

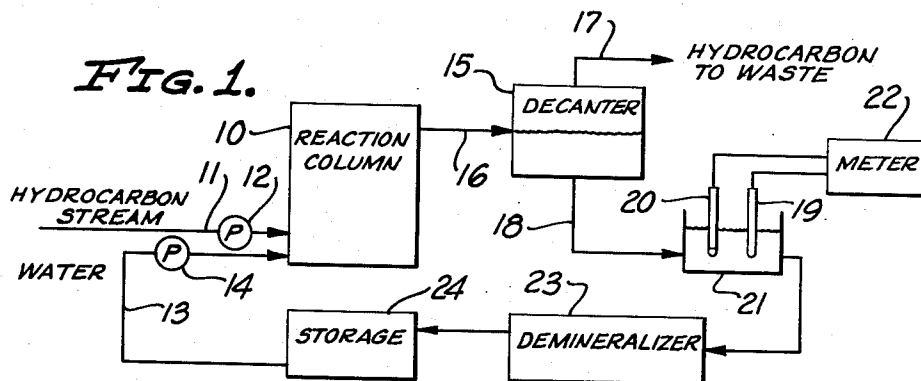
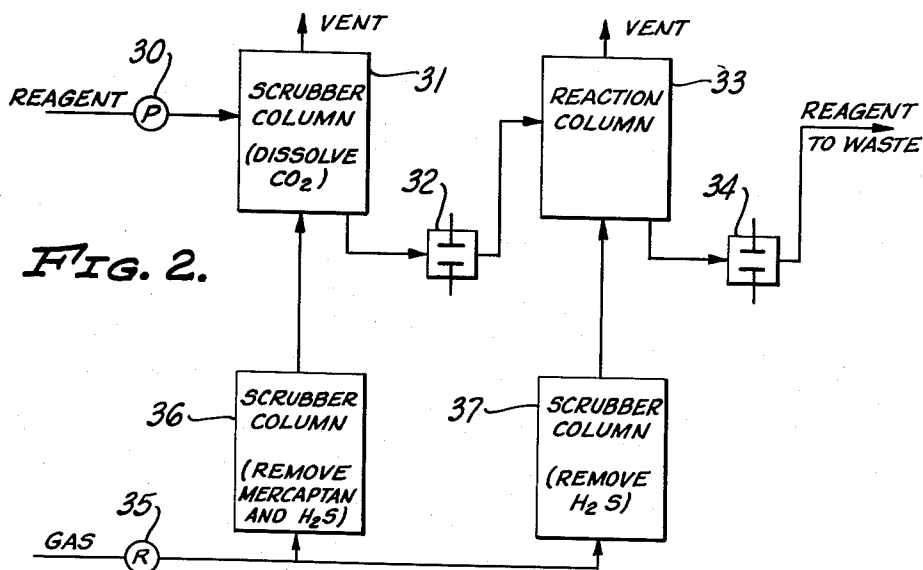
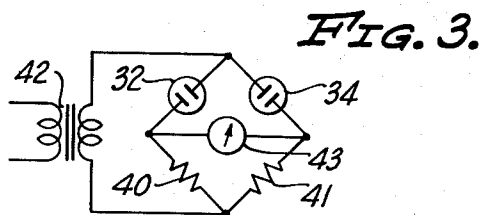
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METHOD AND APPARATUS FOR MERCAPTAN ANALYSIS

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1

3,114,609

METHOD AND APPARATUS FOR MERCAPTAN ANALYSIS

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This invention relates to methods and apparatus for the measurement of mercaptan sulfur and similar materials in hydrocarbon streams, both liquid and gaseous.

Mercaptans are a problem in the hydrocarbon industries, such as petroleum refining and natural gas transmission and distribution. A variety of processes have been developed and are utilized to eliminate mercaptans from hydrocarbons because of the adverse effects on performance due to the presence of mercaptans and also because of the objectionable odor of mercaptans and related materials. Also, small quantities of mercaptan are added to some hydrocarbons to provide a distinguishing odor. Natural gas is a relatively odorless material and mercaptans are added thereto in order to provide the householder with an indicator for gas leaks.

