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METHOD AND APPARATUS FOR CHROMATOGRAPHIC MOISTURE ANALYSIS

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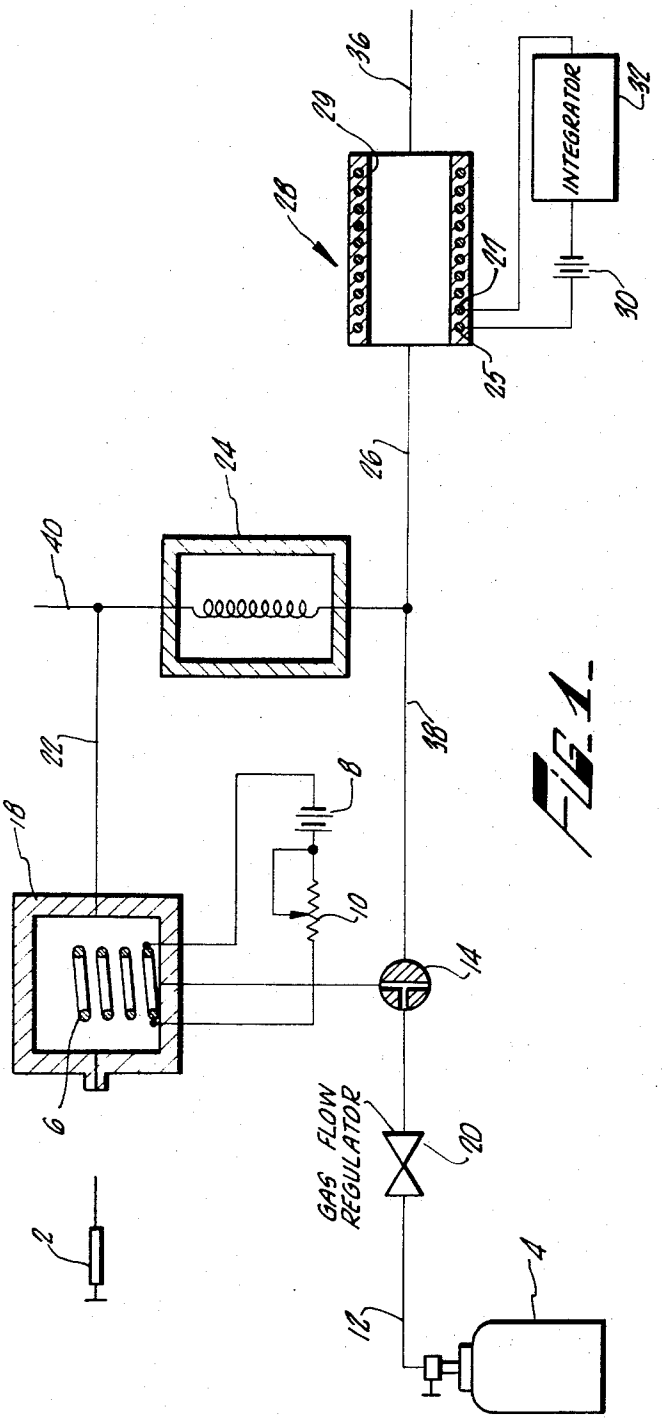
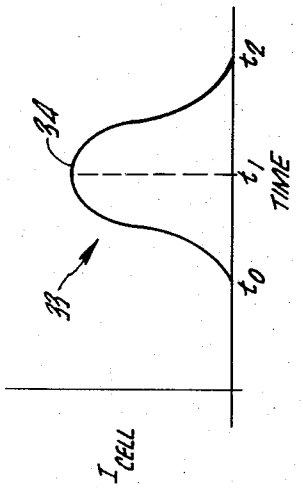



FIG. 1

FIG. 2




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# METHOD AND APPARATUS FOR CHROMATOGRAPHIC MOISTURE ANALYSIS

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6 Claims. (Cl. 204—1)

This invention relates to apparatus for determining the presence of water in non-aqueous fluids and in particular to a laboratory apparatus including a chromatographic column and electrolytic cell detector for measuring the amount of water present in liquid hydrocarbons.

