United States Patent [19]

Grengg

[11] **3,852,604**

[45] **Dec. 3, 1974**

[54] **MERCURY ANALYSIS SYSTEM AND METHOD**

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[73] Assignee: **Pollution Control Technology, Inc.,** Madison, Ill.

[22] Filed: **Aug. 11, 1972**

[21] Appl. No.: **279,820**

[52] **U.S. Cl.** ..... **250/373,** 23/230 R

[51] **Int. Cl.** **G01n 21/26**

[58] **Field of Search** ..... 23/230 R, 230 PC, 232 R, 23/253 R, 254 R; 250/218, 373

[56] **References Cited**

UNITED STATES PATENTS

3,173,016	3/1965	Williston et al.	250/218
3,178,572	4/1965	Williston	250/373
3,544,789	12/1970	Wieder	250/373

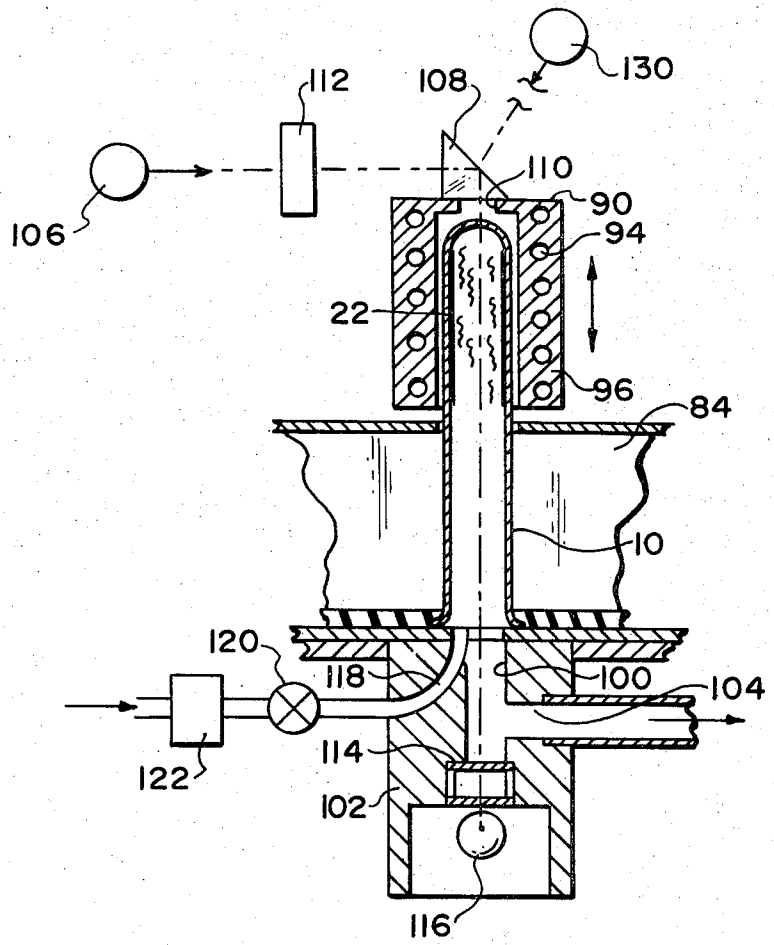
Primary Examiner—James W. Lawrence
Assistant Examiner—C. E. Church
Attorney, Agent, or Firm—Silverman & Cass, Ltd.

[57] **ABSTRACT**

The system and method utilize a vessel, such as a test tube, having a predetermined interior side surface area coated with gold. The closed end of the tube is uncoated. Mercury from a fluid sample is adsorbed by the gold coating, such as by passing a gas through the tube or by placing a liquid in the tube and shaking the tube for a short period of time. After mercury from a given amount of sample has been adsorbed by the gold coating, the test tube is placed in an inverted generally upright position with the closed end of the tube above the open end and with the open end vented. Then the tube is rapidly heated to a temperature in excess of 400° centigrade to vaporize the mercury from the gold coating. The mercury vapor will rise in the test tube to the closed end thereof and form a bubble of mercury vapor mixed with hot air. Ultraviolet light in the 2537 angstrom wave length band is passed endwise through the test tube. Some of the ultraviolet light is absorbed by the mercury vapor in the test tube and the transmitted light is detected and measured. Next, the mercury vapor laden air is flushed from the test tube with mercury free air. Ultraviolet light is again passed through the test tube, this time through mercury-free air and the amount of light transmitted through the mercury-free air is detected and measured. The difference between the light transmission measurements is indicative of the concentration of mercury in the fluid sample.

In addition to the test tube, the system includes structure for carrying out the method steps described above.

