

[54] MERCURY METAL ANALYZER

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[58] Field of Search 23/253 R, 253 PC, 232 R, 23/254 R, 255 R, 230 PC; 423/99; 75/121

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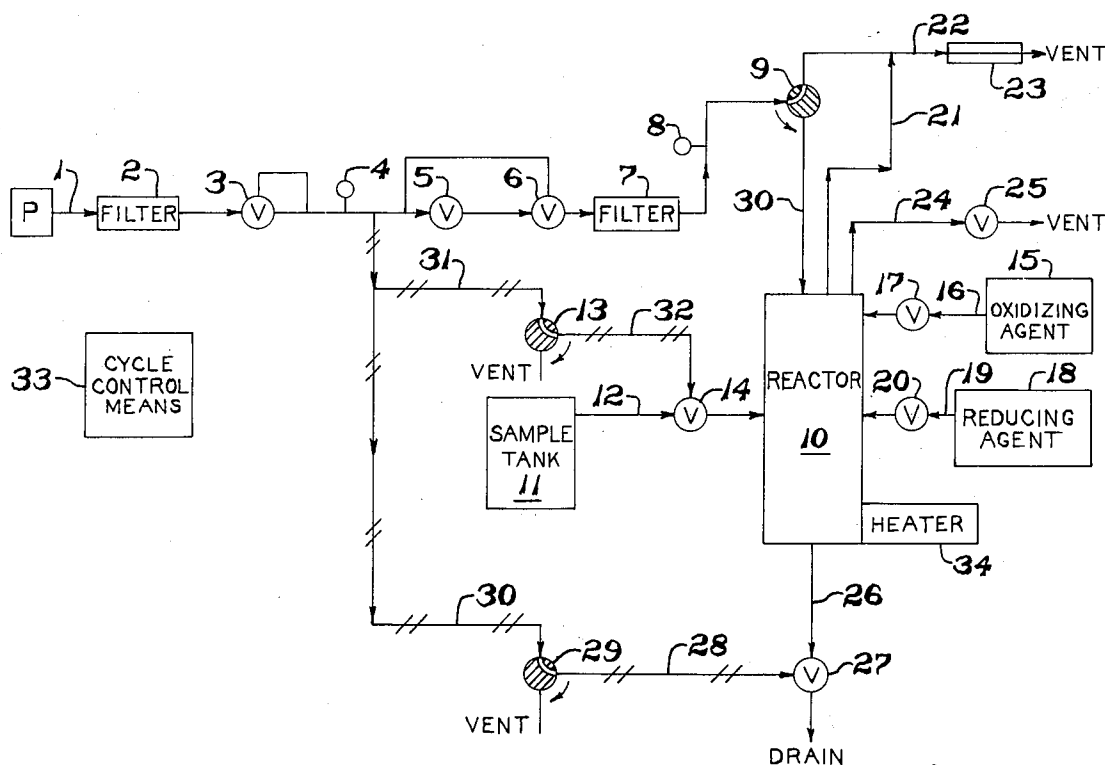
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[57] ABSTRACT

An apparatus for determining the amount of mercury in a liquid or gas sample is provided comprising means for sequentially oxidizing and reducing a non-organic fluid containing mercury combined with organic molecules to form mercury metal and means for passing an inert gas to carry said mercury metal to a UV spectrophotometer wherein the amount of mercury is recorded.