It is an object of the present invention to provide methods and apparatus for continuously measuring the mercaptan sulfur content of hydrocarbon streams, thereby permitting continuous monitoring of mercaptan sulfur content in hydrocarbon processes. A further object is to provide such methods and apparatus which may also be used for measuring hydrogen sulfide content. It is a particular object of the invention to provide such methods and apparatus which may be operable in analyzing hydrocarbon streams which contain carbon dioxide.

It is an object of the invention to provide a process for analyzing a hydrocarbon stream for mercaptan sulfur content including the steps of continuously contacting the hydrocarbon sample with metal ions, such as silver ions, in an aqueous solution to precipitate mercaptide salt and produce ion change in the aqueous solution, and measuring the ion activity in the aqueous solution as a measure of the mercaptan sulfur content of the sample.

It is an object of the invention to provide a mercaptan analysis process including the steps of continuously mixing a stream of hydrocarbon sample with a stream of substantially pure water in the presence of a relatively insoluble metal salt, such as silver chloride, for reaction of the mercaptan and metal cations providing anions and a more insoluble mercaptide salt, separating the hydrocarbon and water streams following the reaction, and measuring the anion content of the separated water stream as a continuous measure of the mercaptan sulfur content of the sample stream. A further object is to provide such a process wherein the pure water may be continuously recirculated with the water being passed through a demineralizer after measurement of the anion content for removing objectionable ions prior to mixing with the hydrocarbon stream. A further object is to provide such a process wherein the sensitivity of the measurement can be increased by controlling the respective flow rates of the hydrocarbon stream and the water stream in predetermined ratios.

It is an object of the invention to provide a process for analyzing a hydrocarbon stream for mercaptan sulfur content including the steps of continuously contacting the sample stream of hydrocarbon gas with a reagent stream including an aqueous solution of metal salt, such as silver sulfate, and measuring the change in conductivity of the reagent stream resulting from such contacting as a measure of the mercaptan sulfur content of the sample. A further object of the invention is to provide such a process for use with sample streams containing carbon

2

dioxide and including the steps of dividing the sample stream into first and second portions, removing mercaptans from the first portion and continuously contacting the reagent stream with the mercaptan free first portion to dissolve carbon dioxide into the reagent stream, then continuously contacting the second portion which contains mercaptan and carbon dioxide with the reagent stream containing carbon dioxide, and measuring the change in conductivity of the reagent stream resulting from contacting the second portion to provide a measure of the mercaptan sulfur content of the sample independent of the carbon dioxide content.

It is a further object to provide such a process for use with hydrocarbon streams containing both carbon dioxide and hydrogen sulfide and including the additional steps of removing hydrogen sulfide from both portions of the sample stream prior to contacting the reagent stream. Another object is to provide a process for measuring hydrogen sulfide content in hydrocarbon streams containing carbon dioxide, including the steps of removing hydrogen sulfide from the first portion prior to contacting the reagent stream with the conductivity change of the reagent stream due to contact with the second portion of the sample stream being a measure of the hydrogen sulfide content of the sample. Another object is to provide a process for determining hydrogen sulfide content in a stream containing hydrogen sulfide, carbon dioxide and mercaptan wherein the mercaptan content is first measured as set out above and then the combined hydrogen sulfide and mercaptan content is measured in a similar manner, with the difference of the two measurements providing a measure of the hydrogen sulfide content.

It is also an object of the invention to provide new and original apparatus for performing the processes of the invention. The invention also comprises novel details of construction and novel combinations and arrangements of parts and steps, which will more fully appear in the course of the following description. The drawing merely shows and the description merely describes preferred embodiments of the present invention which are given by way of illustration or example.

In the drawing:

FIG. 1 is a flow diagram showing a preferred form of the invention for use with liquid hydrocarbon streams;

FIG. 2 is a flow diagram showing a preferred form of the invention for use with gaseous hydrocarbon streams; and

FIG. 3 is an electrical diagram showing the measuring system for the conductivity cells of FIG. 2.