33 Claims, 9 Drawing Figures



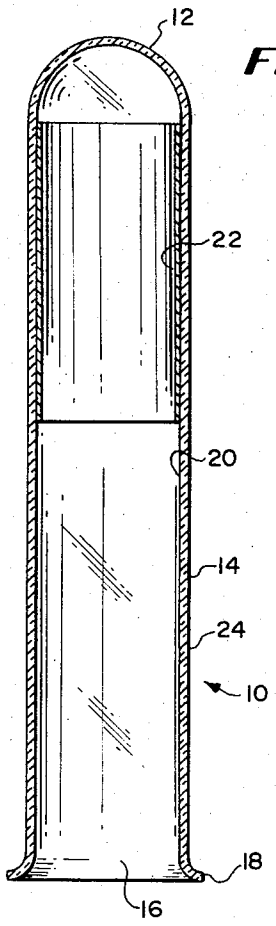


FIG. 1

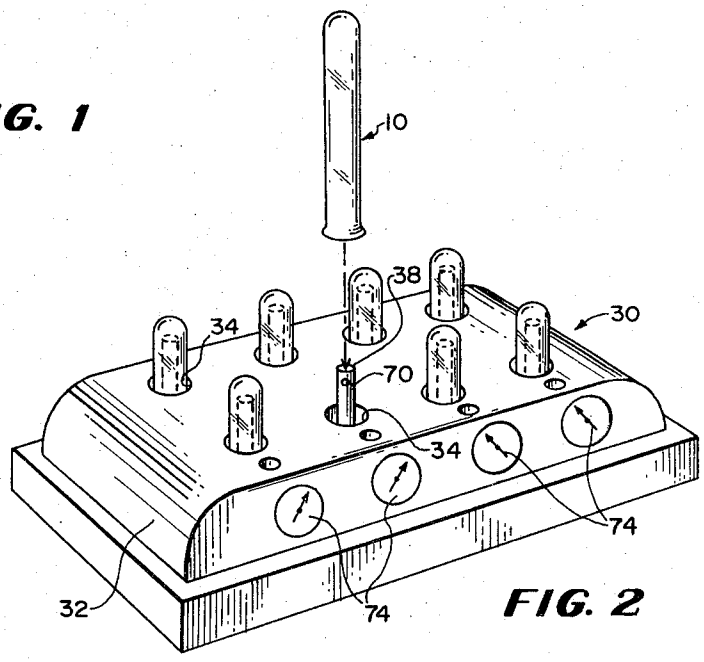


FIG. 2

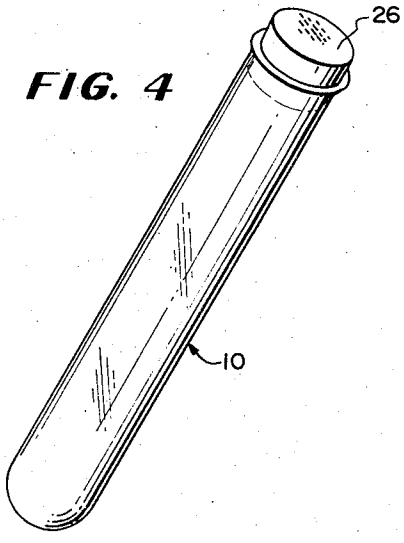


FIG. 4

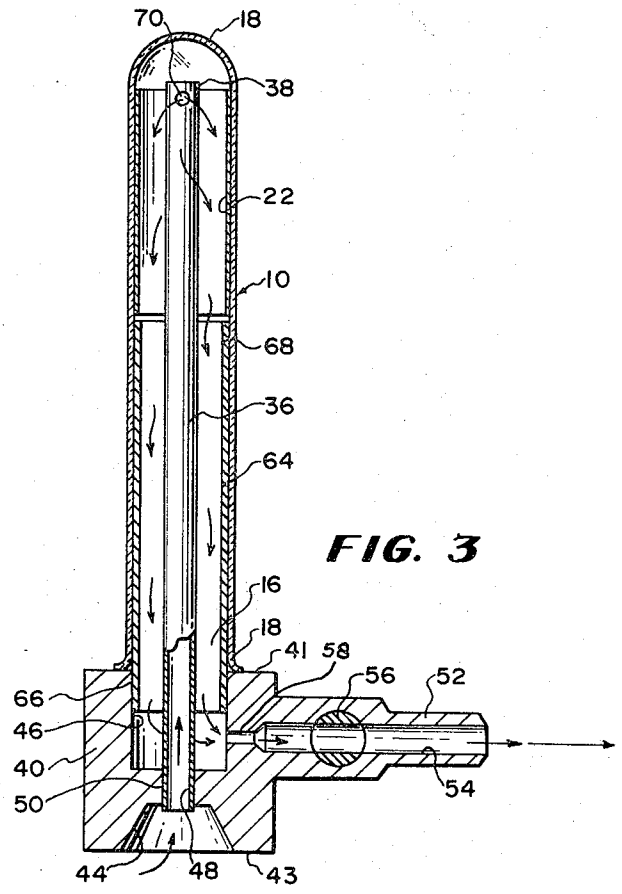


FIG. 3

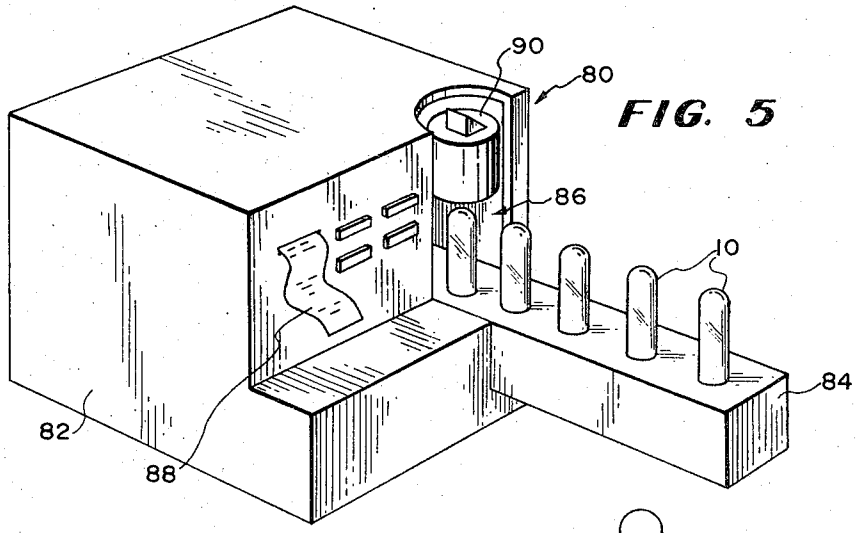


FIG. 5

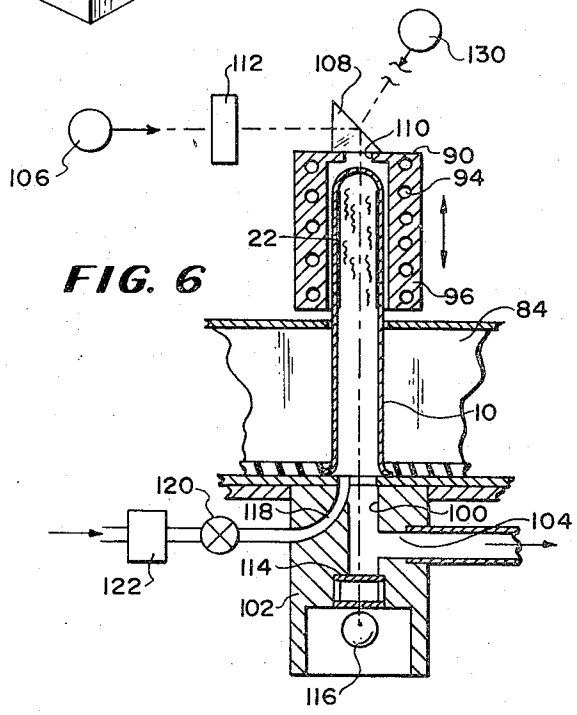


FIG. 6

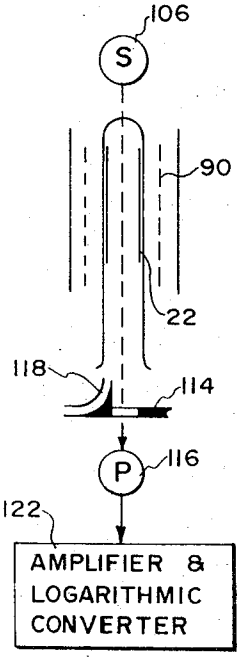
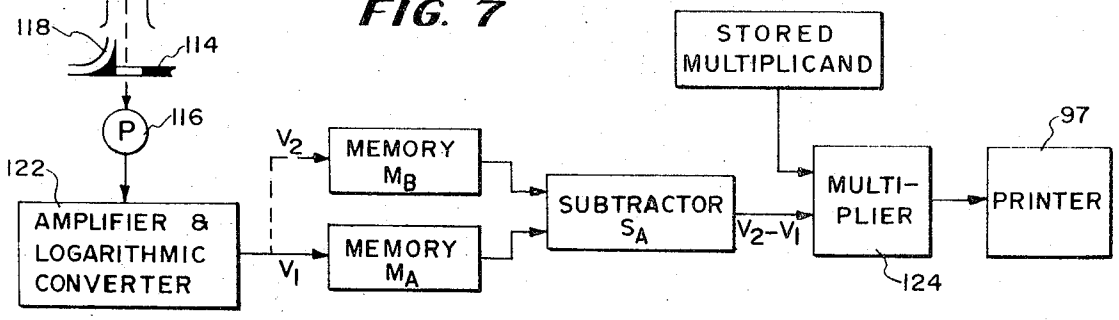


