extending outside of the expansion chamber for indicating the temperature of the expanded mixture. The embodiment illustrated in FIG. 1 is preferably used when the expanded fluid mixture is a gas. When the expanded mixture is partially liquid, measurement of the temperature of the expanded mixture will be more accurate if the modification illustrated in FIG. 2 is used.

The fluid mixture, after expansion, passes into the second side of heat exchanger 3 thereby cooling the incoming mixture on the first side, and thereafter out of the analyzer via exit 10. The whole apparatus is enclosed in casing 11 which optionally and preferably is filled with an insulating means such as insulating foam so that the system functions under substantially adiabatic conditions. Bypass valve 12 is optionally provided to temporarily remove pressure regulator 2 from the system during start-up, thereby bringing the system to operating temperature more rapidly. During start-up, flowing of the binary fluid mixture through orifice 5 is continued until an equilibrium temperature is reached as indicated by a constant temperature reading by temperature sensing means 7.

In FIG. 2 a preferred variation of the device of FIG. 1 is shown. This embodiment is particularly suitable for analyzing fluid mixtures which are present at least partially in liquid form during operation of the device. This device is the same as the device of FIG. 1 until pressure reducing means 5 is reached. In this modification, pressure reducing means 5 is illustrated as a constricting orifice in which case the tubing before and after the orifice can be the same size. A separate expansion chamber 6 is provided into which the mixture is expanded through orifice 5.

When using the embodiment of FIG. 2, the pressure in expansion chamber 6 is preferably not greater than the vapor pressure of the binary fluid mixture at the operating temperature of the expansion chamber. When the fluid mixture has a boiling point in the range of about 25 to 35° C. and the expansion chamber is at substantially atmospheric pressure, the mixture will pass from heat exchanger 3 as a liquid and will only partially vaporize when expanded through orifice 5 into expansion chamber 6. Accordingly, a body of liquid is maintained in expansion chamber 6 by the height of an overflow outlet 9. When the fluid mixture boils in the range of about -40 to +250° C., the body of liquid can be maintained in the expansion chamber by maintaining the necessary pressure above or below atmospheric, as the case may be. For any given sample, the suitable pressure range for maintaining a body of liquid in the expansion chamber is quite broad since pressure variations merely lead to variations in the ratio of liquid to gas leaving the expansion chamber via outlet 9.

Heat sensing means 7 is positioned in the expansion chamber below the liquid level which provides a very accurate method of measuring the temperature of the expanded mixture. The expanded mixture leaves the expansion chamber through overflow outlet 9 and passes into the second side of heat exchanger 3 as in FIG. 1.

In the analyzing device of this invention, heat exchanger 3 may be of any conventional design. The more efficient the heat exchanger is, the more quickly equilibrium is established and the more accurate the analysis will be. Preferably, the incoming sample passes through the coil side of the heat exchanger while the expanded mixture passes through the chamber side.

The actual size of orifice 5 is not important except to the extent of its relationship to the pressure being maintained in pressure regulator 2 and the size of any constrictions beyond the expansion chamber such as outlet 9 and exit 10. In other words, the orifice must be of such size as to provide a pressure drop which causes the binary fluid mixture to pass through it. Preferably the orifice provides a pressure drop of at least 8 p.s.i. and has a diameter of about 0.001 to 0.05 inch, and more preferably about 0.002 to 0.025 inch, and most preferably about 0.004 to 0.02 inch, thereby causing a significant cooling of fluids expanded therethrough. It may be of any available shape, but usually a circular orifice is most convenient.

The size of the tubing used in the analyzing device is not critical so long as it is not smaller than the size of orifice 5. Preferably, the tubing has an internal diameter of about 0.001 to 0.125 inch.

Expansion chamber 6 and subsequent compartments should be sufficiently large to receive the expanding binary fluid mixture passing from orifice 5 without causing back pressure. For such purpose, the expansion chamber preferably should have a volume of at least about 1.5 ml. and most preferably at least about 2 ml., and a diameter at least twice the diameter of exit 9. The expansion chamber may be as large as desired, the maximum size being dictated only by economic considerations and the like.

Temperature sensing means 7 may be a commercial thermistor and may be connected to a Wheatstone bridge circuit as is commonly employed for thermistor type tem-

perature measurements. The circuit contains an ammeter 8 which shows the imbalance of the Wheatstone bridge due to changes in the temperature of the thermistor. The current readings can be converted to temperature readings in degrees, if desired, but this usually is unnecessary as the current readings are equally useful as a measure of the change in the temperature of the thermistor, and it is more convenient to use the current reading for this purpose. Temperature indicating means 8 may also be a potentiometer-recorder used to indicate the bridge output and thereby give a permanent recording of the thermistor temperature. Preferably, the temperature sensing means is a 3000-ohm Precision Thermistor.