The analysis of gases and liquids has recently been improved by the development of electrolytic moisture cells such as described in United States Patents 2,816,067 to F. A. Keidel on Sept. 19, 1957; 2,830,945 to F. A. Keidel on Apr. 15, 1958; 2,994,853 to C. E. Berry on July 25, 1961 and 3,072,556 to Michael Czuha, Jr., on Jan. 8, 1963.

However, electrolytic moisture cells are not readily utilizable for the detection of water in certain non-aqueous fluids because the hygroscopic material with which the electrodes of the cell are coated react with or catalyze a reaction in these fluids. When this happens deposits, as for example, polymers, due to the presence of a hydrocarbon component in the sample are formed which build up to foul and clog the capillary sized tubing of the electrolysis cell and quickly render the cell useless.

The problem then is to provide an apparatus that will accept non-aqueous liquids such as hydrocarbons but will separate the water from the hydrocarbons prior to introduction to the electrolysis cell. The present invention accomplishes this by providing a packed chromatographic column to which a sample of fluid to be analyzed is communicated, wherein an inert carrier is substituted for the non-aqueous fluid. An electrolytic cell having a pair of spaced apart electrodes bridged by a film of hygroscopic material communicates with the output of the column and means for selectively flowing the water-inert carrier combination from the column to the cell are provided. Connected to the spaced apart electrodes are means for impressing a potential across them whereby the water presented to the cell and absorbed by the hygroscopic material is electrolyzed. The electrolysis current is then metered to determine the total amount of moisture present.

The chromatographic column used in conjunction with this invention is a conventional column used in gas chromatography. More specifically, the column is a partition chromatograph in which analysis is accomplished by transporting the water-carrying non-aqueous fluid to be analyzed to the chromatograph and substituting therein an inert carrier gas for the non-aqueous fluid. A typical electrolytic cell utilized with this invention comprises a pair of spaced bifilar wire coils, the coils being supported against the inside wall of an enclosing tube or housing. A film of a desiccant or hygroscopic material, such as phosphorous pentoxide, is deposited on the coils and housing interior to electrically bridge the spaces between adjacent turns of the two wire helices.

A suitable voltage is applied to the two electrode coils, and when the hygroscopic material is conductive, say upon absorption of moisture, an electrolytic path exists between the alternately spaced turns of the coils. In operation therefore, as moisture is absorbed by the hygroscopic material from a gas stream flowing past the coils, the hygroscopic material becomes conductive, current flows between the coils in the regions of conductivity and the water is electrolyzed to hydrogen and oxygen. The electric current that flows is an accurate measure of the rate of moisture absorption in accordance with Faraday's law.



In a typical analysis then involving the use of apparatus according to this invention a moisture bearing sample of hydrocarbons is introduced to a chamber where the sample is heated to a sufficient temperature to flash vaporize all components present. A carrier gas introduced into the chamber transports the vaporized sample to the chromatographic column where the hydrocarbons are separated from the water and the carrier gas substituted therefor. The water-carrier gas combination is then issued first from the column and conveyed to the electrolytic detector where the water is absorbed by hygroscopic material in the cell and electrolyzed by means of a source of potential connected to the electrodes of the cell. The amount of current necessary to completely electrolyze the water is integrated by an instrument included in the potential supplying circuit to indicate the total amount of moisture present. The column is then back-flushed to remove the hydrocarbons which have been retained therein.

Such an apparatus is useful in providing a rapid, accurate analysis in terms of weight of the water content of a liquid hydrocarbon regardless of sample size. Given the total weight of the sample, simple calculations transform this reading into percentages or parts per million of water.

Typical cycle durations, from sample injection to completion of back-flush are approximately fifteen minutes. Disadvantages due to the necessity of establishing equilibrium conditions and providing large sample quantities characteristic of process instruments are avoided since the apparatus is capable of accurately analyzing samples of ½ cc. in volume or less and is restored to essentially its original condition at the completion of each analysis.

These and other details of the apparatus and the operation of the process in accordance with this invention will be made clear by reference to:

FIG. 1 which depicts in schematic form the components of the apparatus of this invention, and

FIG. 2, a graph of the variation of current flowing in the cell during analysis of a typical sample.