In a preferred form of the invention for use with liquid hydrocarbon streams, the liquid hydrocarbon sample stream containing mercaptan is mixed with a stream of substantially pure water in a chamber or column containing a metal salt. This metal salt must be only slightly soluble and the metal ions produced in solution must react with mercaptan to produce a mercaptide salt which is substantially insoluble. The reaction of the metal cations releases anions in the solution for subsequent measurement as an indication of the mercaptan sulfur content of the sample.

Silver chloride is the preferred salt for this reaction, being only slightly soluble and producing an insoluble silver mercaptide salt while releasing chloride ions which are easily measured. Cuprous chloride is an example of another suitable slightly soluble metal salt. Other anions than chloride may be used where suitable anion detecting and measuring equipment is available.

When using silver chloride, an exchange of chloride ion for mercaptide ion in the sample occurs, the silver mercaptide salt being much less soluble than the silver chloride salt. Following the reaction, which is substantially

instantaneous, the hydrocarbon and water layers are separated, as by conventional decanting or by selective filtration, and the chloride ion content of the continuously flowing water stream is measured. Typically, the chloride ion content is measured in a manner similar to pH measurements, using a conventional reference electrode and a silver-silver chloride electrode in place of the pH glass electrode. By knowing the ratio of the flow rates of the hydrocarbon and water streams, the mercaptan sulfur content of the hydrocarbon stream is directly related to the chloride ion content as measured in the separated water stream.

By using a relatively high ratio of hydrocarbon flow rate to water flow rate, the measuring accuracy can be greatly improved. For example, when using silver chloride, with a hydrocarbon having a density of 0.8 gram per cubic centimeter and a volume flow rate ten times that of water, the concentration of chloride ion in the water stream will be approximately ten times that of the initial mercaptan content of the hydrocarbon stream, since the atomic weights of sulfur and chlorine are nearly the same. A measured chloride ion content in the aqueous phase of one hundred parts per million would indicate the mercaptan sulfur content of the sample stream to be 11.3 parts per million with the ratio of flow rates being ten. Similarly, with a flow rate ratio of twenty to one, a chloride ion measurement of one hundred parts per million would indicate a mercaptan sulfur content of 22.6 parts per million.

An apparatus for measuring mercaptan sulfur content of a liquid hydrocarbon stream is shown in FIG. 1. A reaction column 10 is loaded with silver chloride. The hydrocarbon sample stream is introduced into the reaction column 10 through a line 11 having a metering pump 12 therein. The water stream is introduced into the reaction column through a line 13 having a metering pump 14 therein. The effluent from the reaction column is directed to a decanter 15 through a line 16, the effluent being separated into a hydrocarbon phase which leaves the decanter through a line 17, and an aqueous phase which leaves the decanter through a line 18. A reference electrode 19 and a silver-silver chloride electrode 20 are immersed in the water stream in a container 21, the electrodes being coupled as inputs to a conventional chloride ion meter 22.

Following the chloride ion measurement, the water stream may be disposed of. Alternatively, the water stream may be passed through a demineralizer 23 for removing objectionable ions and then to a storage container 24 for re-use in the measuring process. A suitable demineralizer would be a chamber containing a mixed bed of cation and anion exchange resins. Examples are: Barnstead Bantam demineralizer; Rohm and Haas 120 and 400; and Dowex 50 and 1.

This apparatus provides for continuous measurement of the mercaptan sulfur content of the incoming hydrocarbon sample stream. The meter 22 may be used to read anion content or may be calibrated directly in mercaptan sulfur content with the ratio of hydrocarbon to water flow rate being maintained constant. In a typical installation, the apparatus is used to measure mercaptan content in the range of zero to twenty parts per million with the pump 12 providing a hydrocarbon sample stream at a rate of ten cubic centimeters per minute and the pump 14 providing a water stream at a rate of one cubic centimeter per minute. The meter 22 has a sensitivity range of zero to two hundred parts per million of chloride ion.

In a preferred form of the process for use with gaseous hydrocarbon streams, the sample stream of hydrocarbon gas containing mercaptan is continuously contacted with a reagent stream including an aqueous solution of metal salt. The metal ion provided in the solution by the metal salt must react with mercaptan to product a mercaptide salt which is substantially insoluble. Salts of silver, mercury, copper, lead, nickel and zinc are examples of suitable metal salts. The anion released by the reaction must be one which forms an acid that completely dissociates

in solution to provide one hundred percent ionization. Suitable anions are sulfate, chloride and nitrate. The sulfate is preferred since the resultant sulfuric acid is non-volatile and precaution against loss of ions due to volatilization are not necessary.

