United States Patent [19]

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[54] **GAS EMITTING DEVICE**

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[52] **U.S. Cl.** **239/34**

[51] **Int. Cl.** **A24f 25/00**, A611 9/04

[58] **Field of Search** 239/34, 58; 206/5

[56] **References Cited**

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3,412,935	11/1968	O'Keeffe	239/34
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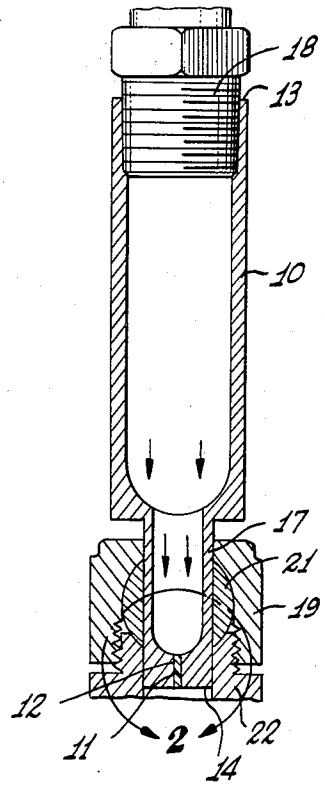
Primary Examiner—Lloyd L. King

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[57] **ABSTRACT**

A device for emitting a gas at a constant rate into a moving fluid medium to produce an accurately known concentration of the gas in the medium. The gas is held in a small cylinder under pressure in equilibrium with its liquid phase or solely in its gaseous phase, and permeates through a silicone material filling an accurately dimensioned passage through one end of the cylinder. Permeation rates may be selected from a wide range by varying the dimensions of the passage, and the device has a relatively low sensitivity to temperature variations.