While a thermistor is the preferred form of temperature sensing means 7, other forms may also be used, particularly thermocouples and other like electronic temperature sensing devices which rapidly detect and measure rather small changes in temperature, particularly those which are accurate to $\pm 1^\circ$ C. Thermometers, such as mercury and toluene filled types, can be used but usually are less desirable because they are slow acting and are not sufficiently sensitive for most applications. Temperature indicating means 8 will be of any conventional form and type that is adapted to indicate and/or record the temperature of the temperature sensing means. In the case of thermometers, means 8 will be the upper portion of the thermometer containing the required temperature markings while temperature sensing means 7 will be the bulb of the thermometer.

The various parts of the analyzer may be constructed of any material which will withstand the temperatures and pressures under which it is to be used and which is substantially inert to the binary fluid mixture to be analyzed under those conditions. Suitable materials include brass, copper, steel, stainless steel, nickel, Monel, Inconel, aluminum, polytetrafluoroethylene, polyethylene and the like.

Examples

The following examples, illustrating the novel method and analyzing device disclosed herein for determining the composition of binary vaporizable fluid mixtures of known components, are given without any intention that the invention be limited thereto. All percentages are by weight.

EXAMPLE 1

Various samples of mixtures containing trichlorofluoromethane and dichlorodifluoromethane (DCDFM) were analyzed on four separate but identical analyzing devices similar to the device illustrated in FIG. 2 with the pressure regulator maintaining a pressure of 8 p.s.i.g. and the expansion chamber at atmospheric pressure. Samples were charged to the analyzers continuously at their own vapor pressure at 25° C. until equilibrium was established as indicated by a constant temperature reading. The following recorder readings were obtained and the corresponding DCDFM contents were determined from a calibration curve based on a series of samples.

TABLE I

Percent DCDFM in sample	Analyzer used	Recorder reading, microamperes	Deviation from actual percent DCDFM
10	A	87.0	+0.25
10	B	85.8	-0.35
10	C	86.8	+0.15
10	D	86.2	-0.15
30	A	48.7	+0.06
30	B	47.4	-0.50
30	C	49.0	+0.30
30	D	49.5	+0.55
50	A	14.0	-0.47
50	B	15.5	+0.53
50	C	13.7	-0.70
50	D	13.8	-0.60
70	A	192.0	-0.30
70	B	194.0	+0.70
70	C	191.8	-0.40
70	D	191.0	-0.80
70	A	156.5	+1.40
70	B	153.0	-0.35
70	C	151.8	-0.95

A high range measuring Wheatstone bridge was used.

EXAMPLE 2

A mixture of dichlorodifluoromethane (DCDFM) and trichlorofluoromethane in a 70:30% ratio was analyzed using the analyzing device illustrated in FIG. 2 with the expansion chamber at atmospheric pressure. Samples were initially at 25° C. Pressures of 8 p.s.i.g. were maintained by the pressure regulator. Initial sample pressures, measured before the pressure regulator, were varied from 40 to 100 p.s.i.g. by pumping N₂ into the container for the liquid mixture. The apparent percent of dichlorodifluoromethane was read from a calibration curve based on a series of samples.

TABLE II

Initial sample pressure, p.s.i.g.	Recorder reading, microamperes	Apparent percent DCDFM
40-----	27.5	69.5
50-----	28.7	69.8
60-----	30.3	70.0
70-----	31.4	70.3
80-----	33.5	70.5
90-----	34.0	70.6
100-----	35.4	70.9

EXAMPLE 3

A mixture of dichlorodifluoromethane (DCDFM) and trichlorofluoromethane in a 70:30% ratio was analyzed using the analyzing device illustrated in FIG. 2 with the expansion chamber at atmospheric pressure. Initial sample pressures were approximately 50 to 80 p.s.i. and were regulated to 8 p.s.i.g. The initial sample temperature before the pressure regulator was varied from 21° to 33° C. The apparent percent of dichlorodifluoromethane was read from a calibration curve based on a series of samples.

TABLE III

Initial sample temp., ° C.	Recorder reading, microamperes	Apparent percent DCDFM
21-----	18.0	69.9
23-----	19.5	69.2
25-----	21.3	70.2
27-----	22.5	70.4
29-----	24.0	70.6
31-----	24.0	70.6
33-----	20.5	70.1

The average deviation of apparent dichlorodifluoromethane analysis was only $\pm 0.3\%$. This is to be compared with a 6% error observed for a 10° C. change in the analyzer device illustrated in FIG. 1 of the Felton and Williams patent.

EXAMPLE 4

Five 145-lb. cylinders were filled with mixtures of dichlorodifluoromethane and 1,2-dichloro-1,1,2,2-tetrafluoroethane (DCTFE) in 10:90, 25:75, 50:50, 75:25 and 90:10% ratios. These mixtures were run through the analyzing device illustrated in FIG. 2 until the recorded voltage output on the Wheatstone bridge became constant. The pressure regulator was set to maintain a pressure of 8 p.s.i.g. and the pressure in the expansion chamber was essentially atmospheric. The temperatures in the cylinders ranged from 20° to 30° C. and the initial pressures ranged from 10 to 100 p.s.i.g. The following data were obtained:

TABLE IV

Percent DCTFE in sample:	Recorder reading, volts D.C.
10-----	8.8
25-----	5.8
50-----	0.8
50-----	19.8
75-----	10.4
90-----	10.4

¹ A high range Wheatstone bridge was used.