When using a solution of silver sulfate as the reagent, there is a reaction which produces silver mercaptide salt and free hydrogen ions in the reagent stream. The increase in hydrogen ion in the reagent stream produces a corresponding increase in electrical conductivity of the stream which is directly related to the mercaptan sulfur content of the hydrocarbon sample. The process includes the step of measuring the change in conductivity of the reagent stream resulting from contact with the hydrocarbon stream. Where the initial conductivity of the reagent stream is known, it is only necessary to measure the conductivity following the reaction. Alternatively, the conductivity of the reagent stream may be continuously measured both before and after the reaction with the difference in conductivity being detected in a bridge circuit to give a measure of the mercaptan content of the sample stream.

Variations of this process permit the measurement of mercaptan sulfur content in sample streams containing carbon dioxide and/or hydrogen sulfide. The process also permits the measurement of hydrogen sulfide content of sample streams.

A preferred form of apparatus for carrying out the invention is shown in FIG. 2, wherein the reagent stream is directed through a metering pump 30, a scrubber column 31, a conductivity cell 32, a reaction column 33, and a conductivity cell 34. The incoming sample stream is directed through a pressure regulator 35, and is then divided into two streams with the first stream going through a scrubber column 36, and the scrubber column 31. The second portion of the sample stream passes through a scrubber column 37, and the reaction column 33, with both gas streams being vented to the atmosphere.

A typical bridge circuit for use with the conductivity cells 32, 34 is shown in FIG. 3. The cells 32, 34 are placed in two adjacent arms of the bridge and resistors 40, 41 comprise the other two arms of the bridge. An A.C. bridge excitation voltage is connected across two opposite corners of the bridge through a transformer 42. An output indicating meter 43 is connected across the other two corners of the bridge. With the resistors 40, 41 of equal value, the meter 43 indicates the difference in conductance measured by the two cells 32, 34. The meter may read conductivity differential or may be calibrated to read mercaptan sulfur content for predetermined rates of flow of reagent and gas sample.

Normally, the scrubber column 36 is used to remove mercaptan and hydrogen sulfide from the sample gas stream and contains a metal salt which reacts with mercaptans and hydrogen sulfide to form an insoluble precipitate. Typically, the column will contain a saturated aqueous solution of silver sulfate. Normally, the scrubber column 37 is used to remove hydrogen sulfide from the sample gas stream and contains a solution which reacts with hydrogen sulfide. Typically, it will contain a buffered aqueous solution of cadmium sulfate.

In the scrubber column 31, the mercaptan and hydrogen sulfide free sample gas stream is contacted with the reagent, and the carbon dioxide in the gas stream is dissolved into the reagent stream. Hence the reagent stream is saturated with carbon dioxide to an equilibrium established by the concentration of carbon dioxide in the sample gas prior to the first conductivity measurement and does not pick up any additional carbon dioxide in the reaction column 33. Therefore, the presence of carbon dioxide in the gas sample does not affect the measured difference in conductivity so that all of the conductivity change is due to the mercaptan reaction.

A typical composition for the reagent is a solution containing 0.125 gram of silver sulfate dissolved in 5 gallons of pure water. Preferably 15 cc. of sulfuric acid solution,

5

made up of 1 cc. of concentrated sulfuric acid diluted with pure water to a volume of 1 liter, is also added to the 5 gallons of solution. The silver sulfate provides the silver ions in the reagent solution. The sulfuric acid slightly acidifies the reagent solution. This suppresses the ionization of carbon dioxide and limits the background conductivity fluctuations due to carbon dioxide. With the rates of flow of the reagent and gas streams through the reaction column known, the change in conductivity of the reagent stream is directly related to the mercaptan sulfur content of the sample stream.