29 Claims, 5 Drawing Figures



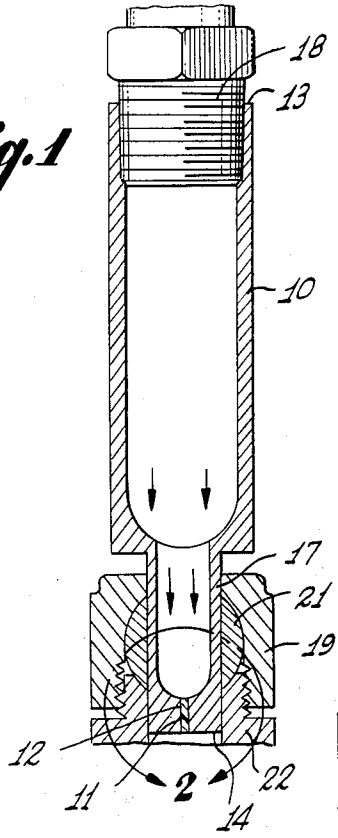


Fig. 1

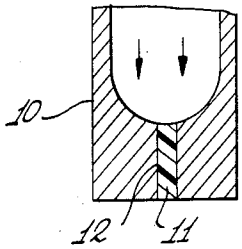


Fig. 2

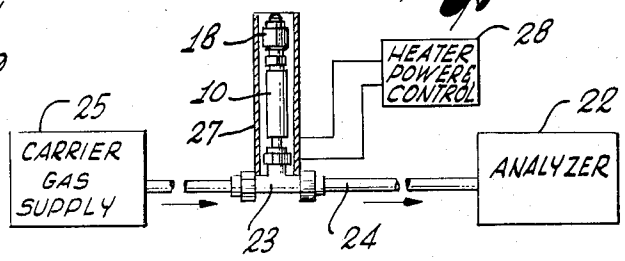


Fig. 3

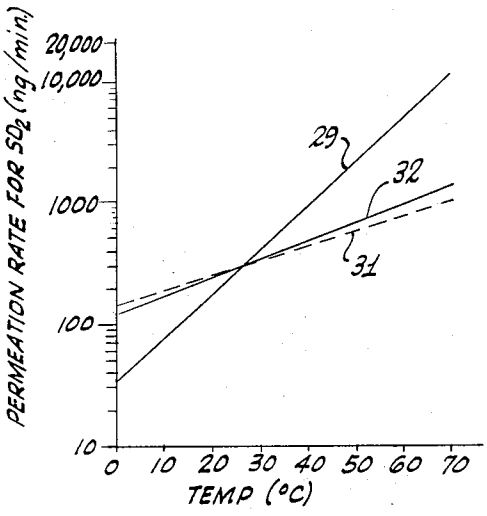


Fig. 4

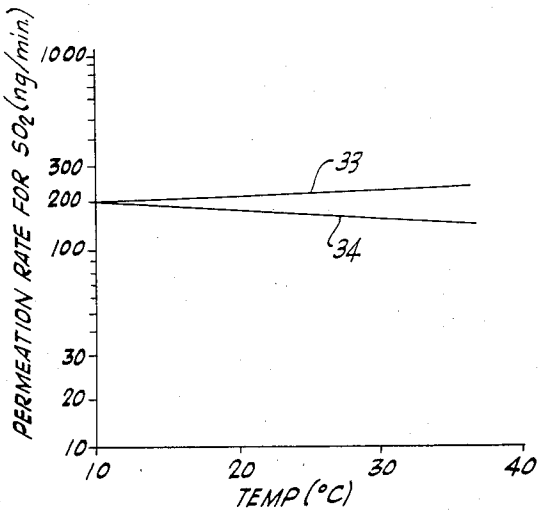


Fig. 5

GAS EMITTING DEVICE

BACKGROUND OF THE INVENTION

This invention relates generally to devices for the emission of a gas at a constant rate, and, more particularly, to such devices used in the production of calibration samples for gas or liquid analyzers, and in which the gas is emitted through a permeable material into a moving fluid medium.

Previously available devices of this type have employed an elongated tube of a permeable, polymeric plastic material to hold a gas under pressure and partially in the liquid phase. At a constant temperature, the vapor pressure of the substance will be constant and molecules of the substance will permeate through the walls of the tube at a constant rate, thereafter to be intermixed or dissolved in a constantly moving fluid medium stream surrounding the tube. Tube devices of this type are described in a patent to O'Keeffe entitled "Gas Dispensing Devices," U.S. Pat. No. 3,412,935.

Although these permeable tube devices were a significant advance in the field, they suffer from two major disadvantages. Firstly, the rate of permeation of the substance through the tube walls is highly sensitive to temperature variations. An increase in permeation rate resulting from an increase in temperature can be considered as having two components: one due to a vapor pressure increase resulting from the temperature increase, and the other due to an inherent property of the permeable material that results in an increase in permeation rate with temperature, at constant pressure. In the prior art tube device, these two components are cumulative, and an adverse temperature characteristic results. Accordingly, the device must be maintained at a constant temperature to a high degree of accuracy if the permeation rate is to be held constant, and this problem is further aggravated if the tube is relatively long, since the constant temperature must be maintained over the entire length of the tube.

The second disadvantage of the prior art tube devices is that they are suited only for the production of very low concentrations of the gaseous substance. In another version of the prior tube devices, the substance permeates through a generally annular permeable element at one end of the tube, but this device produces even lower permeation rates, and concentrations down to 1 millionth of a part per million. For some applications, such as the calibration of "ambient monitors" for the detection of pollutants in the atmosphere, only small concentrations are involved. For example, the concentration of sulfer dioxide (SO_2) in the atmosphere rarely exceeds 1 part per million (ppm), and the tube devices are well enough suited to produce calibration samples with this order of concentration. For other applications, however, such as the calibration of "stack monitors" for the analysis of effluent gases from industrial chimney stacks or from engine exhausts, higher concentrations are often encountered. For example, SO_2 concentrations are typically in the range 100 to 1,000 ppm, and it is difficult and highly inconvenient to obtain calibration samples in this range with the tube devices of the prior art.

Higher concentrations can, of course, be obtained by decreasing the flow rate of the fluid medium used as a carrier, but this has practical limitations and too low a flow rate reduces the concentration accuracy of the resulting mixture. A larger tube will also result in higher concentrations, but again there are practical limitations, since a length or diameter increase of several hundred times may be required to obtain the desired range of permeation rates. As a practical matter, higher concentration calibration samples have hitherto been obtainable only by premixing gases in very large cylinders, and this method produces an inherently unreliable sample, especially after some time has elapsed between preparation and use of the sample, as is usually the case.

