United States Patent

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[54] **DEVICE FOR THE QUANTITATIVE COLORIMETRIC ANALYSIS OF FLUIDS**
8 Claims, 1 Drawing Fig.

[52] **U.S. Cl.** ..... **23/253 R,** 23/253 TP, 23/254 R
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[50] **Field of Search** ..... 23/253 R, 253 TP, 259, 292, 230 B, 254 R

[56] **References Cited**

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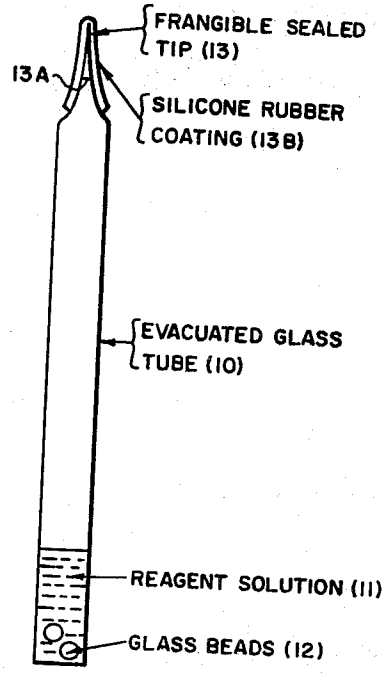
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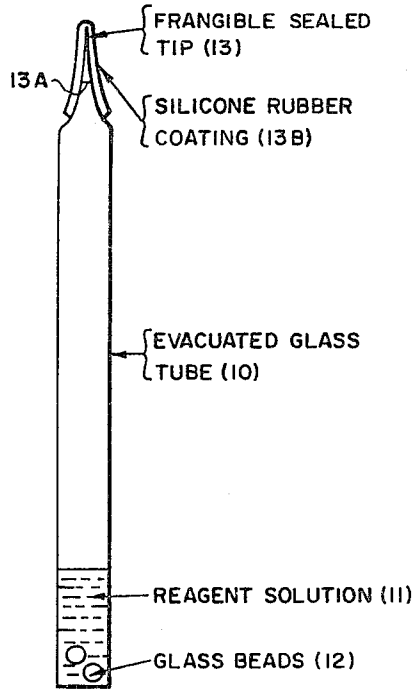
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ABSTRACT: A device for quantitative colorimetric analysis of fluids which consists of a transparent tube of predetermined size with a single frangible tip, containing a liquid colorimetric reagent and evacuated to a predetermined degree to insure that on immersion of the frangible tip in the fluid to be analyzed, followed by fracture of the tip, a predetermined quantity of sample will be forced into the tube so that on mixing of the contents color will be developed proportionately to the concentration of the material being analyzed for in the sample fluid. The amount of material being analyzed for can then be ascertained by comparison with a color chart or a set of color tubes.





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DEVICE FOR THE QUANTITATIVE COLORIMETRIC ANALYSIS OF FLUIDS

FIELD OF THE INVENTION

This invention relates to the quantitative chemical analysis of fluids for a single constituent thereof.

DESCRIPTION OF THE PRIOR ART

The analysis of fluids has very often been facilitated by the use of tubes into which the fluid is introduced together with a material with which it produces a color proportional to the concentration of the material to be analyzed for in the fluid. However, the tubes which have been used are generally rather complicated, very often being calibrated to measure the amount of fluid taken up. They very often involved capillary sections for the introduction of the fluid, and generally have openings at both ends, the force for bringing the fluid into the container being applied at one end and the fluid being taken in at the other end. In one device, described in Furlong U.S. Pat. No. 3,068,855, a sample bulb is filled with a predetermined quantity of a fluid by the use of a predetermined vacuum in the bulb and the fracturing of a frangible tip in the fluid to be tested. However, the complete device therein disclosed is very complicated indeed; the bulb must be shattered for the analysis, and must be protected by an outer tube, so that this device shares the difficulty of other prior art devices, of being expensive to manufacture and complicated to use.