Various modifications of the apparatus of FIG. 2 may be employed. For sample gases containing no carbon dioxide, the scrubber columns 31 and 36 may be omitted. For sample gases containing no hydrogen sulfide, the scrubber column 37 may be omitted. Similarly, for sample gases containing neither hydrogen sulfide or carbon dioxide, columns 31, 36 and 37 may be omitted. If a measure of the combined hydrogen sulfide and mercaptan sulfur content of the sample stream is desired, the scrubber column 37 may be omitted. Similarly, the hydrogen sulfide content of a sample stream containing no mercaptan can be measured by the process of the invention and the apparatus of FIG. 2 with the column 37 omitted.

In another form of the process of the invention, the apparatus of FIG. 2 may be used to measure hydrogen sulfide content of a sample stream which also contains mercaptan. This may be carried out as a two-step process using the apparatus as shown in FIG. 2, or two sets of such apparatus may be operated in parallel. Referring first to the two-step process, the mercaptan sulfur content is measured as described above. Then the scrubber column 37 is bypassed and the combined mercaptan and hydrogen sulfide content is measured. The difference of these two measurements provides a measure of the hydrogen sulfide content. In an alternative form, two sets of apparatus may be utilized with one continuously measuring mercaptan content and the other continuously measuring combined mercaptan and hydrogen sulfide content. The indicated outputs of the two measurements may be noted and subtracted or the indicated outputs may be continuously subtracted in a suitable circuit.

Although exemplary embodiments of the invention have been disclosed and discussed, it will be understood that other applications of the invention are possible and that the embodiments disclosed may be subjected to various changes, modifications and substitutions without necessarily departing from the spirit of the invention.

I claim as my invention:

1. In a mercaptan analyzer, the combination of: a reaction chamber having first and second inlets and an outlet and adapted to contain a slightly soluble metal salt, the metal ion reacting with mercaptan to produce a substantially insoluble metal mercaptide salt; separator means for separating liquids and having an inlet and a pair of outlets; means for measuring only a single anion in a liquid; first flow means for coupling a stream of hydrocarbon containing mercaptan for analysis to said first inlet of said reaction chamber; second flow means for coupling a stream of substantially pure water to said second inlet of said reaction chamber; third flow means for coupling said reaction chamber outlet to said separator means inlet; and fourth flow means for coupling the water outlet of said separator means to said measuring means for measurement of said single anion content of the separated water stream which varies as a function of the mercaptan sulfur content of the incoming hydrocarbon stream.

2. In a mercaptan analyzer, the combination of: a reaction chamber having first and second inlets and an outlet and adapted to contain a slightly soluble metal salt, the metal ion reacting with mercaptan to produce a substantially insoluble metal mercaptide salt; separator means for separating liquids and having an inlet and a pair of outlets; means for measuring only a single anion in a

6

liquid; first flow means for coupling a stream of hydrocarbon containing mercaptan for analysis to said first inlet of said reaction chamber; second flow means for coupling a stream of substantially pure water to said second inlet of said reaction chamber; third flow means for coupling said reaction chamber outlet to said separator means inlet; fourth flow means for coupling the water outlet of said separator means to said measuring means for measurement of said single anion content of the separated water stream which varies as a function of the mercaptan sulfur content of the incoming hydrocarbon stream; a water demineralizer for removing ions from water; and fifth flow means for coupling the water stream from said measuring means to said demineralizer, with said demineralizer providing the pure water for said second flow means.

3. In a mercaptan analyzer, the combination of: a reaction chamber having first and second inlets and an outlet and adapted to contain silver chloride; separator means for separating liquids and having an inlet and a pair of outlets; means for measuring only chloride ions; first flow means for coupling a stream of hydrocarbon containing mercaptan for analysis to said first inlet of said reaction chamber; second flow means for coupling a stream of substantially pure water to said second inlet of said reaction chamber; third flow means for coupling said reaction chamber outlet to said separator means inlet; and fourth flow means for coupling the water outlet of said separator means to said measuring means for measurement of the chloride ion content of the separated water stream which varies as a function of the mercaptan sulfur content of the incoming hydrocarbon stream.