It is apparent, therefore, that there has been an urgent need for a device for the preparation of calibration samples which retains the advantages of prior devices, but which is less sensitive to temperature variations, and which may be made to produce a wide range of concentrations in the samples. The present invention fulfills this need.

SUMMARY OF THE INVENTION

The present invention resides in a new device for emitting a gaseous substance at a predetermined rate into a moving fluid medium. Briefly, and in general terms, the device includes a sealed vessel for holding the substance to be emitted under pressure, the vessel having a passage filled with a permeable polymeric plastic material through which the substance permeates and is emitted outside the vessel.

The permeable polymeric plastic material used in the device has a much higher permeation rate and much less sensitivity to temperature variations than the material used in prior devices. This allows the use of a novel structure having a relatively low cross-sectional area of permeable material, but a relatively high rate of emission of the substance. Furthermore, the substance may be held either in equilibrium with its liquid phase or entirely in its gaseous phase, the latter resulting in an even more favorable temperature characteristic for the device. Also, the rate of emission can be widely and easily varied by employing different dimensions for the passage, without increasing the overall size of the device except as is required to increase the life of the device between refills.

More specifically, in a presently preferred embodiment of the invention, the vessel takes the form of a hollow metal cylinder, closed at one end except for the passage which is formed therethrough, and adapted at the other end to receive a pressure seal. The polymeric plastic, a silicone material in the presently preferred embodiment, is positioned in the passage and cured to form a permanent bond with the metal, after which the vessel is evacuated and filled with a liquefied gaseous substance. In a variation of this preferred embodiment, the gaseous substance is stored in the cylinder under a pressure not sufficient to liquefy the substance. The substance may be any of a wide variety of fluids, including water, and the passage in the vessel can be dimensioned to provide any emission rate over a wide range, to meet the requirements of various applications.

Furthermore, the structure of the present invention allows easy connection with the moving fluid medium by means of a simple T-junction. Thus, the device may be readily adapted for use with any analyzer or may be conveniently housed integrally with an analyzer.

It will be appreciated from the foregoing that the present invention overcomes the major disadvantages of prior art devices, in that sensitivity to temperature

variations is considerably lessened and calibration samples having a wide range of concentrations can be easily produced. Other aspects and advantages of the invention will become apparent from the following detailed description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a device embodying novel aspects of the present invention;

FIG. 2 is an enlarged cross-sectional view of the area of FIG. 1 indicated generally by the numeral 2;

FIG. 3 is a partly schematic view illustrating how the device of FIG. 1 is connected to an analyzer;

FIG. 4 is a graph illustrating the improved temperature characteristic of the device of FIG. 1 utilizing the gaseous and liquid phases of the substance; and

FIG. 5 is a graph illustrating the temperature characteristic of the device utilizing only the gaseous phase of the substance.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As shown in the drawings for purposes of illustration, the device of the present invention is used to dispense a gaseous substance at a constant rate, the gas thereafter being mixed with a moving fluid medium to provide a sample containing a known concentration of the gas, which is then typically used to calibrate an analyzer of gases or liquids. The device includes a sealed vessel **10** (FIGS. 1–3) in which the gaseous substance is held under pressure, and a quantity of permeable polymeric plastic material **11** through which the substance permeates and escapes from the vessel.

In accordance with the present invention, the vessel **10** is formed from a material impervious to the substance contained therein, and the permeable plastic material **11** fills a passage **12,** as best shown in FIG. **2,** extending from the inside to the outside of the sealed vessel. The structure uses a permeable material such as silicone, which has less sensitivity to temperature variations than materials used in prior devices, and a higher permeation rate. Thus, the device has a more desirable temperature characteristic than existing devices, and the rate of emission of the gaseous substance can be preselected from a wide range of rates by proper selection of the dimensions of the passage **12.**

More specifically, the vessel **10** employed in a presently preferred embodiment of the invention is a hollow cylinder of stainless steel or other material impervious to, and practically non-reactive with the substance to be contained therein. As best illustrated in FIG. **1,** the cylinder **10** has an open upper end **13** threaded internally to receive a pressure seal **18,** which is normally not removed except for refilling the cylinder, and a solid lower end **14** of substantial length through which the passage **12** extends along the axis of the cylinder. The terms "upper" and "lower" as used herein are descriptive only with respect to the figures, and the device is not limited to operation in a particular orientation.