OBJECT OF THE INVENTION

This invention aims to provide a very inexpensive disposable device for quantitative colorimetric analysis of fluids, which is characterized by low cost, extreme simplicity of design, and ease of operation. The invention is designed to be so very simple that a person without chemical training can use the device for such simple determinations as active chlorine content of a swimming pool, the amount of oxygen in an inert atmosphere, or the amount of dissolved oxygen in a liquid such as water, or for any one of a host of other similar analyses.

SUMMARY OF THE INVENTION

The device which is the subject of this invention comprises an evacuated glass or other transparent tube with relatively strong walls so that it can be handled without danger of breaking, with a readily frangible sealed tip at one end thereof, the tube being evacuated to a predetermined degree so that on immersion of the tip in a fluid to be tested and fracture of the tip, a predetermined quantity of fluid will be drawn into the tube. The tube contains a liquid colorimetric reagent capable of reacting with the material in the fluid for which an analysis is sought, whereby a color will be developed which is proportional to the concentration of the material in the fluid. The amount of the material to be analyzed for can then be determined as by comparison of the tube, with the color developed therein, with a standard color chart or comparison tube, or by photometric means. Preferably, a stirring device is provided, either in the form of glass beads, or in the form of an air bubble.

BRIEF DESCRIPTION OF THE DRAWINGS

The drawing is a cross section through a glass tube made in accordance with this invention, with an internal stirring device incorporated therein.

DESCRIPTION OF THE INVENTION

As shown in the drawing I use a tube **10** which is preferably of glass, but may be of any transparent or translucent material which does not interfere with the desired analysis, and which can be sealed at the frangible tip and then readily broken there. It is important that the walls of the tube be of sufficient strength to permit handling; ordinary test tube glass is adequate. The tube is filled with a reagent solution **11** and two

glass beads **12** may be placed therein. One end of the tube is then drawn out in a thin walled readily frangible tip **13**, the tube is evacuated to a predetermined degree, and the tip **13** is sealed, and then scored, as by scratching with a file, to produce a score mark **13A** which acts to insure breaking of the tip at that point when pressure is later applied. A silicone rubber coating **13B** covers the tip **13**. For convenience the tube has a flat bottom **14**.

As mentioned above, the frangible tip may be coated with an elastic sleeve **13B** of, for example, silicone rubber. This coating separates only partially on fracture, to permit filling and then snaps back to hold the tip in place and reclose the opening. This protection is important in swimming pool applications where glass fragments would be hazardous and in oxygen analysis where air must be excluded.

In use, the tip is immersed in the fluid to be analyzed and the pressure is applied so that the tip breaks at the score mark **13A**. The ambient outside pressure forces fluid into the tube. Since the outside pressure varies only a few percent from time to time, the amount of fluid which goes into the tube is predetermined by the degree of evacuation of the tube. Since the reagent in the tube is present in amount sufficient to develop color with more than the maximum amount of the material to be analyzed for or which would be expected to be present in the sample, the color developed by the reaction of the fluid with the reagent will be in direct proportion to the concentration of the material to be analyzed for in the fluid.

The color can be developed for comparison simply by placing the operator's finger over the broken tip **13** and turning the tube up and down. The beads **12** help to mix the fluid with the reagent. If the rubber sleeve **13B** has been employed, closure with the finger is not necessary.

As indicated above, the color can be determined visually by comparison with a color chart or a set of color tubes provided with the test kit and calibrated by analyses of fluids of known concentrations. It can of course be observed photometrically where more sophisticated analyses are desired.

Obviously where a high degree of accuracy is desired, it is essential to control the outside pressure and temperature of the fluid. However, for most analyses the ordinary ambient pressure and temperature can be used, since the error introduced is rather small compared with the desired degree of accuracy wanted in analysis.

A convenient size glass tube will be 7.5 to 10 millimeters in outside diameter; 1-millimeter walls are sufficient to give the necessary strength. The taper is drawn to about 2 millimeters in outside diameter, and the score mark **13A** will be conveniently 5–10 millimeters from the actual tip. A filed scratch mark is a convenient method of scoring to insure breaking at the desired point.

Obviously, although I have illustrated a liquid reagent and a coated cellulose reagent in the tube, the tube could also contain a reagent in the form of a solid.