2 Claims, 5 Drawing Figures



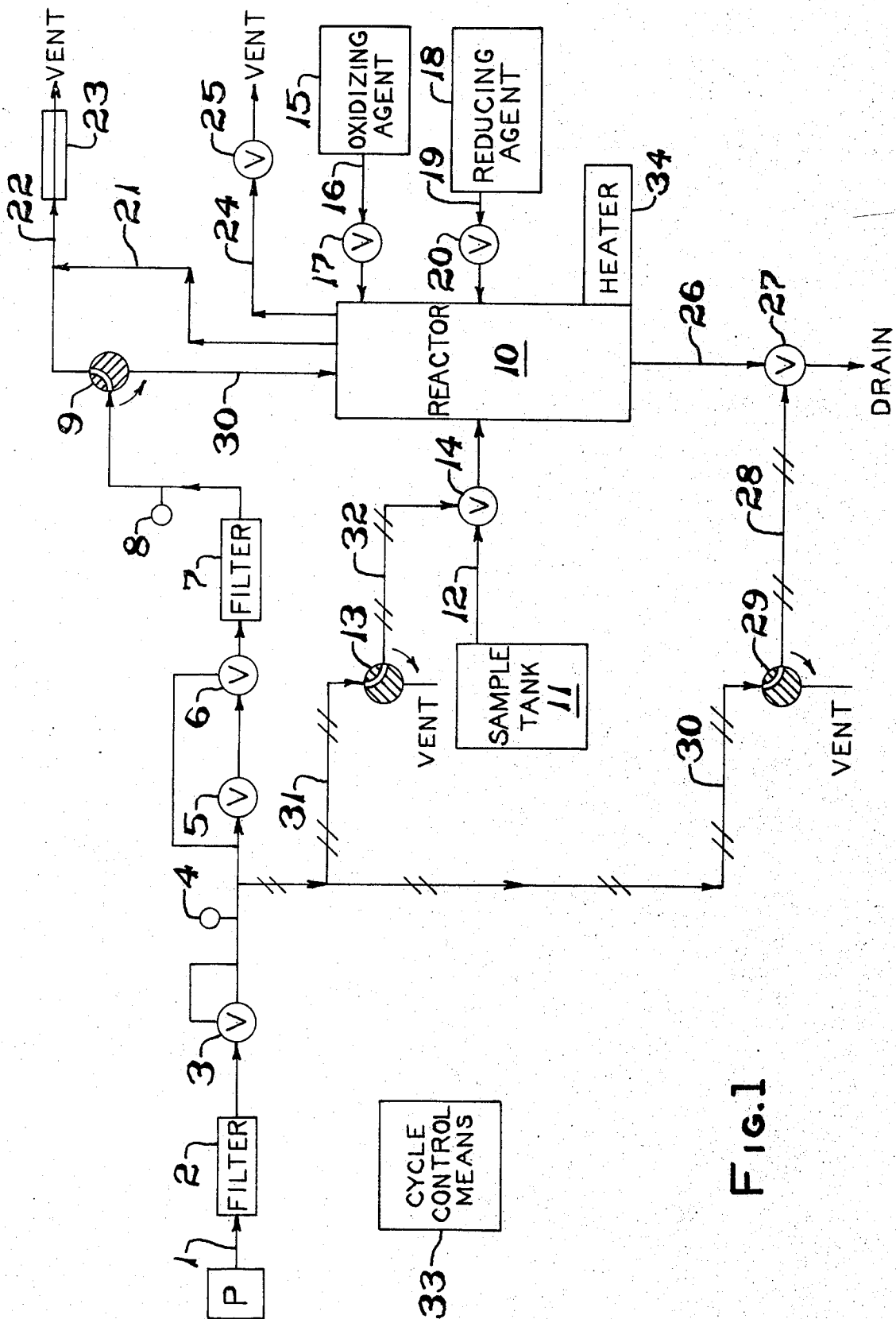


FIG. 1

FIG. 3