In the schematic in FIG. 1 a sample of hydrocarbons to be analyzed is injected in a vaporizer chamber **18** by means of a syringe **2** or similar device. A source **4** of carrier gas is connected through a gas flow regulator **20** to the vaporizer chamber **18**. The carrier gas is normally an inert gas such as nitrogen to which a predetermined amount of moisture, on the order of 100 parts per million, has been added. It has been found that "pre-wetting" of the gas is necessary in order to prevent errors in the operation of the analyzer. The system is calibrated to take into account the predetermined amount of moisture added.

The vaporizer chamber **18** is a heated chamber which is operated at approximately a temperature of 150° C. This is accomplished by such means as an induction coil **6** connected to a source of potential **8** through a variable potentiometer **10**. At this temperature all components present in the sample to be analyzed are flash vaporized when the sample is injected into the chamber. In addition, the carrier gas flowing into the vaporizer chamber also acts to "strip" the moisture from the vaporized sample. The sample is then transported by the carrier gas through line **22** into the chromatographic column **24**.

The column **24** is a conventional gas-liquid partition chromatograph which has been provided with packing such that it is significantly retentive of all components present in the sample except water. For example, one type of packing or substrate to be used within the column is a support of polytetrafluorethylene particles (powdered Teflon) as the solid phase impregnated with an oil or grease such as a #500 silicone oil as the liquid phase.

The packing just illustrated is merely one example of the combination of liquid phase and solid support which can be used in the column. Other possibilities as the substrate include a polychlorine product marketed as Kel-F, which has a paraffin superimposed on it as the liquid phase.

As indicated, the important consideration is that the partitioning material in the chromatograph be selected such that it is highly selective with respect to water. The material is chosen such that the water-carrier combination is the first or last combination eluted from the column. Preferably it is the first and the details of the operation of the analyzer are enumerated herein based on this preferred sequence of operation. By this means, the water is separated from the hydrocarbons in which it was carried when injected into the vaporizer chamber and an inert carrier gas is substituted in its place. The water can now be monitored by the electrolytic cell without the problem of introducing possible contaminants.

The separated water vapor is carried over line **26** to the electrolytic cell **28**. The electrolytic cell or hygrometer **28** is essentially a pair of bifilar helical electrodes **25** and **27** disposed in a cell with the interelectrode space being covered or bridged by means of a hygroscopic material **29** such as phosphorous pentoxide. It is a characteristic of such a cell that when water vapor is passed through it the vapor is sorbed by the hygroscopic material. When water is sorbed by this material a potential such as supplied by source **30** connected to the electrodes **25** and **27** and completing the circuit causes a current to be conducted through the material **29**. This current is conducted so long as moisture is present in the phosphorous pentoxide. As the current is conducted through the hygroscopic material the moisture present is electrolyzed into hydrogen and oxygen and vented by suitable means. At the same time that the water is being electrolyzed the electrolyte is being constantly regenerated in the cell so that when current ceases to flow the cell remains in its original condition ready to receive the next sample.

Like the vaporizer chamber, the electrolytic cell **28** is also operated at an elevated temperature, approximately 50° to 70° C. This is done in order to maintain the moisture carried into the cell **28** in the vapor phase. Liquids of any type entering the cell tend to dissolve the hygroscopic material disposed therein and if allowed to persist ultimately render the cell inactive. The temperature of 50° to 70° is chosen because this is high enough to maintain the moisture in the vapor phase while at the same time not exceeding the vapor pressure of the electrolyte, in this case, the phosphorous pentoxide.

The amount of current flowing in the cell is proportional to the amount of moisture present. If the current flowing in the cell were plotted against time a curve similar to the curve **33** shown in FIG. 2 is the result. As shown in that figure the current at time, $t_0$, begins to flow in the cell, builds up to a maximum **34** indicated at $t_1$ and then diminishes to zero again at a time, $t_2$. The area under the curve **33** is proportional to the total amount of moisture present in the sample. By the mathematical operation of integrating the area under the curve the total amount of moisture present in the sample can be determined. A current integrating device **32** to perform this operation is connected in the circuit with the source of potential **30**. The integrating device **32** may be any of the conventional mechanical or electrical devices which are well known in the art. Readout is normally in terms of the total quantity of sample present. The carrier gas and hydrogen and oxygen liberated in the electrolysis cell are expelled through outlet **36**.