4. In an apparatus for continuously analyzing a liquid hydrocarbon stream for mercaptan content, the combination of: a reaction chamber having first and second inlets and an outlet and adapted to contain silver chloride; separator means for separating water and liquid hydrocarbon and having an inlet and a pair of outlets; means for measuring only chloride ions; a first source providing a stream of hydrocarbon sample at a predetermined rate to said first reaction chamber inlet; a second source providing a stream of substantially pure water at a predetermined rate to said second reaction chamber inlet; means for connecting said reaction chamber outlet to said separator means inlet; and means for connecting the water outlet of said separator means to said measuring means, with the chloride ion content of the water stream being a measure of the mercaptan sulfur content of the hydrocarbon sample.

5. In a mercaptan analyzer, the combination of: a reaction chamber; first means for supplying a stream of hydrocarbon containing mercaptan for analysis to said reaction chamber; second means for supplying a metal chloride salt in water to said reaction chamber to produce a substantially insoluble metal mercaptide salt; means for measuring only the chloride ion content of a liquid stream; and means for conducting a chloride ion bearing liquid stream from said reaction chamber to said means for measuring, with the chloride ion content measurement varying as a function of the mercaptan sulfur content of the hydrocarbon stream.

6. A process for analyzing a hydrocarbon stream for mercaptan content, including the steps of: continuously mixing a stream of hydrocarbon sample containing mercaptan with a stream of substantially pure water in the presence of a slightly soluble metal salt for reaction of the mercaptan and metal ion providing anions of the salt and a substantially insoluble metal mercaptide salt; separating the hydrocarbon and water streams following the reaction; and measuring the anion content of the separated water stream as a continuous measure of the mercaptan sulfur content of the sample stream.

7. A process for analyzing a hydrocarbon stream for mercaptan content, including the steps of: continuously mixing a stream of hydrocarbon sample containing mercaptan with a stream of substantially pure water in the presence of a slightly soluble metal salt for reaction of the

mercaptan and metal ion providing anions of the salt and a substantially insoluble metal mercaptide salt; separating the hydrocarbon and water streams following the reaction; measuring the anion content of the separated water stream as a continuous measure of the mercaptan sulfur content of the sample stream; removing ions from the water stream after the measurement; and recirculating the de-ionized water for mixing with the sample stream.

8. A process for analyzing a hydrocarbon stream for mercaptan content, including the steps of: continuously mixing a stream of hydrocarbon sample containing mercaptan with a stream of substantially pure water in the presence of silver chloride for reaction of the mercaptan and silver providing chloride ions and a substantially insoluble silver mercaptide salt; separating the hydrocarbon and water streams following the reaction; and measuring the chloride ion content of the separated water stream as a continuous measure of the mercaptan sulfur content of the sample stream.

9. A process for continuously analyzing a hydrocarbon stream for mercaptan content, including the steps of: continuously mixing a stream of hydrocarbon sample containing mercaptan with a stream of substantially pure water in the presence of silver chloride for reaction of the mercaptan and silver providing chloride ions and a substantially insoluble silver mercaptide salt; maintaining the rates of flow of the hydrocarbon and water streams at predetermined magnitudes, with the rate of flow of hydrocarbon greater than that of water for producing a chloride ion concentration greater than the mercaptan concentration in a ratio corresponding to the ratio of the rates of flow of hydrocarbon and water; separating the hydrocarbon and water streams following the reaction; and measuring the chloride ion content of the separated water stream as a continuous measure of the mercaptan sulfur content of the sample stream.

10. A process for continuously analyzing a hydrocarbon stream for mercaptan content, including the steps of: continuously contacting a stream of hydrocarbon sample with metal ions in an aqueous solution to precipitate a substantially insoluble metal mercaptide salt and produce ion change in the aqueous solution; and then continuously measuring the ion activity in the aqueous solution as a measure of the mercaptan sulfur content of the sample.

11. In an apparatus for continuously analyzing a hydrocarbon gas containing carbon dioxide for mercaptan, the combination of: first scrubber means for removing mercaptan from a gas stream passing therethrough; second scrubber means for mixing liquid and gas streams passing therethrough; a reaction chamber having a gas inlet and outlet and a reagent inlet and outlet; first and second conductivity cells; first flow means for directing a stream of sample gas through said reaction chamber; second flow means for directing a portion of the incoming sample gas stream through said first scrubber means and then through said second scrubber means; and third flow means for directing a reagent stream including an aqueous solution of a metal salt through said second scrubber means, said first conductivity cell, said reaction chamber, and said second conductivity cell, with the metal cation of the metal salt reacting with mercaptan to produce a substantially insoluble metal mercaptide salt and with the anion of the reaction product producing an acid which completely dissociates, with said reagent stream absorbing carbon dioxide from the mercaptan-free portion of the sample gas in said second scrubber means, and with the change in conductivity of said reagent being a measure of the mercaptan sulfur content of the incoming gas stream.