FIG. 7



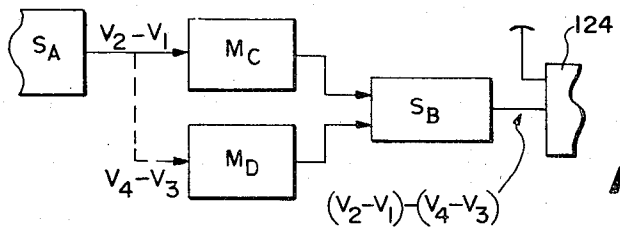
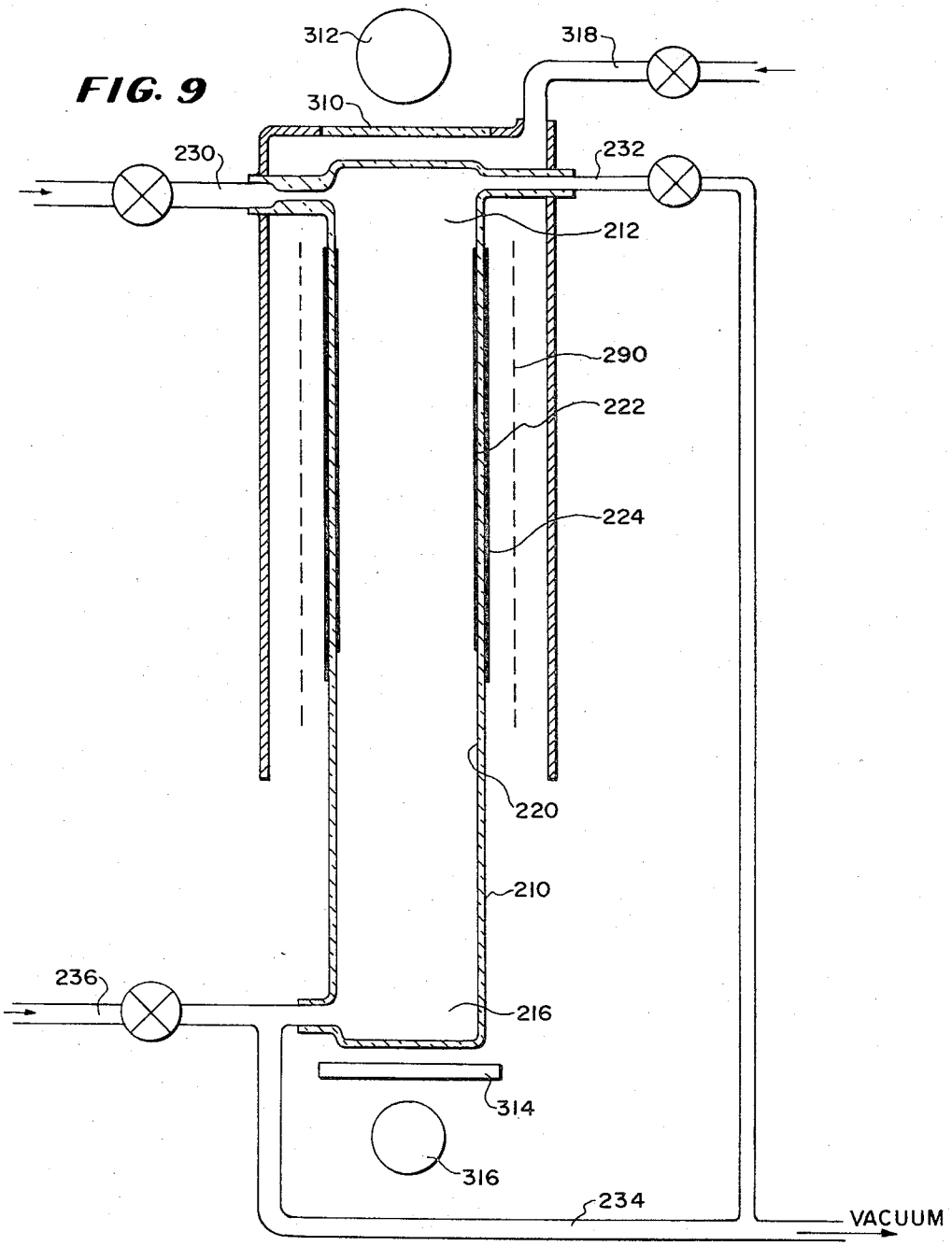

S_A
V_2-V_1
M_C
M_D
V_4-V_3
S_B
124
$(V_2-V_1)-(V_4-V_3)$

FIG. 8

FIG. 9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VACUUM

MERCURY ANALYSIS SYSTEM AND METHOD

BACKGROUND AND SUMMARY OF THE INVENTION

The present invention relates to a method and system for analyzing the mercury concentration in a fluid sample which may be either a gas or a liquid. The field of the invention includes chemical analysis methods and systems, particularly methods and systems which optically measure ray energy which passes through a fluent material. Methods and systems of this type have been classified at this time in Class 23, subclasses 232 and 253, and Class 250, subclass 218.

More specifically, the present invention relates to a method and system which include (a) adsorbing mercury in a noble metal from a fluid sample, (b) vaporizing the mercury from the noble metal by heating the same, (c) passing ultraviolet light in the mercury vapor adsorption wave length band of **2537** angstroms through the mercury vapor, and (d) measuring the amount of ultraviolet light absorbed by the mercury vapor to obtain an indication of the concentration of mercury in the fluid sample.

The technique of measuring the concentration of a gas or vapor by passing radiant energy or light having a specific discrete wavelength band which is absorbed by the particular gas or vapor being studied, is well known. Examples of such procedures or techniques are disclosed in the following U.S. patents:

U.S. Patent 3,174,037

U.S. Patent 3,589,814

U.S. Patent 3,589,868

Also, procedures have heretofore been proposed for measuring the concentration of mercury vapor in a gas sample such as air by passing radiant energy in the 2537 angstrom wavelength band through gas being analyzed, and then measuring the amount of radiant energy absorbed by the gas, the amount of absorbed radiant energy being related to the concentration of mercury vapor in the gas being analyzed. In this respect reference may be had to U.S. Pat. No. 3,173,016 issued to S. H. Williston et al. on Mar. 9, 1965 and to "Trace Mercury Determination" by J. B. Brooks and W. E. Wolfram which appeared in Chemical & Engineering News, Volume 48, Page 37 (June 22, 1970).

One of the disadvantages incurred with previously proposed methods and systems for mercury analysis, is the problem of loss of mercury from the sample and contamination of the sample (carryover) when measuring minute amounts of mercury. As for losses, it is well known that mercury is adsorbed by many different elements and in systems where the sample being analyzed is transferred through tubing or otherwise from one chamber or container to another chamber or container, there is danger of loss of mercury from the sample by reason of the mercury being adsorbed in the walls of the vessel, container or tubing by which it is transferred.

As for contamination, it will be understood that after adsorbing mercury, the transfer vessel, container or tubing may later give off mercury to a succeeding fluid sample and thereby cause an erroneous measurement of the concentration of mercury in the succeeding sample. These problems of losses and contamination are particularly acute when very small concentrations of mercury are being measured such as concentrations in the order of 0.05 parts per billion (PPB).

Another problem incurred with known methods and systems for analyzing mercury concentration in fluid samples by passing ultraviolet light through the sample or through mercury vapors obtained from the samples, is brought about by the fact that the gaseous medium containing the mercury vapor may also contain other gases or vapors such as organic vapors which also absorb radiant energy in the band width of radiant energy absorbed by mercury. When this occurs, an erroneous measurement indicating a larger concentration of mercury than actually exists, will be obtained.

Still another disadvantage incurred with prior art mercury analysis systems and methods is the fact that for measuring very small concentrations of mercury in a fluid sample, a large quantity of the sample must be analyzed and this takes a significant amount of time. It is desirable, therefore, to provide a method and system for analyzing mercury in which the time period for making the analysis is relatively short.

The method and system of the present invention overcome many of the disadvantages incurred with prior art mercury analysis systems and methods by eliminating transfer means such as vessels, containers or tubings, and by eliminating losses between the collection of mercury from a sample and the analysis of the mercury collected. The method and system of the present invention are also very versatile and enable one quickly to make accurate determinations of minute concentrations of mercury in liquids, gases and solids. The method and system of the invention achieve the aforementioned advantages by utilizing one vessel having a predetermined interior surface area thereof coated with a noble metal, such as gold, for the collecting vessel, the vaporizing vessel and the mercury vapor absorption vessel. Heretofore, the use of a vessel, such as a test tube, lined with gold has been proposed but for an altogether different purpose, namely, to provide the interior surface of the tube with an essentially chemically inert lining. In this respect reference may be had to U.S. Pat. No. 3,475,131.