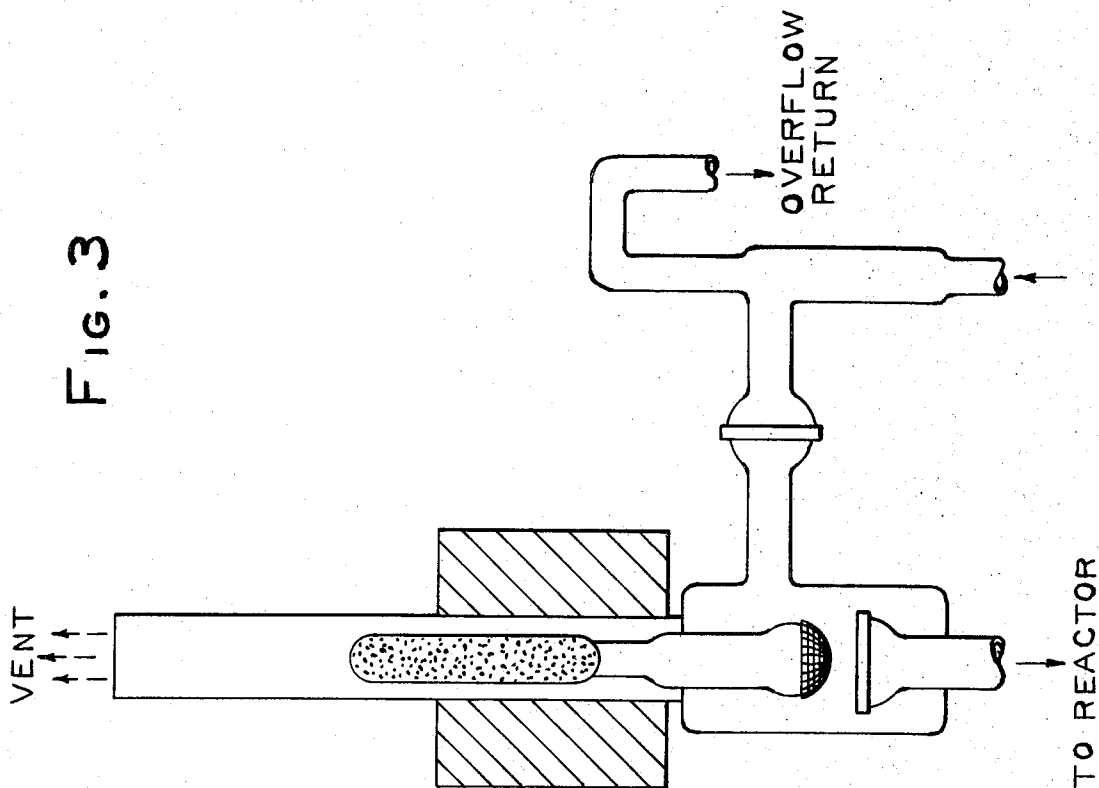
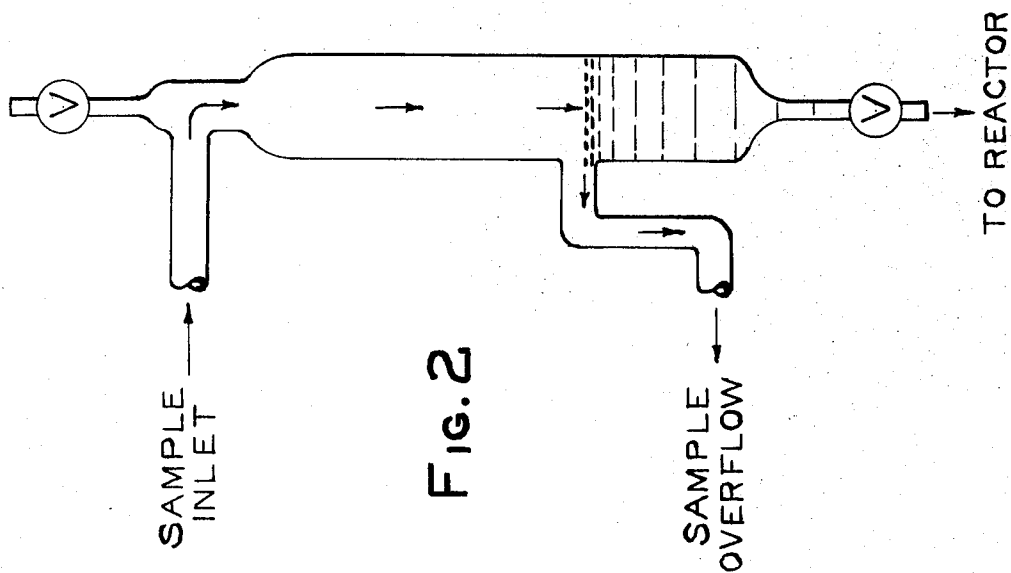