In general I prefer to evacuate to a pressure of the order of 20 millimeters absolute, which is generally sufficient to remove virtually all permanent gases from the sealed tube and insure that only water vapor remains on sealing. Such a tube will fill completely if used with a liquid sample. The glass beads are particularly useful for mixing where one gets complete filling of the tube by a liquid.

An alternate method of mixing is to evacuate less completely so that an air bubble will form in the tube on filling. For example, a tube having internal volume of 5 cubic centimeters can be charged with 0.5 cubic centimeters of aqueous reagent and evacuated to an absolute pressure of 100 millimeters of mercury absolute and then sealed. The partial pressure of air inside the tube will be approximately 76 millimeters of mercury and its volume will be 4.5 cubic centimeters. When actuated at sea level the air inside the tube will then compress to a bubble having a volume of approximately 0.5 cubic centimeters. This bubble will then facilitate mixing of a liquid sample drawn into the tube when the tube is turned up and down.

The great advantages of my analytical device are its low cost and the simplicity of operation, whereby a person untrained in analytical chemistry can readily perform the simple operations necessary to get the result. The device is therefore particularly useful in several contexts. One of these is in and about the home for analyses such as the content of chlorine in swimming pools. Another is in routine testing of fluids in plant operations where operators untrained at chemical work can make limited determinations easily. And yet another is in water pollution testing in the field, where elaborate test facilities are not available. An additional advantage of my invention is that it provides a very convenient means of utilizing reagents which would be ruined if exposed to the atmosphere. Examples 1 and 2 illustrate this advantage in the application of indigo carmine reagent to the quantitative determination of oxygen.

SPECIFIC EXAMPLES OF THE INVENTION

Typical examples of the analyses that can be readily performed are described in the following examples:

EXAMPLE 1

Dissolved Oxygen in Liquids. Range, 0–15 p.p.m.

Reagent: Dissolve 0.12 gram reduced 5,5-indigo disulfonic acid, 1.0 gram sodium carbonate and 1.0 gram dextrose in 100 ml. distilled water. The mixture should be placed in a closed container and blanketed with an inert gas such as nitrogen. The dye will dissolve completely and the solution will change to a light yellow color if stirred periodically over a period of several days at room temperature. Heating to 80° C. reduces this time to about one hour.

The tube is charged with one-fifth of its volume of reagent in an oxygen-free atmosphere, evacuated to an absolute pressure of 40 mm. Hg and sealed.

When the tip is broken under the surface of the liquid to be tested the tube fills almost completely, while mixing with the reagent. Additional mixing, if necessary, may be achieved by shaking or repeatedly inverting the tube.

The hue which develops immediately may be yellow, orange, red, purple, or blue, depending on the concentration of oxygen in the sample fluid.

A quantitative estimate of concentration may be made by comparing the developed color with the colors developed by known concentrations of oxygen in liquids of composition similar to the test liquid. Specially prepared color charts may be used for this purpose.

EXAMPLE 2

Oxygen in "Inert" Atmosphere. Range, 0–0.1 percent by vol.

Reagent: Dissolve 0.012 gram 5,5-indigo disulfonic acid, 1.0 gram dextrose in 100 ml. distilled water. The mixture should be placed in a closed container and blanketed with an inert gas such as nitrogen. The dye will dissolve completely and the solution will change to a light yellow color if stirred periodically over a period of several days at room temperature. Heating to 80° C. reduces this time to about 1 hour.

The tube is charged with one-fifth its volume of reagent in an oxygen-free atmosphere, evacuated to an absolute pressure of 20 mm. Hg and sealed.

When the tip of the tube is broken in the atmosphere to be tested, the tube fills instantly. It is then capped and shaken or repeatedly inverted to assure contact between the reagent and the gas sample.

The hue which develops immediately may be yellow, orange, red, purple, or blue, depending on the concentration of oxygen in the sample fluid.

A quantitative estimate of concentration may be made by comparing the developed color with the colors developed by known concentrations of oxygen in gases of composition similar to the test gas. Specially prepared color charts may also be used for this purpose.

EXAMPLE 3

Ferric Iron in Aqueous Solutions. Range 1–10 p.p.m.

Reagent: Dissolve 20.0 grams potassium thiocyanate in 50 ml. concentrated hydrochloric acid and 50 ml. distilled water.