According to the invention, there is provided for use in a mercury analysis system, a test tube having an open end adapted to be stoppered, an interior side surface area coated with a noble metal, and an uncoated closed end.

Also, according to the invention, there is provided a method for analyzing the concentration of mercury in a fluid including the steps of placing a given amount of fluid sample in a vessel having a noble-metal coating therein, removing the sample for the vessel, positioning the vessel in an inverted generally upright position with the closed end above the open end and with the open end vented, heating the vessel to a given temperature to release mercury vapor from the noble metal coating, passing ultraviolet light of a wave-length band which is absorbed by mercury vapor endwise through the vessel, measuring the amount of light transmitted through the mercury vapor laden air within the vessel, flushing the mercury vapor laden air from the vessel with mercury free air, again passing ultraviolet light endwise through the vessel now having mercury-free air therein, measuring the amount of light transmitted through the mercury-free air, and comparing the first light transmission measurement with the second light transmission measurement, the difference between the measurements

being indicative of the concentration of mercury in the fluid sample.

Further according to the invention there is provided a mercury analysis system including a vessel supported in a generally upright position with a first end of the vessel above a second end and with the second end vented, a mechanism for vaporizing mercury stored in the noble metal coating on the interior surface of the vessel, and apparatus for analyzing the mercury vapor, the analyzing apparatus including a source of ultraviolet light which is positioned to pass ultraviolet light endwise through the vessel, a detector for detecting the amount of light transmitted through the vessel, and a mechanism for flushing mercury vapor laden air from the test tube. Preferably the mercury analysis system also includes electronic circuitry for converting the signals generated by the detector into signal values directly related to the numerical concentration of mercury in the fluid sample in parts per billion (PPB).

Further, according to the invention there is provided for use in a mercury analysis system a device for sampling a gas including a vessel positioned to receive a gas therein, a suction mechanism for drawing a gas through the vessel and a control mechanism for controlling the rate of flow and the time period of flow of the gas through the vessel.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a sectional elevational view of the test tube of the invention.

FIG. **2** is a perspective view of a device for obtaining multiple samples of a gas by drawing the gas through a plurality of test tubes of the invention.

FIG. **3** is a sectional elevational view showing the drawing of a gas through one of the test tubes shown in FIG. **2.**

FIG. **4** is a perspective view of a stoppered test tube after a fluid sample has been passed therethrough.

FIG. **5** is a perspective view of the apparatus of the mercury analysis system for vaporizing mercury from the gold coating in each test tube and for measuring the concentration of mercury vapor.

FIG. **6** is a fragmentary sectional elevational view showing the apparatus for vaporizing and analyzing the mercury stored in one test tube.

FIG. **7** is a schematic diagram of the mercury analysis system of the invention and of the electronic circuitry therefor.

FIG. **8** is a fragmentary schematic diagram of a modification to the electronic circuitry shown in FIG. **7.**

FIG. **9** is a fragmentary schematic diagram of a modified mercury analysis system where a fixed cell is utilized in place of movable test tubes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In FIG. **1** is illustrated a test tube **10** made in accordance with the teachings of the present invention. The test tube **10** is basically of conventional design having a closed generally semi-spherical end **12,** a generally cylindrical elongate side wall **14,** and an opened end **16** defined by an outwardly flared flange **18** extending from the cylindrical side wall **14.** According to the invention a portion of interior side surface **20** of the tube **10** is coated with a noble metal **22.** Any one of the noble metals which have a strong afinity for mercury can be utilized for the noble metal coating **22.** One noble metal which has worked very well is gold, and hereinafter the noble metal coating **22** will be simply referred to as the gold coating **22.**

The gold coating **22** extends along the length of the side wall **14** starting at a point at or adjacent the junction between the closed end **12** and the side wall **14,** and extending toward the open end **16.** Empirical tests have shown that good results are obtained when the ratio of the length of the gold coating **22** to the length of the tube **10** is a number equal to approximately 0.4. The limitations on the length of the gold coating **22** will be explained in greater detail in connection with the description of FIG. **6.**

The gold coating or film **22** on the interior surface **20** of the tube **10** can be applied by several methods which are as follows: (a) high vacuum vapor deposition; (b) ionic sputtering in a low pressure inert gas electrical discharge; (c) chemical reduction of a solution initially containing the metal in soluble form; and (d) thermal decomposition of a metal-organic compound which has been applied to the inside by painting a solution of the metal-organic compound in an organic solvent on the interior surface **20** of the test tube **10,** drying the solvent, and then converting the remaining film to metallic gold (or other noble metal) by heating the test tube **10** above the decomposition temperature of the metal-organic compound.

To facilitate heating of the test tube for purposes to be described hereinafter, outer surface **24** of the test tube **10** preferably has a black coating thereon. Such a black coating can consist of a black oxide coating which is applied to the outer surface **24** after the outer surface **24** has been sandblast roughened. After being applied, the black oxide coating is fused in place.

According to the teachings of the invention, the test tube is preferably made from a glass which transmits infra-red radiation and ultraviolet light radiation. In this respect the test tube **10** is preferably made from high silica **2537** angstrom transmitting glass.

The flared flange **18** at the open end **16** facilitates the insertion of a stopper **26** in the tube **10** as shown in FIG. **4.** However, for practicing the method or for utilizing the system of the invention, a flared open end is not essential.

The test tube **10** with the gold coating **22** enables one to utilize a very simple and accurate procedure for analyzing the concentration of mercury in a sample. Briefly this procedure involves the placing of a sample, or the passing of a given amount of sample through the test tube **10** in such a way that at least a portion, if not substantially all of the mercury in the sample, is adsorbed by the gold coating **22.** Then the sample is removed from the tube **10** and the tube **10** is stoppered as shown in FIG. **4.** It is now ready for making an analysis of the mercury in the sample by analyzing the mercury adsorbed by the gold coating **22.** This is accomplished by rapidly heating the test tube **10** to vaporize the mercury from the gold coating **22.** Ultraviolet light in the mercury absorption band width, namely, **2537** angstrom ultraviolet light is passed axially through the tube and the amount of light which is transmitted through the tube is detected and compared with a measurement of light through the tube with mercury-free air therein. The difference in the light transmission measurements is indicative of the concentration of mercury in the sample.

As will be described hereinafter, the sample can be a liquid or gas. A device **30** is shown in FIG. **2** for sampling a gas. The device **30** includes a housing **32** having a plurality of openings or ports **34** which extend through the upper surface of the housing **32.** In FIG. **2,** the housing **32** has eight such ports **34.** Each of the ports **34** is adapted to receive one of the test tubes **10** in inverted position, that is to say, with the closed end **12** up, as shown in FIG. **2.**

Positioned within each one of the openings **34** is a pipe **36,** a portion of which extends above the upper surface of the housing **32** such that an upper end **38** of each pipe **36** extends into a test tube **10** received in the associated opening **34** and opens at the upper end **38** into the test tube adjacent the closed end **12** of the test tube **10.** In this way gas sample which is injected into the tube **10** through the pipe **36** will enter the test tube **10** adjacent the closed end **12** and flow downwardly therefrom along and past the gold coating **22** in the test tube **10** as best shown in FIG. **3.** It will be appreciated that by injecting the gas sample into the test tube **10** with the pipe **36** one is assured that substantially all of the gas sample will flow past the gold coating **22** on the inner surface **20** of the test tube **10.**

In FIG. **3** is illustrated the structure within the housing **32** beneath one of the openings **34.** This structure for receiving and holding a test tube in proper location relative to the pipe **36** includes a block **40.** The block **40** has a top side **41** and a bottom side **43** with an inlet opening **44** opening onto the bottom side **43** and a cavity **46** which opens onto the top side **41.** Extending between and communicating with the cavity **46** and the inlet opening **44** is a passageway **48** in which an inner end **50** of the pipe **36** is received and fixed in place. As shown in FIG. **3** the block **40** has a spigot **52** and an outlet opening or passageway **54** which extends through the spigot **52.** The spigot **52** has a valve member **56** mounted therein for controlling the flow of gas through the outlet passageway **54.** A constriction **58** between the cavity **46** and the passageway **54** limits the rate of flow when the valve member **56** is fully open.

As shown in FIG. **3,** the inverted test tube **10** is supported on the block **40** with the flange **18** resting on the top side **41** and with the open end **16** of the test tube **10** positioned over the cavity **46.** To facilitate proper locating of the test tube **10** over the cavity **46,** a tubular guide member or pipe **64** is positioned in and extends outwardly from the cavity **46.** In this respect one end **66** of the pipe **64** is received and fixed in the cavity **46** with the remainder of the pipe **64** extending outwardly from the cavity **46.** The pipe **64** is shorter in length than the pipe **36** such that an outer end **68** of the pipe **64** is located beneath the upper end **38** of the pipe **36** and beneath the gold coating **22** in the test tube **10** when the test tube **10** is positioned as shown in FIG. **3.** Thus, the outer pipe **64** serves as a means for supporting and holding the test tube **10** in a desired location with the upper end **38** of the inner, smaller pipe coaxial with the test tube **10.**

Since it is not necessary to eject gas toward the closed end **12** of the test tube **10,** the upper end **38** of the pipe **36** ejects air through ports or holes **70** in the side walls of the pipe adjacent the upper end **38** as shown in FIGS. **2** and **3.** In this way a gas is injected into the test tube **10** radially outwardly from the center of the test tube **10** toward the gold coating **22** on the interior surface **20** of the test tube **10.**

The cavity **46** and associated openings located beneath each housing opening **34** can be formed in an individual block or in a large block which contains a plurality of cavities and associated openings.

To minimize undesired adsorption and cross-contamination between samples, it is desirable to coat the gas conducting channels, such as the interior of the pipe **36,** which carry the gas to be analyzed into the test tube **10** with a material which has a very low adsorption of mercury. It has been discovered that fluorocarbon plastic such as plastic sold under the trademark Teflon is one such material which adsorbs very little mercury. Thus, according to the teachings of the invention the fluid conducting channels in a mercury analysis apparatus, e.g., in the sampling device **30,** are coated with or made of a fluoro-carbon plastic such as Teflon.

The device **30** is particularly adapted for sampling ambient air by drawing air from the underside of the housing **32** into the opening **44** through the pipe **36** and into the interior of the test tube **10.** This is accomplished by applying a suction to the outlet passageway **54.** The rate of flow of air drawn through the test tube **10** is determined by the size of the flow limiting constriction **58** and the partial vacuum in the outlet passageway **54.** The initiation and termination of the sample air flow is provided by a **90°** rotation of the valve member **56** which is controlled by a timer **74** mounted in the housing **32** adjacent each housing opening **34.** The amount of air sampled will be directly proportional to the duration of the interval during which the valve member **56** is open. Thus, to sample a given quantity of air at a desired time, an operator first places one of the test tubes **10** in one of the openings **34** and over the outer pipe **64** within the housing **32.** Then the operator sets the appropriate timer **74** to initiate the known rate of air flow at the desired time, and to terminate the air flow after a predetermined interval.

It will be understood that since the air or other gas which is sampled is passed through the test tube **10,** not all of the mercury in the gas or air is adsorbed by the gold coating **22.** However, it has been found that for a particular gas, a specific percentage of mercury will be adsorbed by the gold coating **22** from the gas depending upon the flow rate. Accordingly, in practicing the method of the invention, an operator will first draw a sample of air containing a known quantity of mercury through the test tube at a known flow rate. Then after determining the amount of mercury adsorbed by the gold coating **22,** and knowing the amount of air which has been passed through the test tube **10,** the operator can calibrate the sample analyzing device accordingly. Empirical tests have shown that measurements of a standard can be reproduced very accurately with not more than plus or minus 6% error.

With one working model of the test tube **10** and sampling device **30,** a time period of 200 seconds was found to be very adequate for sampling air. The test tube utilized in this working example had an overall length of approximately **15** centimeters with the length of the gold coating within the tube being approximately 6 centimeters. The internal diameter of the test tube was approximately 16 millimeters.

After a predetermined quantity of gas such as air has been drawn or sucked through the test tube **10,** the test tube is removed from the sampling device **30** and stoppered with the stopper **26** as shown in FIG. **4,** unless, of course, an immediate analysis of the contents of the

test tube is to be made. It is contemplated that the device **30** may be used at various locations far removed from analysis equipment hereinafter to be described. Thus, it is contemplated that after the sample is collected in the gold coating **22** of a test tube **10,** the tube **10** will be stoppered as shown in FIG. **4,** and then sent, such as by mail, to an analyzing station or laboratory.

The method and system of the invention can also be utilized in collecting a sample of mercury from a solid by thermally decomposing a solid and passing the vapors resulting from the thermal decomposition through the test tube **10** by suitably connecting the outlet from a thermal decomposition chamber to the inlet opening **44** of the block **40.**

Another way for obtaining an analysis of a solid is by dissolving the solid with an acid, diluting the dissolved solidacid mixture and placing the aqueous solution into test tube **10** and adding a reducing agent to obtain free mercury. Likewise, for making an analysis of a liquid, one can simply place liquid in an aqueous solution into test tube **10** and add a reducing agent. Empirical tests have shown that almost all of the mercury in the solution will be picked up by the gold coating if the solution is agitated, such as by shaking, for at least 5 minutes. In this respect empirical tests have shown that shaking for 20 minutes or more results in an adsorbtion of practically all of the mercury in the liquid by the gold coating **22.** Of course, when analyzing a liquid sample one would first make an analysis of a liquid having a known concentration of mercury therein in order to properly calibrate the analyzing equipment hereinafter to be described.

One procedure which worked very well for analyzing the mercury concentration in a water sample involved the placing of ten cubic centimeters of the water sample directly into the test tube **10** and then adding 2 cubic centimeters of a 1.5 percent hydroxylamine hydrochloride solution. The test tube **10** was then stoppered and shaken for at least fifteen minutes.

When a liquid sample is being analyzed, the test tube **10** is rinsed after the sample is removed therefrom and then dried before being stoppered or before making an analysis of the mercury picked up and adsorbed by the gold coating **22.**

Since mercury is vaporized from the gold coating **22** for ultraviolet light absorption within the tube **10,** the tube **10** can be referred to as an absorption cell in addition to a sample collecting tube. By combining the absorption cell into the collecting and sampling tube, the present invention obviates, if not altogether eliminates, the problems incurred with previously proposed mercury analysis systems. In this respect, there is no transferring of a fluid sample from a collecting container or tube to an absorption cell for analysis of the mercury concentration in the fluid sample.

After each sample is made, the test tube will be given an identification marking or number to identify what was sampled, where and when. This information will preferably be in a code which can be sensed and then printed with the analysis of the mercury adsorbed by the gold coating **22.**

As previously described, the analysis involves driving out or vaporizing the mercury from the gold coating **22** and then making an analysis of the amount of mercury vapor driven from the gold coating **22.** This is accomplished according to the method and system of the invention with a vaporizing and analyzing apparatus **80** shown in FIG. **5.** The apparatus **80** includes a housing **82** in which are mounted components of the apparatus **80** including electronic circuit elements. The apparatus **80** also includes a test carrier **84** in which a plurality of test tubes **10** are carried in a generally inverted upright position. The carrier is received in an opening **86** in the front side of the housing **82.** Preferably the housing **86** includes a suitable mechanism for indexing the carrier **84** into and through the housing **82** each time the analysis of the mercury in the gold coating **22** in one of the test tubes **10** is completed whereby a plurality of test tubes **10** can be analyzed automatically. Also the apparatus **80** includes a printer **87** (FIG. **7**) which provides a print-out tape **88** on which the analysis of the mercury adsorbed by the gold coating **22** in each of the test tubes **10** is printed together with identifying code information carried by each test tube **10.**

A generally cylindrical device **90** for vaporizing mercury from the gold coating **22** in each of the test tubes **10** carried by the carrier **84** is situated above the opening **86.** The interior diameter of the device **90** is slightly larger than the outer diameter of the test tube **10,** so that the device **90** can be easily received over the closed end **12** of the test tube **10.** Also, the device **90** is movably mounted in the opening **86** for movement from a raised position shown in FIG. **5** to a lowered position shown in FIG. **6** where the vaporizing device **90** is received over the portion of one of the test tubes **10** extending upwardly from the carrier **84.**

The vaporizing device **90** consists essentially of an infra-red heater which includes a heating coil or element **94** imbedded in a material **96** having high emissivity in the infrared spectral region. The vaporizing device or heater **90** is designed to rapidly heat the upper portion of the inverted test tube including the closed end **12** and the portion of the tube **10** which has the gold coating **22** on the inner surface **20** thereof. It will be appreciated that the black coating on the exterior surface **24** of the test tube **10** enhances the rapid heating of the portion of the test tube **10** located within the heater **90.** Also the black coating prevents undesirable reflection, of the infra-red heat applied to the test tube **10,** by the gold coating **22.** The heater **90** is operable to heat the gold coating **22** to a temperature between 400° centigrade and 1,300° centigrade. The higher the temperature the faster the mercury in the gold coating **22** is vaporized. However, the higher the temperature the greater the insulation required for the various components of the apparatus **80.** Experience has shown that the higher temperatures, although desirable for rapid heating of the test tube **10,** are somewhat undesirable in view of the heat-dissipation problems incurred therewith. Very good results have been obtained however, by utilizing an electric current through the heating element **94** which is sufficient to raise the temperature of the test tube **10** to approximately 1000° centigrade.

The rapid heating of the test tube **10** to a temperature on the order of 1,000° centigrade produces very desirable results in that a thin film of hot air and mercury vapor is quickly generated along the surface of the gold coating **22.** This vapor rises in the inverted test tube **10** and forms a bubble of hot air and mercury vapor at the closed end **12** of the test tube **10.** Although mercury vapor is heavier than air, the heated air and mercury vapor mixture is buoyant on the cooler air within the

test tube. As a result, the mercury vapor tends to remain at the upper end of the test tube **10** as shown in FIG. **6**.

During the heating of the test tube **10**, the heated gas within the upper part of test tube **10** expands and it is desirable to allow the displaced cooler gas (air) to escape from the test tube **10**. For this reason, the test tube **10**, when positioned underneath the heater **90**, has the lower end thereof in communication with a passageway **100** in a block **102** as shown in FIG. **6**. The passageway **100** extends vertically downwardly into a block **102** and then communicates with an outlet or vent passageway **104** in the block **102**. Typically, the passageway **104** vents to atmosphere.

From the foregoing description it will be understood that when a test tube is indexed to a position beneath the heater **90**, the lower open end **16** of the test tube **10** is in registry with the passageway **100** so that the test tube is vented. Then, when the upper portion of the inverted test tube **10** is heated and the gases in the test tube expand, the cooler gas or air within the test tube is forced out of the test tube by the expanding heated gases and mercury vapor.

It will be appreciated that if the gold coating **22** on the interior surface **20** of the test tube **10** extended further toward the open end **16** thereof, a greater amount of mercury vapor would be vaporized from the gold coating **22** into the test tube **10**, and very possibly forced out of the test tube **10** through the vent passageway **104** by the heated expanding gases within the test tube **10**. This possibility of losing some of the mercury vapor creates a limitation on the length of the gold coating **22** relative to the overall length of the test tube **10**. As described previously, a gold coating length to tube length ratio of approximately 0.40 has been found to work quite satisfactorily for obtaining a significant sample of mercury none of which is lost during heating of the test tube **10**.

After the mercury in the gold coating **22** has been vaporized, an analysis of the amount of mercury vapor to determine the concentration of mercury in the sample from which the mercury vapor was originally obtained, is made by passing ultraviolet light axially through the test tube **10** and the mercury vapor therein. In the illustrated embodiment of the apparatus **80**, this is accomplished with a light source **106** which directs light to a prism **108** mounted above the heater **90** in position to reflect light downwardly through an opening **110** in the top of the heater **90**. The prism **108** is located to direct light downwardly along the axis of the test tube **10**.

The ultraviolet light from the source **106** is in the **2537** angstrom band width which is the band width of ultraviolet light that is absorbed by mercury vapor. To minimize any optical aberrations which may be incurred as a result of passing the ultraviolet light through the heated closed end **12** of the test tube **10** and the heated gases within the test tube **10**, a quartz diffuser **112** is situated between the source **106** and the prism **108** for diffusing the light that is passed through the test tube **10**. As shown in FIG. **6**, the light passing through the test tube **10** passes through the passageway **100** and thence through an ultraviolet band width pass filter **114** to a photodetector **116**. The filter **114** prevents any extraneous light or radiant energy from reaching the photodetector **116** such as light from the heated gold coating **22**. Typically the light source **106** is continuously on such that ultraviolet light is continuously passing through the test tube **10**. The detector **116**, however, is only switched on at certain times. In carrying out the method, the apparatus **80** is programmed to heat the test tube **10** for a predetermined period of time and then to switch on the photodetector **116** which will immediately sense the amount of ultraviolet light passing through the mercury vapor in the test tube **10**. Then, after a measurement has been made of the ultraviolet light passed through the test tube **10**, the detector **116** will be turned off. Next, the mercury vapor laden air is flushed from the test tube **10** with mercury-free air. This is accomplished by injecting mercury-free air into the test tube **10** from a nozzle **118** mounted in the block **102** in position to direct air therefrom upwardly along one side of the test tube **10** as best shown in FIG. **6**. The flow of air through the nozzle **118** is controlled by a valve shown schematically at **120**. Typically, the flushing air is ambient air which is passed through a filter **122**. The filter **122** can contain manganese dioxide and/or activated charcoal.

After the mercury vapor laden air has been flushed from the test tube **10** and only mercury free air is therein, the photodetector **116** is again activated and another measurement of ultraviolet light reaching the photodetector **116** is made. The difference between these measurements is indicative of the amount of mercury vapor in the test tube **10**.

In FIG. **7** is illustrated a schematic block diagram of an electronic circuit for comparing the light transmission measurements and then converting the difference to a signal value which is related to the numerical value in parts per billion (PPB) of mercury in the fluid sample. This numerical value is then printed out on the tape **88**. The electronic circuit can also be calibrated to print out the concentration of mercury in nanograms. As shown in FIG. **7**, the signal generated by ultraviolet light reaching the photodetector **116** is first applied to a circuit **122** where it is amplified and logarithmically converted such that the output signal from the circuit **122**, typically a voltage signal, is proportional to the logarithm of the intensity of the 2537 angstrom radiation striking the photodetector **116**. The first signal obtained from ultraviolet light passing through the mercury vapor laden air is identified as V_1 and is stored in a first memory M_A. The second voltage signal derived from ultraviolet light passing through mercuryfree air in the test tube **10**, is designated V_2 and is stored in a memory M_B. The two voltage signals V_2 and V_1 are then applied to a subtractor S_A where the first voltage signal V_1 is subtracted from the second voltage signal V_2. The difference signal (V_2-V_1) is then applied to a multiplier **124**. A stored multiplicand which is determined from the measurement of a fluid sample standard having a known concentration of mercury therein is applied to the multiplier **124** for multiplying the difference signal to obtain an output signal from the multiplier **124** which is directly related to the numerical value of the concentration of mercury in parts per billion. This signal is then applied to the printer **97** which prints out the numerical value of the tape **88**.

Ultraviolet light is also absorbed by some organic vapors and, to avoid inaccurate measurements of light intensity as may be occasioned by the absorption of some of the ultraviolet light by organic vapors in the test tube **10**, it may be desirable to make measurements of ultraviolet light of a wavelength which is not absorbed by mercury. For this purpose the apparatus **80** of the mer-

cury analysis system can include a second light source **130** as shown in FIG. **6.** Also the electronic circuit can be modified to include the additional memories M_C and M_D and an additional subtractor S_B as shown in FIG. **8** connected between the subtractor S_A and the multiplier **124.** The light from the source **130** is preferably of a wavelength band which is near to the 2537 angstrom band but which does not include the 2537 angstrom wavelength which is absorbed by mercury vapor.

With the modifications to the system as just described, the analyzing procedure is modified in the following manner. After passing light from the light source **106** through the mercury vapor laden air in the test tube **10** to obtain the signal V_1, light from the light source **130** is passed through the mercury vapor laden air to obtain a second signal V_2 which is stored in the memory M_B. The difference $V_2 - V_1$ is determined by the subtractor S_A and the result stored in the memory M_C. Then, after the mercury laden air has been flushed from the test tube **10** by mercury free air, a third signal V_3 is obtained by passing light from the source **106** through the mercury free air and the logarithmic signal value V_3 is stored in the memory M_A. Then a fourth signal V_4 is obtained by passing light from the source **130** through the mercury free air and stored in the memory M_B. The difference $V_4 - V_3$ is determined by the subtractor S_A and the result stored in the memory M_D.

The two difference signals stored in the memories M_C and M_D are then applied to the subtractor S_B where the second difference signal (V_4–V_3) is subtracted from the first difference signal (V_2–V_1), the resulting difference signal then being applied to the multiplier **124.** In this way, any ultraviolet radiation which is absorbed by vapors in the test tube other than mercury vapor, are cancelled out of the measurement of mercury vapor so that the numerical value printed out on the tape **88** by the printer **126,** is more accurate.

Experience has shown however, that the modified circuit and the additional light source **130** may not be necessary since in most cases the vapors in the tube are oxidized by the heat from the infra-red heater **90** and the oxidized organic vapors generally do not absorb ultraviolet light in the mercury absorption band width of **2537** angstroms.

In FIG. **9** there is illustrated a modified mercury analysis system or apparatus **180** where a fixed cell or vessel **210** is utilized in place of movable tubes **10.** The apparatus **180** is particularly useful for "on-the-spot" analysis of food (by thermal decomposition) or gases. The vessel **210** is positioned in a generally upright position and has an upper end **212,** a lower end **216,** an inner surface **220** with a gold coating or film **222** thereon and an infra-red absorbing layer **224** on the outer surface of the vessel **210.** A gas input line **230** is connected to the upper end **212.** A vacuum line **232** also is connected to the upper end **212.** A second vacuum line **234** and a clean air input line **236** are connected to the lower end **216.** An infra-red heater **290** surrounds the vessel **210** in the general area of the gold coating **222.** A reflector **292** surrounds the heater **290** and has a quartz window **310** therein above the upper end **212.** An ultraviolet light source **312** is situated above the quartz window. Beneath the lower end **216** is a **2537** angstrom band pass filter **314** and a photo detector **316.** Cooling air is supplied to the interior of the reflector through line **318.**

Each gas or air line has a suitable control valve therein and by programming the operation of the valves, the heater **290** and the detector **316,** mercury from a given amount of a gas sample first can be concentrated in the gold coating **222** followed by the thermal release of mercury vapor from the coating **222** and buoyant maintenance of the vapor in the generally vertical optical path between light source **312** and photodetector **316.** Then a first light transmission measurement is made, the vessel **210** is flushed with mercury-free air, a second light transmission measurement is made and the measurements are compared to determine the concentration of mercury in the gas sample.

It has been found that the mercury analysis system of the present invention utilizing the apparatus **80** or **180** enables an operator to make a mercury concentration analysis in a time period from three to five minutes which is a much faster time than obtained with many of the previously proposed mercury analysis systems. Also it has been found that the mercury analysis system of the present invention is very sensitive in that readings of 0.01 parts per billion (PPB) can be obtained therewith.

From the foregoing description it will be readily apparent that the mercury analysis system and method of the present invention provide a number of advantages some of which have been described above and others of which are inherent in the invention. Some of these advantages are as follows: (1) The system is very sensitive. (2) It is very flexible and enables one to make analysis of gases, liquids and solids such as food stuffs. (3) The system is very simple and the simplicity is enhanced by combining the sample collection tube and absorption cell into one test tube. (4) This simplicity also minimizes, if not altogether eliminates, losses and cross-contamination. (5) The fluid sampling time and the analysis time are very short, thereby facilitating the analysis of numerous samples. (6) The system is very economical in that one vaporizing and analyzing apparatus can be used for any number of field collecting test tubes **10.** (7) The results obtained are readily reproducible within a plus or minus 6 percent error.

From the foregoing description it will also be apparent that modifications and variations can be made to the test tube, method and system of the present invention without departing from the spirit or scope of the invention. Accordingly, the present invention is only to be limited as necessitated by the accompanying claims.

What it is desired to be secured by Letters Patent of the United States is:

1. A method for analyzing the concentration of mercury in a fluid including the steps of: placing a given amount of a fluid sample in a vessel having a predetermined interior side surface area coated with a noble metal which has a strong affinity for mercury, such that at least a portion of the mercury in said sample is adsorbed by said noble metal coating; removing said sample from said vessel; positioning said vessel in a generally upright position with a first end of said vessel above a second end of said vessel and with said second end vented; heating said vessel to a given temperature to release mercury vapor from said noble metal coating; passing endwise through said vessel an ultraviolet light of a wave length band which is absorbed by mercury vapor; measuring the

amount of said light transmitted through the mercury vapor laden air within said vessel; flushing said mercury vapor laden air from said vessel with mercury-free air; passing said ultraviolet light endwise through said vessel having mercury-free air therein; measuring the amount of said light transmitted through said mercury-free air; and comparing the first light transmission measurement with the second light transmission measurement, the difference between said measurements being indicative of the concentration of mercury in said fluid sample.

2. The method according to claim 1 wherein said fluid is a gas and said steps of placing sample and removing sample from said vessel consists in passing said gas through said vessel at a given flow rate for a given time period.

3. The method according to claim 2 wherein said gas is injected into said vessel at a point near said first end of said vessel so that said gas flows along and adjacent the interior noble-metal-coated surface of said vessel and out said second end of said vessel.

4. The method according to claim 2 wherein said gas is injected into said vessel through a pipe which extends into said vessel at said second end and opens into said vessel adjacent said first end and said gas is caused to flow through said pipe into said vessel along and adjacent the interior noble-metal-coated surface of said vessel and out said second end of said vessel by applying a vacuum to said second end of said vessel.

5. The method according to claim 2 wherein said vessel is positioned in a generally upright position while said gas is being passed through said vessel.

6. The method according to claim 1 wherein said fluid sample is an aqueous solution and said method includes the steps of adding a reducing agent to the given amount of aqueous solution in said vessel; sealing said vessel; and agitating said aqueous solution and reducing agent for a given period of time to facilitate reduction of mercury compounds to free metal mercury and to facilitate adsorption of said mercury by said noble metal coating.

7. The method according to claim 6 wherein said aqueous solution sample includes dissolved solids and said method includes the initial steps of; dissolving a solid in an acid and diluting the acid-dissolved solid with water to form the aqueous solution sample.

8. The method according to claim 7 wherein said solid is a foodstuff.

9. The method according to claim 6 wherein said step of agitating said solution consists essentially in shaking said vessel.

10. The method according to claim 6 wherein said aqueous solution is agitated for at least five minutes.

11. The method according to claim 6 including the steps of rinsing and drying said vessel prior to heating said vessel.

12. The method according to claim 6 wherein said sample consists essentially of approximately ten cubic centimeters of water and said reducing agent consists essentially of approximately two cubic centimeters of an approximately 1.5 percent hydroxylamine hydrochloride aqueous solution.

13. The method according to claim 1 wherein said fluid sample is a gas sample including vapors from a thermally decomposed solid and said method includes the initial step of thermally decomposing a solid to obtain vapors which form said fluid sample.

14. The method according to claim 1 wherein said noble metal is gold.

15. The method according to claim 1 wherein said vessel is heated to a temperature between 400°C and 1,300°C.

16. The method according to claim 1 wherein said vessel is heated by infra-red radiation.

17. The method according to claim 2 including the initial step of filtering said gas to remove undesirable particles therefrom.

18. The method according to claim 1 wherein said ultraviolet light is diffused before being passed endwise through said vessel.

19. The method according to claim 1 including the step of preheating said fluid sample to vaporize mercury in any solid particles carried in said sample.

20. The method according to claim 1 including the steps of amplifying and logarithmically converting the light measurements to signal values which are directly related to the concentration of mercury in said fluid sample.

21. The method according to claim 20 including the steps of subtracting said first signal value from said second signal value; multiplying the difference by a predetermined multiplicand to obtain a numerical value in parts per billion; and printing said numerical value.

22. The method according to claim 1 including the steps of: passing through said mercury vapor laden air ultraviolet light of a second wavelength band which is near to, but which does not include, said mercury absorption band; measuring the amount of said light having said second wave length which is transmitted through said mercury vapor laden air to obtain a light transmission measurement; passing said light having said second wave length band through said mercury-free air; measuring the amount of said light having said second wave length band which is transmitted through said mercury-free air to obtain a light transmission measurement; amplifying and logarithmically converting said light transmission measurements to signal values proportional to the logarithm of said light transmission measurements; subtracting said first signal value derived from the measurement of transmission through said mercury vapor laden air of ultraviolet light of a wavelength band which is absorbed by mercury vapor, from said signal derived from the measurement of transmission through said mercury vapor laden air of ultraviolet light of said second wave length band to obtain a first difference signal; subtracting said signal value derived from the measurement of transmission through said mercury-free air of ultraviolet light of said wave length band which is absorbed by mercury vapor from said signal derived from the measurement of transmission through said mercury-free air of ultraviolet light of said second wave length band to obtain a second difference signal; and subtracting said second difference signal from said first difference signal to obtain a signal value which is related to the concentration of mercury in said fluid sample and which has had subtracted therefrom the undesired effects of ultraviolet light absorption by other vapors which may be in said vessel in addition to mercury vapor.

23. The method according to claim 22 including the steps of multiplying said last signal value by a given multiplicand to obtain a numerical value in parts per billion; and printing said numerical value.

24. A mercury analysis system including a vessel having a noble metal coating on an interior side surface thereof and being supported in a generally upright position with an upper end of the vessel above a lower end and with the lower end of the vessel vented, means for vaporizing mercury stored in said noble metal coating, and means for analyzing the mercury vapor, said analyzing means including a source of ultraviolet light of a wave length band which is absorbed by mercury vapor, said source of ultraviolet light being positioned to pass ultraviolet light endwise through the vessel, means for detecting the amount of light transmitted through the vessel, and means for flushing mercury vapor laden air from the vessel.

25. The system according to claim 24 including an electronic circuit connected to said detecting means, said electronic circuit including means for amplifying signals generated by light detected by said detecting means and for logarithmically converting the generated signals to signal values related to the concentration of mercury in the mercury vapor laden air, means for memorizing a first generated signal related to the light transmitted through mercury-laden-vapor, means for memorizing a second generated signal related to the light transmitted through mercury-free air, and means for subtracting the first signal from the second signal to obtain difference signal directly related to the concentration of mercury in the mercury vapor laden air.

26. The system according to claim 25 including means for printing the mercury analysis measurement in parts per billion and wherein said electronic circuit includes a multiplying means connected between said subtracting means and said printing means for multiplying the difference signal by a predetermined multiplicand.

27. The system according to claim 25 including a second source of ultraviolet light of a wavelength band which is near, but which does not include, the mercury vapor absorption band, said second source being positioned to pass ultraviolet light endwise through the vessel at predetermined times, and wherein a memorizing means is operable to memorize a generated signal obtained when ultraviolet light from said second source is passed through the mercury vapor laden air in the vessel; a memory means is operable to memorize a generated signal obtained when ultraviolet light from said second source is passed through mercury-free air in the vessel, said subtracting means being operable to subtract said first signal obtained when ultraviolet light from said first source is passed through the mercury vapor laden air in the vessel from said signal obtained when ultraviolet light from said second source is passed through the mercury vapor laden air in the vessel to obtain a first difference signal, memory means operable to memorize a third signal obtained when ultraviolet light from said first source is passed through mercury-free air in the vessel, memory means operable to memorize a fourth signal obtained when ultraviolet light from said second source is passed through mercury-free air in the vessel, said subtracting means being operable to subtract said third signal from said fourth signal to obtain a second difference signal, and said electronic circuit includes a means for memorizing said first difference signal and a means for memorizing said second difference signal and a second subtracting means for subtracting said second difference signal from said first difference signal to obtain a third difference signal which is directly related to mercury vapor vaporized in the test tube and which has had subtracted therefrom the undesired effects of ultraviolet light absorption by other vapors which may be in the vessel in addition to mercury vapor.

28. The system according to claim 27 including means for printing the mercury analysis of a fluid sample in parts per billion and wherein said electronic circuit includes multiplying means connected between said second subtracting means and said printing means for multiplying said third difference signal by a predetermined multiplicand to obtain a numerical value in parts per billion of the mercury concentration in the fluid sample.

29. The system according to claim 24 wherein said flushing means includes a filter for removing mercury vapors from air used as a flushing medium, and a flush nozzle having its outlet orifice arranged to inject flushing air into the lower end of the vessel adjacent one side of the vessel and in a direction generally parallel to the longitudinal axis of the vessel.

30. The system according to claim 24 including an ultraviolet band pass filter situated between one end of the vessel and said detecting means.

31. The system according to claim 24 wherein said vaporizing means is an infra-red heater.

32. The system according to claim 24 wherein said light source is horizontally spaced from the upper end of the vessel and a prism is situated above the upper end of the vessel for reflecting light from said light source downwardly through vessel.

33. The system according to claim 24 including means interposed between said light source and the vessel for diffusing the light from said light source.

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