FIG. 2



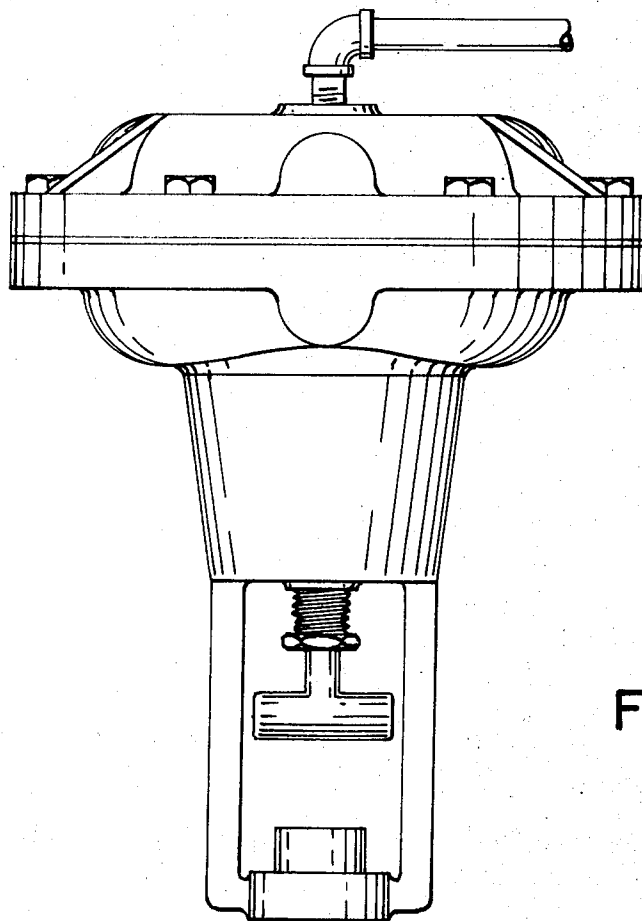
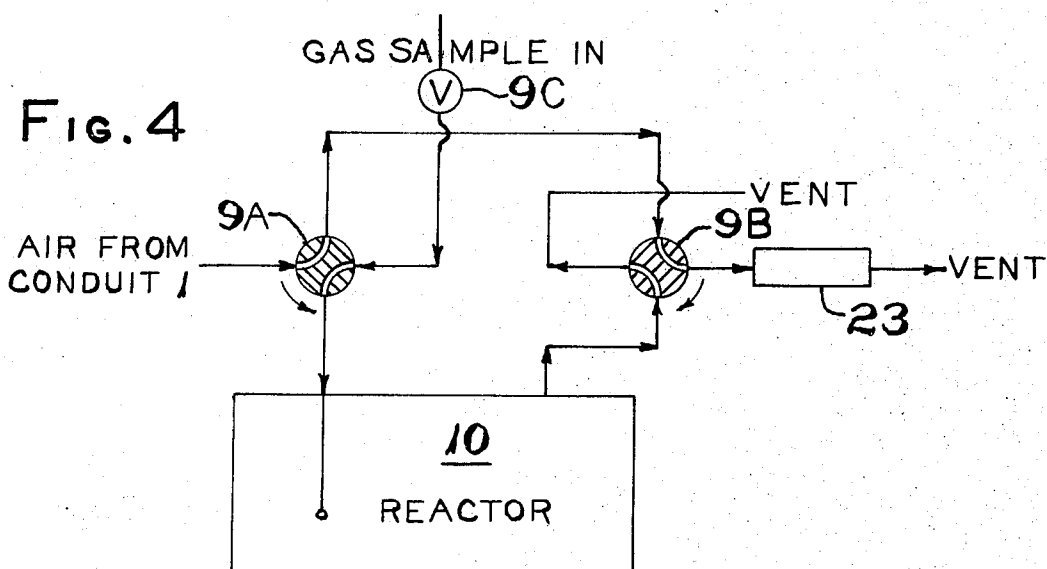