When the percent 1,2-dichloro-1,1,2,2-tetrafluoroethane

is graphically plotted against the recorder reading in volts, a straight line curve is obtained in spite of the variations in temperature and pressure.

EXAMPLE 5

Three 145-lb. cylinders were filled with mixtures of dichlorodifluoromethane (DCDFM) and isobutane in 25:75, 30:70 and 35:65% ratios. These mixtures were run through the analyzing device illustrated in FIG. 2 until the recorded voltage output on the Wheatstone bridge became constant. The pressure regulator was set to maintain a pressure of 8 p.s.i.g. The temperatures in the cylinders ranged from 20° to 30° C. and the initial pressures ranged from 70 to 150 p.s.i.g. The following data were obtained.

TABLE V

Percent DCDFM in sample:	Recorder reading, volts, D.C.
25-----	9.0
30-----	5.2
35-----	1.4

When the percent dichlorodifluoromethane is graphically plotted against the recorder reading in volts, a straight line curve is obtained in spite of the variations in temperature and pressure.

Although the invention has been described and exemplified by way of specific embodiments, it is to be understood that it is not limited thereto. As will be apparent to those skilled in the art, numerous modifications and variations in the composition of the samples, the conditions of the analysis and the details of the analyzing devices illustrated above may be made without departing from the spirit of the invention or the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for determining the composition of a binary vaporizable fluid mixture of known components which comprises:

- (a) regulating the pressure of a stream of the binary vaporizable fluid mixture so that it flows at a constant pressure,
 - (b) passing the mixture at a constant pressure through the first side of a heat exchanger,
 - (c) rapidly reducing the pressure of the mixture thereby expanding and cooling the mixture,
 - (d) measuring the temperature of the mixture just after expansion,
 - (e) passing the expanded mixture through the second side of the heat exchanger,
- said steps being carried out continuously until the temperature just after expansion remains substantially constant, and

(f) comparing this temperature with the temperatures recorded for a series of similarly expanded binary fluid mixtures of the same components of known varying composition.

2. The method of claim 1 which comprises:

- (a) passing the mixture through a pressure regulator which passes the mixture at a constant pressure of at least 8 p.s.i.g.,
- (b) passing the mixture from the pressure regulator through the first side of the heat exchanger wherein the temperature of the fluid is reduced,
- (c) passing the mixture from the first side of the heat exchanger through a constricted orifice into an expansion chamber containing a body of liquid binary fluid mixture, thereby rapidly reducing the pressure of the mixture at least 8 p.s.i. under substantially adiabatic conditions with a resulting expansion and cooling of the mixture, said expanded mixture discharging from the orifice below the surface of the body of liquid,

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- (d) measuring the temperature of the body of liquid,
- (e) passing the expanded mixture through the other side of the heat exchanger whereby the incoming mixture is cooled to approximately its boiling point at the pressure after the orifice, and

- (f) comparing the measured temperature of the body of liquid within the temperatures recorded for a series of similarly expanded binary fluid mixtures of the same components of known varying composition.

3. The method of claim 2, in which the incoming binary fluid mixture is initially at a pressure of 8 to 2,000 p.s.i.g., and is regulated to a constant pressure of 8 to 12 p.s.i.g., the constricted orifice has a diameter of 0.001 to 0.05 inch, and the pressure after the constricted orifice is substantially atmospheric.

4. An analyzing device for determining the composition of binary vaporizable fluid mixtures of known components which comprises:

- (a) an inlet for passing the binary vaporizable fluid mixture into the device,
- (b) a pressure regulator connected to said inlet which passes the mixture at a constant pressure,
- (c) a heat exchanger having the inlet to the first side connected to the pressure regulator,
- (d) a pressure reducing means connected to the outlet from said first side of the heat exchanger, said pressure reducing means causing a rapid pressure reduction as the binary fluid mixture passes there-through,
- (e) temperature sensing means positioned just after the pressure reducing means so as to measure the temperature of the mixture just after it passes through the pressure reducing means,
- (f) means for connecting the pressure reducing means to the second side of the heat exchanger, and

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- (g) an outlet connected to said second side of the heat exchanger for removing the mixture from the device.

5. The analyzing device of claim 4 in which the pressure reducing means is a constricting orifice which causes a rapid pressure reduction of at least 8 p.s.i., said orifice being connected to an expansion chamber having an overflow outlet for retaining a body of liquid mixture, said orifice discharging binary fluid mixture in the expansion chamber below the level of the overflow outlet, and the temperature sensing means is positioned in the expansion chamber below the level of the overflow outlet and includes means extending outside the extension chamber for indicating the temperature.

6. The analyzing device of claim 5 in which the pressure regulator maintains a constant pressure of 8 to 12 p.s.i.g., and the constricting orifice has a diameter of 0.001 to 0.05 inch.

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