The tube is charged with one-tenth its volume of reagent, evacuated to an absolute pressure of 40 mm. Hg and sealed.

When the tip is broken under the surface of the liquid to be tested the tube fills almost completely, while mixing with the reagent. Additional mixing, if necessary, may be achieved by shaking or repeatedly inverting the tube. A red color develops immediately, the intensity of which is proportional to the concentration of ferric iron in the test solution.

A quantitative estimate of concentration may be made by comparing the developed color with the colors developed by known concentrations of ferric iron in liquids of composition similar to the test liquid. Specially prepared color charts may also be used for this purpose.

EXAMPLE 4

Orthophosphate in Aqueous Solutions. Range 10–120 p.p.m.

Reagent: Dissolve 0.06 gram ammonium metavanadate, NH_4VO_3, in 50 ml. distilled water and 5 ml. 70 percent perchloric acid. Then add 3.0 grams ammonium molybdate $(NH_4)_6 \cdot Mo_7 O_{24} \cdot 4H_2O$, mix and dilute with water to 100 ml. Filter the solution before using.

The tube is charged with one-fifth its volume of reagent, evacuated to an absolute pressure of 40 mm. Hg and sealed.

When the tip is broken under the surface of the liquid to be tested the tube fills almost completely, while mixing with the reagent. Additional mixing, if necessary, may be achieved by shaking or repeatedly inverting the tube. A yellow color develops rapidly and is suitable for quantitative measurement in 15 minutes. The intensity of the color is proportional to the concentration of orthophosphate in the test solution.

A quantitative estimate of concentration may be made by comparing the developed color with the colors developed by known concentrations of orthophosphate in liquids of composition similar to the test liquid. Specially prepared color charts may also be used for this purpose.

EXAMPLE 5

Free Chlorine in Water. Range 0–10 p.p.m.

Reagent: Dissolve 0.30 gram orthotolidine hydrochloride in 25 ml. concentrated hydrochloric acid and dilute to one liter with distilled water.

The tube is charged with one-fifth its volume of reagent, evacuated to an absolute pressure of 40 mm. Hg and sealed.

When the tip is broken under the surface of the liquid to be tested the tube fills almost completely while mixing with the reagent. Additional mixing, if necessary, may be achieved by shaking or repeatedly inverting the tube.

A yellow color develops if chlorine is present in the sample. After 15 minutes, a quantitative estimate of concentration may be made by comparing the color with the colors developed by known concentrations of chlorine in liquids of composition similar to that of the test liquid. Specially prepared color charts may be used for this purpose.

In the above examples, no attempt has been made to describe in detail the limits of accuracy, effects of interfering species or stabilities of the colors which form. That information is readily available in standard treatises dealing with colorimetric analysis and has no direct bearing on the applicability of this invention.

Obviously the examples can be multiplied indefinitely without departing from the scope of the claims.

I claim:

1. A device for quantitative chemical analysis of fluids, comprising a transparent cylindrical tube of predetermined size and of uniform cross section and of sufficient wall strength to permit ready handling, having one end thereof drawn to a frangible tip, said tube containing a liquid

colorimetric reagent and being evacuated to a predetermined degree and means for mixing the liquid colorimetric agent with the fluid to be analyzed, which is drawn into the tube on fracture of the tip in the fluid to be analyzed.

2. The tube of claim 1, in which the mixing means is glass beads included in the tube with the liquid colorimetric reagent.

3. The tube of claim 1, in which the reagent is an aqueous solution of reduced 5,5-indigo disulfonic acid.

4. The tube of claim 1, in which the reagent is an aqueous acidified solution of potassium thiocyanate.

5. The tube of claim 1, in which the reagent is an aqueous acidified solution of orthotolidine.

6. The tube of claim 1, in which the vacuum in the tube ensures that, on breaking the tip in the fluid to be analyzed, the tube will be essentially full of liquid except for a gas bubble which facilitates mixing.

7. The tube of claim 1 in which the tube is of glass.

8. The tube of claim 7 in which the frangible tip portion is coated with an elastic coating which retains the glass fragments formed on breaking the tip to introduce sample into the device.

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