The cylinder **10** has a reduced diameter, both inside and outside, over a substantially long lower end portion **17** of the cylinder, to facilitate fitting the device to pipes containing the moving fluid into which the gaseous substance is to be emitted. Accordingly, the lower end portion **17** has a threaded nut **19** and an associated sealing ring **21** fitted thereto for engaging a threaded pipe fitting **22.**

For relatively low permeation rates, the cylinder **10** is typically 0.5 inch in outside diameter, reducing to 0.25 inch in diameter at its lower end **17** for convenient fitting to quarter-inch diameter gas lines. The passage **12** in this size of cylinder **10** is typically a few hundredths of an inch in diameter and about a quarter-inch long. For higher permeation rates, the cylinder **10** may be 2 or more inches in diameter and 8 or 9 inches long, to provide a reasonably long life between refills, and the passage **12** may be a half-inch or more in diameter. The higher permeation rates may be obtained by increasing the diameter of the passage **12** or decreasing its length, or both.

The permeable material **11** used in the presently preferred embodiment is a silicone polymeric compound chemically classified as dimethyl polysiloxane. Many compounds of this type are commercially available and can be used in the present invention. By way of example, the dimethyl compound PR1939, manufactured by Products Research and Chemical Corp., Los Angeles, California, and dimethyl RTV compound 630, manufactured by General Electric Co., Waterford, New York, have each been found suitable in the presently preferred embodiment.

Before the silicone material **11** is positioned in the passage **12,** the entire cylinder **10** is cleaned with a degreasing agent to remove any possible contaminants. Then the silicone material **11,** which is typically relatively viscous, is drawn into the passage **12** by applying a partial vacuum to the cylinder **10** at its upper end **13.** When the silicone material **11** completely fills the passage and any trapped air bubbles have been removed, the partial vacuum is removed and the silicone material is cured at a temperature of approximately 120°F, preferably for at least 24 hours. During curing, the silicone material **11** hardens and becomes permanently bonded to the walls of the passage **12.**

Two variant forms of the preferred embodiment are presently contemplated. In the first, the gaseous substance is introduced into the cylinder **10** in a liquefied state, and is held there under pressure with its liquid and gaseous phases in equilibrium, as was the case in the prior tube devices. In the second form, the substance is held at a lower pressure entirely in its gaseous phase. Although this latter form suffers from a shorter life between refills and a gradual fall in permeation rate as the cylinder **10** is emptied of gas, it can still be designed as a practical device, and, as will be discussed in detail below, it has the advantage of a very favorable temperature characteristic.

After the silicone material **11** has been cured in the cylinder passage **12,** the cylinder **10** is evacuated and filled with the desired gaseous substance through the open upper end **13.** If the substance is normally gaseous at room temperature, and is to be introduced in the liquid state, the cylinder **10** is usually cooled below the boiling point of the substance to minimize loss of liquid when the cylinder is sealed.

FIG. **3** diagrammatically illustrates how the device of the present invention would typically be connected for use. For calibrating an analyzer **22,** the cylinder **10** is connected by a T-junction **23** to emit the gaseous substance at a constant rate through the silicone **11** into the fluid medium flowing at a constant rate along a pipe **24** to the analyzer. The fluid medium may be an inert

gas, such as nitrogen, in which the emitted substance is mixed, or, in some applications, it may be a liquid in which the emitted substance is dissolved. The fluid medium is drawn from a supply system **25,** which typically includes a pump, a pressure regulator and a flow meter, none of which is illustrated.

A constant temperature is preferably maintained by means of some heating element **27** wrapped around the cylinder **10** and supplied with power through a control unit **28** which includes an adjustable thermostat (not illustrated), thus maintaining a constant rate of emission of the substance contained in the cylinder **10.** When liquefied gas is used, it has been found that a constant temperature need be maintained only to within approximately 0.5°C, whereas a variation of 0.1°C was all that could be tolerated in prior devices with comparable accuracy. In the form of the invention in which the substance is held entirely in its gaseous phase, the temperature tolerance is even greater, and, in somce cases, temperature control may be unnecessary.