12. In an apparatus for continuously analyzing a hydrocarbon gas containing carbon dioxide and hydrogen sulfide for mercaptan, the combination of: first scrubber means for removing mercaptan and hydrogen sulfide from a gas stream passing therethrough; second scrubber means for mixing liquid and gas streams passing therethrough; third scrubber means for removing hydrogen sulfide from

a gas stream passing therethrough; a reaction chamber having a gas inlet and outlet and a reagent inlet and outlet; first and second conductivity cells; first flow means for directing a stream of sample gas through said third scrubber means and then through said reaction chamber; second flow means for directing a portion of the incoming sample gas stream through said first scrubber means and then through said second scrubber means; and third flow means for directing a reagent stream including an aqueous solution of a metal salt through said second scrubber means, said first conductivity cell, said reaction chamber, and said second conductivity cell, with the metal cation of the metal salt reacting with mercaptan to produce a substantially insoluble metal mercaptide salt and with the anion of the reaction product producing an acid which completely dissociates, with said reagent stream absorbing carbon dioxide from the mercaptan and hydrogen sulfide free portion of the sample gas in said second scrubber means, and with the change in conductivity of said reagent being a measure of the mercaptan sulfur content of the incoming gas stream.

13. In an apparatus for continuously analyzing a hydrocarbon gas containing carbon dioxide for mercaptan, the combination of: first scrubber means containing a saturated solution of silver sulfate for removing mercaptan from a gas stream passing therethrough; second scrubber means for mixing liquid and gas streams passing therethrough; a reaction chamber having a gas inlet and outlet and a reagent inlet and outlet; first and second conductivity cells; first flow means for directing a stream of sample gas at a predetermined flow rate through said reaction chamber; second flow means for directing a portion of the incoming sample gas stream at a predetermined flow rate through said first scrubber means and then through said second scrubber means; and third flow means for directing a reagent stream including an acidified aqueous solution of silver sulfate through said second scrubber means, said first conductivity cell, said reaction chamber, and said second conductivity cell, with said reagent stream absorbing carbon dioxide from the mercaptan-free portion of the sample gas in said second scrubber means, and with the change in conductivity of said reagent being a measure of the mercaptan content of the incoming gas stream.

14. A process for analyzing a hydrocarbon stream for mercaptan content, including the steps of: continuously contacting a sample stream of hydrocarbon gas containing mercaptan with a reagent stream including an aqueous solution of a metal salt producing a substantially insoluble metal mercaptide salt and an acid which completely dissociates resulting in an increase in hydrogen ions in the reagent stream; and measuring the change in conductivity of the reagent stream resulting from such contacting as a measure of the mercaptan sulfur content of the sample.

15. A process for analyzing a hydrocarbon stream containing carbon dioxide for mercaptan content, including the steps of: dividing a sample stream of hydrocarbon gas containing carbon dioxide and mercaptan into first and second sample streams; removing mercaptan from the first sample stream; continuously contacting the first sample stream with a reagent stream including an aqueous solution of a metal salt, with the metal cation of the metal salt reacting with mercaptan to produce a substantially insoluble metal mercaptide salt and with the anion of the reaction product producing an acid which completely dissociates, with the carbon dioxide being dissolved into the reagent stream; continuously contacting the second sample stream with the reagent stream containing dissolved carbon dioxide producing the mercaptide salt and an increase in hydrogen ions in the reagent stream; and measuring the change in conductivity of the reagent stream resulting from contacting the second sample stream as a measure of the mercaptan sulfur content of the sample.