FIG. 5

MERCURY METAL ANALYZER

This invention relates to a semi-automatic or automatic mercury analyzer for determining contamination levels of mercury in a non-organic fluid such as an aqueous solution or gas. More particularly, this invention relates to an analyzer suitable for determining mercury contamination levels in sodium chloride or potassium chloride brines from mercury electrolytic cells and particularly in sewer streams from said cells. Mercury electrolytic cell brines contain from 10 grams to 300 grams per liter of sodium chloride or potassium chloride and, in addition, metallic mercury, mercury ions and mercury combined with organic compounds as a result of bacteria fixation. Sewer samples from mercury operations contain in addition silt, asbestos, calcium and iron compounds and various flocculents.

Because of the desire to minimize mercury pollution and particularly mercury pollution from mercury electrolytic cells, it has become necessary to regularly analyze for mercury in waste streams. Moreover, because the amount of mercury pollution varies from time to time during the operation of an electrolytic cell, it is desirable to make regular analyses. Accordingly, an apparatus has been desired which is semi-automatic or preferably automatic and which can regularly analyze for mercury metal in aqueous and gas fluids particularly mercury electrolytic cell sewer brines.

It has now been discovered that the amount of mercury in a fluid can be periodically and automatically determined by a novel apparatus which can be installed as part of a fluid system or employed as a self-contained portable unit. Moreover, said apparatus is suitable for analyzing all types of non-organic fluids including inert gases such as air, and liquids such as water but is particularly efficacious for mercury electrolytic cell sewer brines.

The term "non-organic" means that the fluid does not contain any appreciable amount of organic material (other than the minor amount combined with the mercury) such as oil, or an unusually large amount of oxidizing agent will be required to free the mercury as the metal. Generally the fluid will not contain more than trace amounts of organic material uncombined with mercury.

Reference is now made to the accompanying drawings in which:

FIG. 1 is a schematic illustration of the overall system of the present invention;

FIG. 2 is a gravity flow sample dispenser;

FIG. 3 is a gravity flow oxidant or reductant dispenser;

FIG. 4 is a complex valve system; and

FIG. 5 is a free-flowing pneumatic pinch clamp valve.

Referring now to FIG. 1 wherein reference numerals are used to indicate parts in the analyzer, the following description is a preferred embodiment of the invention adapted for liquids such as aqueous samples.

The system comprises a gas inlet pressure header connection feed suitable for connection to a gas line containing contaminant-free air or other inert gas. A conduit 1 connects the inlet header P to a filter 2, a pressure regulator 3, a pressure indicator 4, a hand control valve 5, a differential flow control regulator 6, a filter 7, a flow indicator 8, a three-way solenoid control valve 9, and in turn to reactor 10. The pressure reg-