This important aspect of the invention, that the operation of the device is much less sensitive to temperature variations than was the case with previously available devices, is well illustrated in FIG. **4,** which is a graph showing the variation of permeation rate of sulfur dioxide (SO_2) in nanograms (grams $\times 10^{-9}$) per minute (ng/min), plotted on a logarithmic scale, with temperature in degrees centigrade (°C). The solid line **29** is typical of previous devices made for this purpose, while the broken line **31** shows the improvement effected by the present invention, in which the SO_2 is held in liquefied form. For example, the permeation rate for both devices is approximately 315 ng/min at 26.2°C. At 36.2°C, the permeation rate of the old tube device increases to 730 ng/min, while the rate for the new device increases to only 410 ng/min; i.e., an increase of 132 percent, or approximately 13 percent per degree centigrade, for the old device compared with an increase of 30 percent, or only 3 percent per degree centigrade, for the new device of this invention. In that particular temperature range, then, the new device is approximately only one-fourth as sensitive to temperature changes as the prior device.

The variation of permeation rate with temperature can be considered as having two components: one due to a vapor pressure change resulting from the temperature change, and the other due to an inherent property of the permeable material that results in a change in permeation rate when the temperature is varied at constant pressure. The first component can be easily determined from vapor pressure tables. For example, for SO_2, the vapor pressure increases from 33.45 p.s.i. to 66.45 p.s.i. for a temperature change from 10°C to 30°C, i.e. the vapor pressure increases almost exactly by a factor of two. Thus, the permeation rate will be doubled by an increase of temperature from 10°C to 30°C because of the vapor pressure increase.

This first component of the permeation rate variation is shown graphically by the curve **32** in FIG. **4.** Note that only the slopes of the lines **29, 31** and **32** are of interest, since the points of intersection with the y axis can be varied by changing the cross-sectional area of the permeable material.

Note also that the second component of the permeation rate variation, the component inherent to the permeable material, is positive for the prior device, resulting in the steeper characteristic curve **29,** but is negative for the new device of this invention, resulting in the improved characteristic curve **31.** Using the same SO_2 example, the permeation rate for the prior device increases from 80 ng/min at 10°C to 440 ng/min at 30°C. Of this 360 ng/min increase, only approximately 80 ng/min results from the vapor pressure increase (a two-fold increase), and the remaining 280 ng/min results from the unfavorable temperature characteristic of the permeable material of the prior device. For the device of this invention, over the same temperature range, the permeation rate increases from 200 ng/min to 350 ng/min, and a 200 ng/min increase due to the vapor pressure change is offset by a 50 ng/min decrease due to the different permeable material of the invention.

If the substance in the cylinder **10** is entirely in its gaseous phase, the variation of pressure in the cylinder will be nearly directly proportional to the absolute temperature, in accordance with the ideal gas laws. Thus, the permeation rate will also vary in direct proportion to the absolute temperature because of this pressure change, as shown by the curve **33** in FIG. **5.** A temperature change from 10°C to 30°C results in a first component of permeation rate increase of approximately 7 percent, or from 200 ng/min to 214 ng/min in the curve **33** as illustrated.

As was seen in the foregoing discussion relating to the liquefied gas form of the invention, an increase in temperature from 10°C to 30°C results in a second component of permeation rate change of minus 50 ng/min for the new device. Thus, the combined effect of the two components is, as shown at **34** (FIG. **5**), a net decrease of 36 ng/min, i.e., approximately 18 percent change in permeation rate for 20°C temperature change, or less than 1 percent per °C. With temperature sensitivity this low, temperature control would be totally unnecessary in some situations. Using only the gaseous phase of the substance in the prior devices does not, of course, greatly improve the temperature characteristic for those devices, since there is still a large second component of permeation rate increase inherent to the material of the devices.

Although the form of the invention using only the gaseous state of the substance suffers from a shorter life between refills and a gradual decline in permeation rate, the device is still a practical one. Again using SO_2 as an example, if the cylinder **10** is 8 or 9 inches long and 2 or 3 inches in diameter, it will contain approximately 3 grams of SO_2 at twice atmospheric pressure. At a permeation rate of 1000 ng/min, this will last for more than 5 years, so that the permeation rate decrease is less than 2 percent per month, an entirely acceptable figure for most applications.