16. A process for analyzing a hydrocarbon stream con-

taining carbon dioxide and hydrogen sulfide for mercaptan content, including the steps of: dividing a sample stream of hydrocarbon gas containing carbon dioxide, hydrogen sulfide and mercaptan into first and second sample streams; removing mercaptan and hydrogen sulfide from the first sample stream; removing hydrogen sulfide from the second sample stream; continuously contacting the first sample stream with a reagent stream including an aqueous solution of a metal salt, with the metal cation of the metal salt reacting with mercaptan to produce a substantially insoluble metal mercaptide salt and with the anion of the reaction product producing an acid which completely dissociates, with the carbon dioxide being dissolved into the reagent stream; continuously contacting the second sample stream with the reagent stream containing dissolved carbon dioxide producing the mercaptide salt and an increase in hydrogen ions in the reagent stream; and measuring the change in conductivity of the reagent stream resulting from contacting the second sample stream as a measure of the mercaptan sulfur content of the sample.

17. A process for analyzing a hydrocarbon stream containing carbon dioxide, hydrogen sulfide and mercaptan, including the steps of: dividing the sample stream of hydrocarbon gas into first and second sample streams; removing mercaptan and hydrogen sulfide from the first sample stream; removing hydrogen sulfide from the second sample stream; continuously contacting the first sample stream with a reagent stream including an aqueous solution of a metal salt, with the metal cation of the metal salt reacting with mercaptan to produce a substantially insoluble metal mercaptide salt and with the anion of the reaction product producing an acid which completely dissociates, with the carbon dioxide being dissolved into the reagent stream; continuously contacting the second sample stream having hydrogen sulfide removed with the reagent stream; measuring the change in conductivity of the reagent stream resulting from contacting the second sample stream as a measure of the mercaptan sulfur content of the sample; continuously contacting the second sample stream having hydrogen sulfide therein with the reagent stream containing dissolved carbon dioxide; measuring the change in conductivity of the reagent stream resulting from contacting the second sample stream as a measure of the total hydrogen sulfide and mercaptan sulfur content of the sample; and determining the difference in the two measurements providing a measure of the hydrogen sulfide content of the sample.

18. A process for analyzing a hydrocarbon stream containing carbon dioxide and hydrogen sulfide, including the steps of: dividing the sample stream of hydrocarbon gas into first and second sample streams; removing hydrogen sulfide from the first sample stream; continuously contacting the first sample stream with a reagent stream including an aqueous solution of a metal salt, with the metal

cation of the metal salt reacting with hydrogen sulfide to produce a substantially insoluble metal sulfide salt and with the anion of the reaction product producing an acid which completely dissociates, with the carbon dioxide being dissolved into the reagent stream; continuously contacting the second sample stream with the reagent stream containing dissolved carbon dioxide producing the sulfide salt and an increase in hydrogen ions in the reagent stream; and measuring the change in conductivity of the reagent stream resulting from contacting the second sample stream as a measure of the hydrogen sulfide content of the sample.

19. A process for continuously analyzing a hydrocarbon stream for mercaptan content, including the steps of: continuously contacting a sample stream of hydrocarbon gas containing mercaptan with a reagent stream including an aqueous solution of silver sulfate producing silver mercaptide salt and an increase in hydrogen ions in the reagent stream; and continuously measuring the change in conductivity of the reagent stream resulting from such contacting as a measure of the mercaptan sulfur content of the sample.

20. A process for analyzing a hydrocarbon stream containing carbon dioxide for mercaptan content, including the steps of: dividing a sample stream of hydrocarbon gas containing carbon dioxide and mercaptan into first and second sample streams; removing mercaptan from the first sample stream; continuously contacting the first sample stream with a reagent stream including an aqueous solution of silver sulfate with the carbon dioxide being dissolved into the reagent stream; continuously contacting the second sample stream with the reagent stream containing dissolved carbon dioxide producing silver mercaptide salt and an increase in hydrogen ions in the reagent stream; and measuring the change in conductivity of the reagent stream resulting from contacting the second sample stream as a measure of the mercaptan sulfur content of the sample.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,114,609

December 17, 1963

Robert H. Jones

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 74, for "relased" read -- realeased --;
column 4, line 22, for "of" read -- in --; column 10, line
51, for "1952" read -- 152 --.

Signed and sealed this 30th day of June 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents