United States Patent [19]

Ritter

[11] **3,911,723**

[45] **Oct. 14, 1975**

[54] **EXPONENTIAL DILUTION FLASK**

[75] Inventor: **Joseph J. Ritter,** Mount Airy, Md.

[73] Assignee: **The United States of America as represented by the Secretary of Commerce,** Washington, D.C.

[22] Filed: **Aug. 8, 1974**

[21] Appl. No.: **495,754**

[52] **U.S. Cl.** .... **73/1 R**

[51] **Int. Cl.²** **B01F 3/02**

[58] **Field of Search** .... 73/1 R; 48/180 B, 180 S, 48/180 R

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

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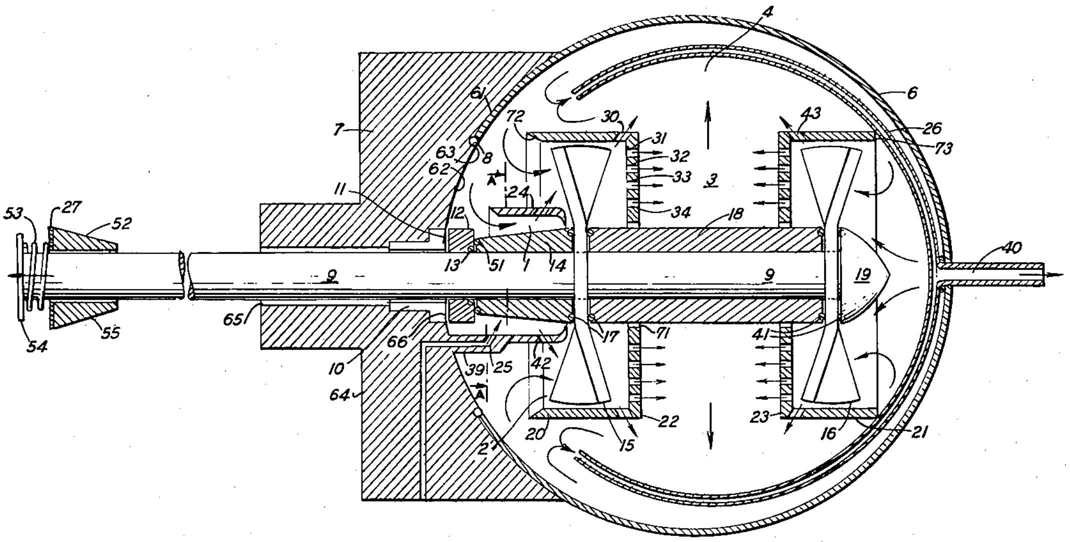
Primary Examiner—S. Clement Swisher
Attorney, Agent, or Firm—David Robbins; Alvin Englert

[57] **ABSTRACT**

An exponential dilution flask for the calibration of gas detectors or for use as a dynamic gas blender or an efficient flow-through reactor for gas phase reactions. A nearly ideal first order exponential decay characteristic for the flask is obtained by introducing sample and carrier gases to a spherical shell and providing means in the shell for completely mixing incoming carrier fluid with the contents of the flask within the response time of a gas detector being calibrated. The fluid is moved by two fans of equal but opposite pitch rotating on a common shaft through oppositely facing corresponding holes in a pair of plates forming a mixing region therebetween. The fluid is thus divided by the holes into a plurality of separate streams which collide in the mixing region. A small portion of the combined fluid exits from the shell through a narrow outlet tube and the remainder is recycled for further division and combination.

15 Claims, 3 Drawing Figures



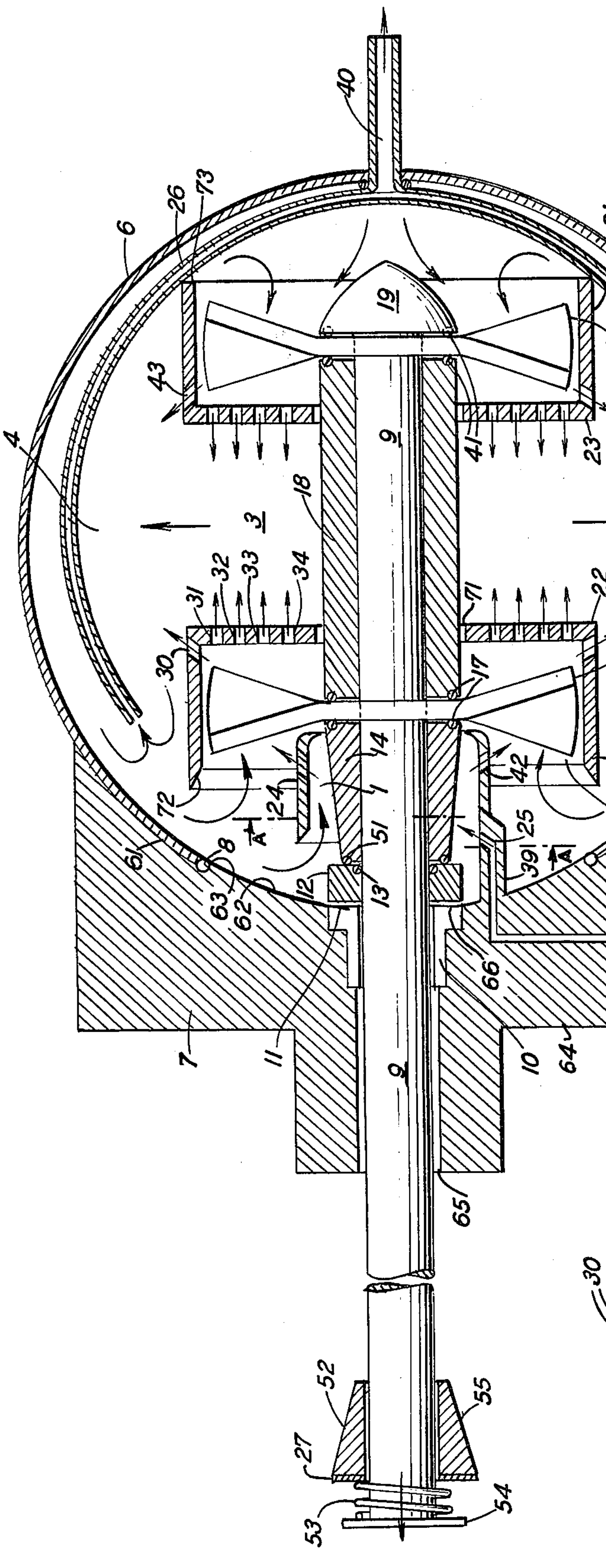


Fig. 1

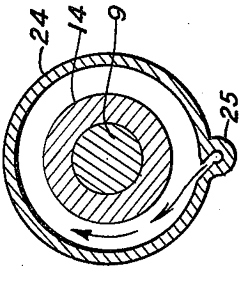


Fig. 2

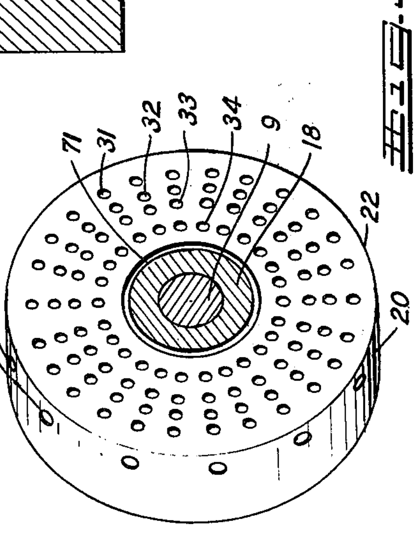


Fig. 3

EXPONENTIAL DILUTION FLASK

The present invention relates to an improved exponential dilution flask which facilitates more accurate calibration of gas detectors such as in air pollution monitoring instruments and which can also be used as a dynamic gas blender and as an efficient flow-through reactor for gas phase reactions.

It has been known in the prior art to utilize exponential dilution techniques for the calibration of gas detectors. However, due to the deficiencies of prior art exponential dilution flasks, the calibrations performed in the prior art have generally not been reliable.

The calibration of a gas detector with an exponential dilution flask is based on the theoretical expectation that the concentration of a sample injected into an exponential dilution flask through which a carrier gas is flowing will decay exponentially with time according to the expression $c_o e^{-kt}$ where c_o is the initial concentration and k is a constant which can be computed from the known system parameters. However, it has been observed that the dilution processes in prior art flasks do not follow an ideal first order exponential decay process according to the equation and that such flasks further exhibit poor slope reproducibility on a day-to-day basis which renders them unsuitable for providing reliable calibrations.

The exponential dilution flasks of the prior art are basically spherical, cylindrical or bell-shaped vessels containing either flat solid paddles or unshielded fans. It is suggested that the observed unreliability of these devices is due to inefficient blending of the sample and carrier gases which comprise the flask contents.

According to the invention it has been found that an exponential dilution flask will follow the desired first order exponential decay equation only if the sample is randomly distributed throughout the flask at all times. Since exponential dilution is a continuous dynamic process involving a steady influx of pure carrier gas and corresponding efflux of mixture of sample and carrier, the blending of incoming gas with the flask contents should ideally be instantaneous. In a practical system it takes a finite time to move gas from one place to another to achieve mixing but since all detector systems which will be measuring the efflux have a finite response time (typically 0.1 to 0.5 seconds), it has been found that ideal behavior may be achieved to within a first approximation if the mixing is essentially complete within the response time of the detection and display system. According to the invention then a novel structure for an exponential dilution flask which meets the above criteria has been provided.

It is thus an object of the invention to provide an improved exponential dilution flask which is useful in the calibration of gas detectors such as concentration detectors and detectors used in air pollution monitoring instruments and in determining the linearity of such detectors.

It is a further object of the invention to provide an improved exponential dilution flask which more nearly follows an ideal first order exponential decay process.

It is still a further object of the invention to provide an exponential dilution flask which achieves reproducible performance.

It is still a further object of the invention to provide an exponential dilution flask in which the mixing of the incoming increment of fluid is essentially complete within the response time of a typical detection and display system.

It is still a further object of the invention to provide a structure which may be used as a dynamic gas blender and as an efficient flow-through reactor for gas phase reactions.

According to the invention, an exponential dilution flask for mixing a sample and carrier gas is provided which is comprised of a spherical vessel which houses two ducted fans of equal but opposite pitch which rotate with a common shaft. Gas is admitted into the vessel through an inlet tube and the fans move the gas at a relatively high volume flow through corresponding holes in opposing perforated plates. The gas is thus divided into laminar streams which collide head-on and blend. The resultant mixture is then rapidly recirculated, redivided, blended further, and a portion of the fluid exits through one of two portions of a C-shaped exit tube provided in the vessel. The probability of a short circuit developing between the inlet and outlet is minimized since gas entering the device must pass through four mixing regions before having access to the exit tube.

A better appreciation of the novel structure of the flask may be had by referring to the figures which will be discussed in detail below but first, so that the advantages of the invention may be better appreciated gas detector calibration techniques in general utilizing exponential dilution will be discussed.

The basic calibration technique involves coupling the output of an exponential dilution flask to a gas detector (e.g., a flame ionization detector). The object of the calibration is to correlate the gas detector signal outputs as displayed on a display device with actual concentration values. Since in the ideal case the concentration of the gas exiting from the flask follows the formula $c = c_o e^{-kt}$ where c_o is the initial concentration, k is a constant known for the parameters of the system, and t is time, theoretically the concentration is known for each instant of time following t_o and this information may be used to calibrate the detector. The advantage of this method as opposed to inputting several discrete samples of different known concentrations to the detector is that it rapidly provides a continuous concentration spectrum over several orders of magnitude.

Basically an exponential dilution flask is a gas mixing device of known volume Vo. A suitable carrier gas is purged through the flask at a known constant rate r. A premeasured quantity of pure sample N_o (moles) to which the detector will respond is introduced into the exponential dilution flask (EDF) at some time t_o. If the sample is prefectly and instantaneously mixed with the carrier gas at all times after its introduction then the instantaneous rate at which the sample leaves the flask ($-dN/dt$) is proportional to the amount of sample within the flask at that instant. Thus $-dN/dt \sim N$ or $-dN/dt = kN$ where k is a constant. These equations are the basic mathematical expressions which describe a simple first order decay process and the concentration c of the sample at any time t after t_o becomes $c = c_o e^{-kt}$. In the ideal case the initial concentration of the sample $c_o = N_o/Vg$ where Vg is volume of gas within the exponential dilution flask (EDF) under actual operating conditions, $k = r/Vg$ and the sample concentration c at any time t after t_o can be calculated.

If the gas detector to which the EDF is coupled responds in a linear fashion it provides a signal (usually a voltage) $S = Ic$ where $I =$ constant. The area A under the curve generated by the detector is $\int_0^\infty S dt$. By substitution of the above signal-concentration relationship and integration between appropriate limits the constant I is found to be $I = Ar/N_0$. Moreover, the slope k_s of the signal curve should be identical to that calculated for the concentration curve, i.e. $k_s = r/Vg$. For non-linear detectors the quotient of k_s and k can be used as a monitor of detector linearity. The linearity factor n is given by k_s/k.

Thus for calibration purposes exponential dilution offers a rapid means of providing a continuous concentration spectrum over several orders of magnitude, a signal-concentration relationship, and an assessment of detector linearity.

Of course, the above theory presupposes that the flask provides dilution of the sample according to the ideal first order exponential decay equation and that the performance of the flask is reproducible, and it is in these areas where the exponential dilution flasks of the prior art have fallen short. On the other hand, the structure described of the present invention in detail below provides a dilution flask which permits the desired theoretical results to be more nearly realized.

The invention will be better appreciated by referring to the Figures in which:

FIG. **1** is a schematic representation of an exponential dilution flask according to the invention.

FIG. **2** is a cross-sectional view taken at A—A of FIG. **1.**

FIG. **3** is a perspective view of elements **20,22** of FIG. **1.**

Referring to FIG. **1,** it is seen that the flask is spherical in shape. The sphere was chosen as the basic flask shape because it has no corners and offers the smallest surface area for a given volume of all the regular geometric shapes thus maximizing the effective mixing region.

In FIG. **1** the sphere is formed partly of glass shell **6** and partly of the inside surface **62** of metallic member **7** which may be brass. Member **7** may have a circular cross-section in the plane perpendicular to the plane of the paper and parallel to wall **64.** The inside surface **61,62** of the member is spherical in shape and has a ledge **63** into which the glass shell **6** is pressure fitted and sealed by O ring **8.** A simple clamping frame (not shown) is used to retain the glass and metal sections.

Drive shaft **9** extends through longitudinally extending cylindrical opening **65** in member **7** and into the interior of the sphere. The shaft is supported in carbon filled PTFE bushing **10** and a simple rotary face seal **11** to contain the gases within the sphere is comprised of the inner face **66** of the bushing and a face of stainless steel ring **12** which is statically sealed and fixed to the drive shaft with an O ring **13.** The inside diameter of stainless steel ring **12** is bored slightly larger than the drive shaft diameter to permit the ring face to move parallel to the bushing face. The seal is kept under tension by any mechanical arrangement known to those skilled in the art for exerting a pulling force on shaft **9** which force will cause O ring **51** and member **14** to push ring **12** against face **66.** One such exemplary arrangement is shown in FIG. **1** wherein spring **53** pushes thrust washer **27** against a face of bushing **52** at one end and against a face of ring **54** at the other end. Bushing **52** is arranged to be immovable (not shown) and ring **54** is attached to the shaft **9** so that the effect of the spring is to continuously pull the shaft **9** outwardly from the sphere. The type of seal used besides being simple has the advantage of improving rather than deteriorating with use.

A conical aluminum member **14** is locked to the drive shaft by means of a small set screw, not shown. Also mounted on the shaft and locked thereto with set screws are cylindrical spacer **18** and conical member **19.** Two fans **15** and **16** of equal but opposite pitch are made to rotate with the drive shaft by being frictionally locked between members **14** and **18** and **18** and **19** respectively by O rings **17** and **41.** In the preferred embodiment the fans may be made of aluminum, the pitch of the fan blades is 30° and the diameter thereof is 3.8 centimeters.

Fan blade **15** is surrounded by a stationary brass shroud **20** and fan blade **16** is surrounded by a stationary brass shroud **21.** Each shroud has 16 equally spaced peripheral holes, **30** and **43** respectively, drilled therein at 45° to the drive axis. Shroud **20** is fitted with a facing place **22** which in the preferred embodiment may be 1/16 of an inch thick brass and shroud **21** is fitted with a similar facing place **23.** Each facing plate contains four concentric groups of holes, and groups **31, 32, 33** and **34** of plate **22** are arranged to be situated exactly opposite from the corresponding groups of plate **23.** A perspective view of shroud/facing plate unit **20,22** is shown in FIG. **3** and as illustrated, in the preferred embodiment each concentric group of holes has 25 holes. As will be described below, the perforated plates serve both to remove the rotational components induced in the gas by the fans and to divide the gas into separate streams.

Shroud assemblies **20,22** and **21,23** may be mounted in the flask by any convenient mechanical means so long as no part of the assembly touches spacer **18,** the annulus **71** preferably being about 1/32 inch in width. One mounting mode found to be advantageous is to connect the two shroud assemblies together by three metal supports soldered to members **22** and **23** at their outer peripheries at positions 120° displaced from each other and extending parallel to shaft **9.** Member **20** is provided with three metal feet supports which may be straight rods also soldered to edge **72** at positions 120° displaced from each other, extending parallel to shaft **9** and resting at their other ends on portion **62** of metal member **7** just below O ring **8.** Three phosphor bronze spring clips are attached to edge **73** of member **21** at positions 120° displaced from each other. The spring clips also extend parallel to shaft **9** and the outside ends spring against the inside of spherical glass shell **6** thereby pushing both shrouds to the left in the drawing and forcing the feet connected to edge **72** against portion **62** of metallic member **7.**

Conical member **14** is enclosed by stationary brass shroud **24** which contains 16 equally spaced peripheral holes drilled at 60° to the drive shaft axis. The input end of inlet passageway **25** is drilled in metallic member **7** as shown in FIG. **1,** and the output portion extends through tube **39** which is soldered or welded to member **7,** shroud **24** being soldered to tube **39.** The output of passageway **25** is arranged to discharge tangentially into the annular space between shroud **24** and conical member **14** as shown more clearly in the cross-sectional view of FIG. **2.**

The blended gas escapes from the sphere by entering C-shaped tube **26** at either end thereof. C-shaped tube

26 terminates at its middle in flask outlet tube **40** which provides an outlet for the gas. Tube **26** is relatively narrow and in the preferred embodiment has an inside diameter of 0.102 centimeters.

In the operation of the device, shaft **9** is driven at approximately 5500 rpm by an air turbine and the sample and carrier gases are admitted through inlet tube **25.** The incoming gas enters tangentially to the spiral flow pattern generated in the fluid between spinner member **14** and its stationary shroud **24** as shown in FIG. **2** to the region denoted as **1** in FIG. **1.** Upon reaching the end of the shroud, the now pre-mixed inlet gas is divided into sixteen separate streams by the sixteen peripheral holes **42** and is discharged into region **2** where the first fan is located. In so doing, the streams must transverse the fluid being drawn into the fan and further blending is effected. Conical spinners **14** and **19** on the intake sides of fans **15** and **16** respectively assist flow into the working region of the blades and reduce fluid stagnation near the shaft.

The mixture is moved by the motion of fan **15** to the area at the far end of shroud **20** which has 16 peripheral holes therein and to face plate **22** which has 100 holes therein. At the same time, fluid mixture is being drawn past conical spinner **19** by fan blade **16** and is moved to face plate **23** and the far end of shroud **21.** Thus the mixture, after it has moved past each of the fan blades, is subdivided into 116 streams, 100 of which collide head-on at velocities of between 160 to 200 centimeters per second in region **3** shown in FIG. **1.** The resulting blend is then forced by pressure differential and the radial pumping induced by the rotating shaft to move outwardly towards the walls of the sphere to region **4.** In so doing, it must traverse a cross-fire of 32 streams emanating from the peripheral holes **30** and **43** of shrouds **20** and **21** respectively. The angle of holes **30** and **43** is arranged so that the streams do not collide, but rather pass each other inducing vortex formation and mixing at the point of passing. Most of the fluid thus compounded is recycled while a small portion finds exit through one of the entrance ends of C-shaped tube **26** to the outlet **40.**

The probability of a short circuit developing between inlet and outlet is very low, since any gas entering the device must traverse all four mixing regimes before having access to the exit tubes. The effects of fluid stagnation near the walls and other stationary portions of the devices are minimized by providing polished surfaces and gentle curves wherever possible. At a shaft speed of 5500 rpm the estimated recirculation rate within a flask having a volume of 150 ml is 20 times per second. In experiments performed with the structure of the invention the sample propane was investigated using a carrier gas of air or nitrogen.

Two calibration methods utilizing the exponential dilution flask of the invention which have been found to be particularly suitable will now be described. In the first method, an approximate quantity of pure sample gas is introduced into the flask which is purged with carrier gas and the detector output as a function of time is recorded. This is used to compute the detector linearity factor *n* which is the ratio of the observed slope of the log of the recorded signal versus time curve to the theoretical value discussed above computed from the volume of gas in the EDF, Vg, and gas flow rate. All gas volumes and flow rates are corrected to STP. A single high-level response So within the concentration region covered by the dilution curve is established with a certified span gas of known concentration. All responses S below the span gas level can now be expressed in terms of calibrant concentration *c* by use of the equation

$$S = \frac{S_o}{c_o^n} c^n.$$

In a second method of calibration, a precisely known quantity N_o of pure calibrant gas is introduced into the dilution flask which is purged with carrier gas. The resultant detector signal curve is integrated to establish the area A. The linearity factor *n* for the detector is obtained as above, the carrier gas flow rate *r* is measured and the volume of carrier gas in the flask under actual operating conditions Vg is determined. The response S is then related to sample concentration through the equation

$$S = \frac{ArnVg \quad \mathrm{n}}{VgN_o^n} c^n.$$

This technique does not require the use of a precalibrated span gas mixture as does the above method. It further should be noted that apart from calibrating the detector it is sometimes necessary only to determine the linearity factor of the detector and the exponential dilution flask of the invention may be used for this purpose.

While I have disclosed and described the preferred embodiments of my invention, I wish it understood that I do not intend to be restricted solely thereto, but that I do intend to include all embodiments thereof which would be apparent to one skilled in the art and which come within the spirit and scope of my invention.

I claim:

1. An exponential dilution flask comprising a substantially spherical shell, means for introducing sample and carrier fluid to said shell, means in said shell for dividing said introduced fluid into a plurality of separate fluid streams and for combining said fluid streams, outlet means for outputting a small portion of said combined fluid from said shell, and means for recylcling the remainder of said combined fluid to said means for dividing and combining for re-division and recombination.

2. The exponential dilution flask of claim **1** wherein said means for dividing and combining comprises first and second members located in said shell downstream of said introduction means and forming a mixing region therebetween, each of said members having a plurality of corresponding holes therein which face each other across said mixing region, and means for simultaneously moving fluid through the holes in each of said members towards said mixing region whereby the fluid is divided by said holes in each of said members and combined in said mixing region.

3. The exponential dilution flask of claim **2** wherein said means for simultaneously moving said fluid is comprised of first and second fan means of equal but opposite pitch located outside of the sides of said first and second members respectively which face away from said mixing region, and means for simultaneously rotating said first and second fan means.

4. The exponential dilution flask of claim **3** wherein said means for simultaneously rotating comprises a shaft which passes through the centers of said fan means.

5. The exponential dilution flask of claim **4** wherein said shaft has first and second conical spinners mounted thereon adjacent said first and second fan means respectively to assist fluid flow into said fan means.

6. The exponential dilution flask of claim **5** wherein said first and second members each comprise a flat plate having a plurality of rings of concentric holes therein, said plates being perpendicular to said shaft.

7. The exponential dilution flask of claim **6** wherein said means for dividing further includes first and second cylindrical members which are concentric with said shaft and surround said first and second fan means respectively, said cylindrical members having a plurality of holes in the periphery thereof cut at an acute angle to the direction of said shaft, said first and second cylindrical members being joined at the ends thereof to said first and second plane members respectively.

8. The exponential dilution flask of claim **7** wherein said outlet means comprises a narrow tube which leads to the exterior of said shell.

9. The exponential dilution flask of claim **8** wherein said tube comprises a C-shaped tube each open end of which admits fluid, said tube providing a passageway to the exterior of said shell at its mid-section.

10. The exponential dilution flask of claim **8** wherein said introduction means for said fluid comprises an inlet opening which directs fluid into said spherical shell at said first spinner in a direction tangential to the surface of said first spinner.

11. The exponential dilution flask of claim **10** wherein said first spinner is surrounded by a cylindrical member concentric with and spaced from said spinner, said cylindrical member have a plurality of holes in the periphery thereof cut at an acute angle to the direction of said shaft.

12. The exponential dilution flask of claim **11** wherein said spherical shell is sealed by a seal comprised of a bushing in which said shaft rotates and an axially movable ring mounted on said shaft, means being provided for pulling said shaft outwardly from said sphere so that said first spinner pushes said ring against said bushing to form said seal.

13. The exponential dilution flask of claim **12** wherein said means for pulling includes a spring means and a thrust washer.

14. The exponential dilution flask of claim **4** wherein said spherical shell is comprised partly of a glass shell and partly of the interior of a metallic frame member said metallic member having a longitudinal hole therein through which said shaft passes.

15. A method of mixing a sample gas and a carrier gas comprising,

providing a substantially spherical shell,

introducing said sample gas and said carrier gas to said shell,

dividing said introduced gas into a plurality of gas streams,

causing some of said streams to collide head on with others of said streams to effect mixing,

outputting a small portion of said mixed gas from said shell,

recycling the remainder of said mixed gas for re-division and re-combination.

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