Another important aspect of the invention is that the passage **12** can be easily dimensioned to select any of a wide range of permeation rates. Since the permeation rate is inversely proportional to the length of the passage **12** and directly proportional to the cross-sectional area of the passage, the rate may be varied by changing the length or diameter of the passage. In one form of the presently preferred embodiment, the passage is accurately machined to be 0.016 inch in diameter and 0.25 inch long. By way of example, a 100-fold increase in permeation rate can be achieved by a 10-fold diameter increase, to 0.160 inch, with the length kept constant. No increase in the size of the cylinder **10** would be required unless it was needed to compensate for the

shorter life of the device between refills, due to the faster permeation rate.

This availability of higher permeation rates allows the convenient production of accurate calibration samples with concentrations in the hundreds of parts per million, for use in the calibration of industrial "stack monitors," for example, where accurate calibration was previously cumbersome and difficult. For example, a high emission rate SO_2 tube of the old type would need to be about 50 inches long to generate 100 ppm of SO_2 at 22°C in a carrier gas flowing at 1 liter per minute. Using the present invention, a passage diameter of only approximately 0.5 inch would be needed, and the device need only be 2 inches in diameter and 8 or 9 inches long to attain a life between refills comparable with the old device. Lower concentrations in the order of one part per million are, of course, still obtainable from the device if an appropriately smaller diameter passage is employed.

The substance to be stored in and emitted from the cylinder **10** may be any of a wide range of fluids including, but not limited to, sulfur dioxide, nitrogen dioxide, hydrogen sulfide, ammonia, chlorine, bromine, hydrogen fluoride, propane, propylene, methyl mercaptan, ethyl oxide, n-butane, carbon tetrachloride, formaldehyde, acetaldehyde, and even water. The use of water as the "gaseous substance" has important application in the accurate calibration of industrial hygrometers, widely used to monitor the environment for certain manufacturing processes. It will be understood that some of the substances named are not suitable for storage entirely in the gaseous phase at ordinary temperatures.

From the foregoing, it will be seen that the invention described herein satisfies a need for accurate, high concentration calibration samples, which were not hitherto conveniently available. Furthermore, the invention is a significant improvement over prior devices of the same type in that sensitivity to temperature variations is greatly decreased, and the device may be more easily connected to a fluid supply line.

Although one embodiment of the invention has been described in detail for purposes of illustration, it will be appreciated that various modifications may be made without departing from the spirit and scope of the invention.

I claim:

1. A device for emitting a gaseous substance at a predetermined rate, comprising:

a sealed vessel for holding said substance under pressure, said vessel being impermeable to said substance and having an exit for emission of said substance; and

a quantity of permeable polymeric silicone material positioned in said exit, said material having a permeability which decreases with increasing temperature and constant pressure in said vessel, whereby said substance permeates through said material and is emitted from said vessel at the predetermined rate, and said device has a characteristically low overall sensitivity to temperature variations.

2. A device as set forth in claim **1,** wherein said quantity of permeable polymeric silicone material is a dimethyl polysiloxane.

3. A device as set forth in claim **1,** wherein said substance is held by said sealed vessel partially in the liquid phase.

4. A device as set forth in claim **3,** wherein said permeable polymeric silicone material is a dimethyl polysiloxane.

5. A device for emitting a substance at a predetermined rate, comprising:

a sealed vessel for holding said substance under pressure, said vessel being impermeable to said substance and having an exit passage for emission of said substance; and

a quantity of permeable polymeric plastic material completely blocking said passage, said material having a permeability which decreases with increasing temperature and constant pressure in said vessel, whereby said substance permeates through said material blocking said passage and is emitted from said vessel at the predetermined rate, and said device has a characteristically low overall sensitivity to temperature variations.

6. A device as set forth in claim **5,** wherein said permeable polymeric plastic is a silicone polymer.

7. A device as set forth in claim **6,** wherein said silicone polymer is a dimethyl polysiloxane.

8. A device as set forth in claim **6,** wherein said substance is held by said sealed vessel partially in the liquid phase.

9. A device as set forth in claim **5,** wherein said permeable polymeric plastic is a silicone polymer and said substance is held by said sealed vessel partially in the liquid phase, said device further including temperature control means to maintain said vessel and said substance at a substantially constant temperature.