ulator 3 controls the operating pressure of the system and furnishes air pressure to the flow control system comprising hand control valve 5, differential flow control regulator 6, and flow indicator 8, and said pressure regulator 3 also furnishes air pressure to control valves 14 and 27. Filter 7 is a chemical filter containing suitable chemicals to remove residual contaminants which could be detected by spectrophotometer 23. The hand control valve 5 provides a means for setting the flow of air within the system. A liquid, containing mercury compounds, contained in sample tank 11 (sample tank is illustrated in FIG. 2) is connected through conduit 12 to pressure operated valve 14 to reactor 10. Said pressure operated valve is operated by activating solenoid valve 13 allowing the air pressure in conduit 32 to pass to valve 14. Oxidizing agent contained in tank 15 is connected through conduit 16 to solenoid valve 17 and to reactor 10. Reducing agent contained in tank 18 (dispensers for tanks 15 and 18 are illustrated in FIG. 3) is connected through conduit 19 to solenoid valve 20 and reactor 10. Spectrophotometer 23 is connected by conduits 21 and 22 to reactor 10. A recorder, not shown, can be a part of the spectrophotometer or electrically connected to said spectrophotometer. Conduit 24, connected to reactor 10 and solenoid valve 25, provides a means for removing air pressure so that the oxidant, reductant and sample can be gravity fed to the reactor. Conduit 26 between reactor 10 and pressure operated valve 27 is for draining the reactor, and conduit 28 connected to pressure operated valve 27 and solenoid valve 29 is joined with conduit 30 so that said pressure operated valves can be activated. Electrical cycle control means 33 is connected to said solenoid valves, and pumps (not shown) and to the spectrophotometer and recorder by conventional time cycling units which control the solenoid valves. These time cycling units include the other electrocomponents of the system and may be set by suitable manual switches so as to initiate an automatic cycle of operation. This type of cycling circuitry is widely utilized in control of process gas chromatographs, and automatic washers and dryers. The invention is not directed to the details of any specific cycling circuit, and thus the details of such circuits are not necessary to the understanding of the invention.

Heater 34 is for heating the reactor, oxidant and sample.

The particular sequence of the functions of operations of the valves and electrical components is as follows for a liquid sample. Upon initiation, valves 14 and 25 open allowing a measured amount of sample to drain into the reactor. Said valves close after valve 17 opens and closes to deliver the predetermined amount of oxidizing agent into the reactor. Heater 34 begins to heat the sample and shuts off after the mercury-containing sample is oxidized. Valve 25 opens allowing the pressure to be released, followed by the opening of valve 20 which allows reducing agent to be passed into the reactor and then said valves close. The UV spectrophotometer 23 is then set for a 0 reading of mercury with air passing through the spectrophotometer from solenoid valve 9. After the mercury in the sample is reduced to free mercury metal, solenoid valve 9 is activated and the mercury metal is carried from the reactor through conduits 21 and 22 to spectrophotometer 23 by the contaminant-free air entering from conduit 30 at 1 to 2 liters per minute. The spectrophotometer and

recorder are activated and the amount of mercury is recorded as the mercury is passed through the spectrophotometer to a vent. Valves 29 and 27 are then activated so that the reactor may drain. Valve 27 is closed and the system is purged by deactivating solenoid valve 9.

FIG. 3 is an oxidizing or reducing agent dispenser depicted in the open position. The central stopper containing iron filings is raised by means of the adjacent electromagnetic coil.

FIG. 4 is a complex valve system which adapts the analyzer for use with both liquid and gas samples. The system comprises a sample inlet valve 9C and two four-way solenoid valves 9A and 9B which replace valve 9. These valves are shown in the position to permit air entering from conduit 1 to be shunted past the reactor. Oxidizing agent is fed from valve 17, heater 34 is activated and then a measured amount of mercury-containing gas sample is passed through valve 9A to reactor 10. The mercury-containing gas sample is oxidized and the mercury-free air vented through valve 9B. Valve 9C closes, and the reducing agent is introduced into the reactor through valve 20. Valves 9A and 9B are then simultaneously rotated 90° in the direction as indicated, valve 9C opens again and air from conduit 1 is fed through valve 9A into reactor 10 to strip the mercury metal from the solution and carry it through valve 9B to spectrophotometer 23 for analysis, and then vented. Valve 14 which regulates liquid samples would be inactivated when the apparatus was employed for gas samples.

To adapt the analyzer for use only on mercury-containing gas samples, conduits 12, 31, 32 and valves 13 and 14 would be eliminated.

Another preferred embodiment of the invention is the pneumatic pinch clamp of FIG. 5. This valve permits unrestricted flow of sample so that samples containing up to 10 or 15 percent solids by volume can be handled without the deposit of solids in the valves. The sample conduit made of a flexible material such as rubber, Neoprene, or other material, which can be pinched to stop flow through it and be restored to its original internal diameter when relaxed, is inserted between the stopper and the rod. The stopper is made of a partly flexible material such as hardened rubber. When the valve is air activated, the rod is extended to restrict flow of the conduit. When the air source is removed, a spring returns the rod to a position of rest (as shown) and unrestricted flow of sample containing solids is permitted as the conduit returns to its previous unrestricted internal diameter.

The oxidizing agent preferred for mercury electrolytic cell brines is a solution of 2 percent by weight potassium persulfate in 20 percent by volume sulfuric acid and the reducing agent is preferably a 10 percent solution by weight of stannous chloride in an equal volume of concentrated hydrochloric acid and water. Other conventional reagents can be employed, however, providing that the mercury metal is released in a finely-divided form so that it can be easily removed by the inert gas and passed to the UV spectrophotometer.

The inert gas employed is preferably air but other gases such as nitrogen, and argon can be employed.

The gas flow must be sufficient to strip or carry the mercury metal from the reactor to the spectrophotometer and this will depend upon the size of the reactor,

viscosity of the sample mixture and other variables but can be easily determined by one of ordinary skill. Generally a rate of 1 to 2 liters per minute will be sufficient.

The temperature at which the oxidation and reduction is conducted will depend upon the materials in the solution but generally a temperature of from between about 170°C. and about 200°C. will be sufficient. The oxidation reaction will generally be complete from between 5 and about 10 minutes depending upon the temperature. The reduction reaction is almost instantaneous at room temperature.

When it is desired to analyze for mercury in gaseous mediums such as air, the gas can be sparged into a suitable oxidizing agent, such as sulfuric acid acidified permanganate, while in the reactor.

The rate for gas-containing samples will depend upon the quantity of mercury in the sample and should be adjusted to provide a reading within the limits of the spectrophotometer. All gases shunted to the spectrophotometer must be contaminant free, i.e., be free of materials which prevent an accurate determination of mercury.

While there are above described a number of specific embodiments of the present invention, it is obviously possible to produce other embodiments in various equivalent modifications thereof without departing from the spirit of the invention.

I claim:

1. A mercury-metal analyzer comprising:

- a. a reactor including reactor vent means;
- b. a sample feed means to said reactor;
- c. a reducing agent feed means to said reactor;
- d. a separate oxidizing agent feed means to said reactor;
- e. a separate elevated pressure gas feed means to said reactor;
- f. a means for maintaining said gas feed means at an elevated pressure with respect to ambient pressure;

g. an U.V. spectrophotometer means in series with said reactor for measuring the absorbance of mercury-metal in the product of said reactor; and

h. an electric cycle control means for sequentially and repetitively:

1. simultaneously feeding sample to the reactor from the sample feed means and venting the reactor;
2. feeding oxidizing agent to the reactor from the oxidizing agent feed means;
3. sealing the reactor during oxidation of the sample;
4. venting the reactor after oxidation of the sample;

5. feeding reducing agent to the reactor from the reducing agent feed means;

6. thereafter feeding the reaction product from the reactor to the U.V. spectrophotometer means by gas from the elevated pressure gas feed means; and

7. purging the reactor with gas from the elevated pressure gas feed means.

2. The mercury-metal analyzer of claim 1 wherein the electric cycle control means comprises means for first passing air through the U.V. spectrophotometer means whereby to set the spectrophotometer means to a zero reading of mercury, and thereafter feeding the reaction product from the reactor to the spectrophotometer means.

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