10. A device as set forth in claim **9,** further including removable vessel sealing means.

11. A device as set forth in claim **5,** wherein said substance is selected from the group consisting of sulfur dioxide, nitrogen dioxide, hydrogen sulfide, ammonia, chlorine, bromine, hydrogen fluoride, propane, propylene, methyl mercaptan, ethyl oxide, n-butane, carbon tetrachloride, formaldehyde, acetaldehyde, and water.

12. A device for emitting a substance at a predetermined rate into a moving fluid stream to produce a desired concentration of said substance in the stream, said device comprising:

a sealed vessel for holding said substance under pressure, said vessel being impermeable to said substance and having a passage through which said substance is emitted into the moving fluid stream;

a quantity of a permeable silicone polymeric material completely filling said passage and bonded to the walls thereof, said material having a permeability which decreases with increasing temperature and constant pressure in said vessel;

connection means for connecting said device to the moving fluid stream, whereby said substance permeates through said silicone material at the predetermined rate and is emitted into the moving fluid stream through said connection means, and said device has a characteristically low overall sensitivity to temperature variations.

13. A device as set forth in claim **12,** further including sealing means removably attached to said vessel to allow filling and refilling thereof with said substance.

14. A device as set forth in claim **13,** wherein:

said vessel is a hollow cylinder; and

said passage is a tube through one end of said cylinder.

15. A device as set forth in claim **14,** wherein said connection means includes a T-shaped pipe fitting connecting said cylinder to a line enclosing the fluid stream.

16. A device as set forth in claim **12,** wherein said substance is selected from the group consisting of sulfur dioxide, nitrogen dioxide, hydrogen sulfide, ammonia, chlorine, bromine, hydrogen fluoride, propane, propylene, methyl mercaptan, ethyl oxide, n-butane, carbon tetrachloride, formaldehyde, acetaldehyde, and water.

17. A device as set forth in claim **12,** wherein said substance is held by said sealed vessel partially in the liquid phase in equilibrium with the gaseous phase.

18. A device as set forth in claim **12,** wherein said substance is held by said sealed vessel solely in the gaseous phase.

19. A device as set forth in claim **12,** further including temperature control means for maintaining said sealed vessel and said substance at a substantially constant temperature, and thereby maintaining a constant rate of emission of said substance.

20. A device as set forth in claim **19,** further including sealing means removably attached to said vessel to allow filling and refilling thereof with said substance.

21. A device as set forth in claim **20,** wherein:

said vessel is a hollow cylinder; and

said passage is a tube through one end of said cylinder.

22. For use with apparatus for the analysis of fluid mixtures, a device for generating a calibration mixture with a predetermined concentration of a substance, said device comprising:

a vessel for holding said substance under pressure, said vessel being impermeable to said substance and having a passage through which said substance is emitted into a moving stream of an inert fluid medium;

a body of a permeable silicone polymeric material completely filling said passage and bonded to the walls thereof to limit emission of said substance to a constant rate for a constant temperature, said material having a permeability which decreases with increasing temperature and constant pressure in said vessel, thereby providing for said device a characteristically low overall sensitivity to temperature variations.

23. A device as set forth in claim **22,** wherein:

said vessel is a hollow cylinder; and

said passage is located at one end of said cylinder.

24. A device as set forth in claim **23,** wherein said connection means includes a T-shaped pipe fitting connecting said cylinder to a pipe enclosing the moving stream of fluid.

25. A device as set forth in claim **22,** wherein said substance is selected from the group consisting of sulfur dioxide, nitrogen dioxide, hydrogen sulfide, ammonia, chlorine, bromine, hydrogen fluoride, propane, propylene, methyl mercaptan, ethyl oxide, n-butane, carbon tetrachloride, formaldehyde, acetaldehyde, and water.

26. A device as set forth in claim **22,** wherein said substance is held by said sealed vessel partially in the liquid state in equilibrium with the gaseous phase.

27. A device as set forth in claim **22,** wherein said substance is held by said sealed vessel solely in the gaseous phase.

28. A device as set forth in claim **22,** further including temperature control means for maintaining said sealed vessel and said gaseous substance at a constant temperature.

29. A device as set forth in claim **1,** wherein said substance is held by said sealed vessel entirely in the gaseous phase.

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