After the current in the electrolytic cell has diminished to zero indicating that the moisture present has been completely electrolyzed the flow of carrier gas is reversed by means of valve **14** and is redirected through line **38** into the outlet of the chromatograph **24**. By this means the other sample components, most of which are still collected in the column, are back-flushed from the chromatograph and eliminated through auxiliary outlet **40**. The analyzer is then ready for the next analysis.

The analyzer is also useful in measuring the water content of certain gases such as ammonia and gaseous amines. In the same manner as liquid analysis, injection of a known weight of sample under reference temperature, pressure and volume conditions into the analyzer results in an output in terms of the total weight of water present in the sample. In addition to use as a batch or laboratory analyzer it is also possible to adapt the analyzer of this invention to process applications. Operation of the analyzer would still be on a discontinuous, batch type basis with the apparatus being connected to a process stream and provided with the capability of periodically extracting suitable samples. In this adaptation the order of component elution can also be altered to provide that water is the last component of the sample to be eluted from the chromatographic column. If such a sequence is chosen all components except the water are eluted from the column and vented and thereafter the water and inert carrier are transported to the electrolysis cell for water content measurement.

What has been provided is a laboratory-type analyzer for determining the total amount of moisture present in non-aqueous fluids such as ammonia and hydrocarbons. Such a device is especially useful in liquid polymer analysis applications where it is possible to obtain the quick, accurate indications of an electrolytic detector while at the same time protecting the hygroscopic material of the detector from polymer formation. Since the amount of the sample is controllable, problems of overloading of the electrolytic cell are avoided simply by adjusting the size of the sample taken. Control of sample size also means that it is possible to operate this instrument over wide water content ranges, from a lower limit of 100 parts per million of water to small percentages, i.e., parts per hundred, of water as the upper limit.

I claim:

**1.** Apparatus for determining the amount of water present in a non-aqueous fluid sample, comprising:

a partition chromatograph having a column packed with a liquid solvent disposed on a solid support, the solvent and solid support being selected such that water has the lowest adsorbability therein of the components in the fluid sample,

means comprising a source of inert carrier gas to which a predetermined amount of moisture has been added for eluting the sample through the column,

an electrolytic cell having a pair of spaced apart electrodes,

a body of hygroscopic material interconnecting the electrodes,

means for selectively communicating the water eluted from the column through the cell for absorption by the hygroscopic material, and

means coupled to the cell for impressing a potential across the cell electrodes for electrolysis of the water absorbed by the hygroscopic material, the electrolysis current flow between the electrodes through the hygroscopic material being related to the quantity of moisture electrolyzed in the cell.

**2.** An apparatus according to claim **1** wherein the solid support and liquid solvent packed in the column are Teflon particles and a silicone oil respectively.

**3.** A process for determining the amount of water present in liquid hydrocarbons comprising the steps of:

vaporizing a sample of the water-bearing liquid hydrocarbons,

passing the vaporized sample with an inert carrier gas which has been pre-wetted with a predetermined amount of moisture to a suitable chromatographic column, and substituting the inert carrier gas for hydrocarbons by passing the sample therethrough,

selectively flowing the water and inert carrier gas from the column to an electrolytic cell having a pair of

electrodes bridged by a film of hygroscopic material interiorly of the cell, and

impressing an electric potential across the cell electrodes to electrolyze moisture absorbed by the hygroscopic material.

4. A process according to claim 3 including the steps of integrating the electrolysis current to indicate the total amount of moisture absorbed and back-flushing the chomatographic column to remove the hydrocarbons retained therein.

5. A process for determining the amount of water present in fluid hydrocarbons comprising the steps of introducing a hydrocarbon sample with an inert carrier gas which has been pre-wetted with a predetermined amount of moisture to a suitable chromatographic column, and substituting the inert carrier gas for hydrocarbons by passing the sample therethrough, selectively flowing the water and inert carrier gas from the column to an electrolytic cell having a pair of electrodes bridged by a film



of hydroscopic material interiorly of the cell, and impressing an electric potential across the cell electrodes to electrolyze moisture absorbed by the hygroscopic material.

6. A process according to claim 5 including the steps of integrating the electrolysis current to indicate the total amount of moisture absorbed and back-flushing the chromatographic column to remove the hydrocarbons retained therein.

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# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,355,367 November 28, 1967

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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 1, line 19, for "2,994,853" read -- 2,993,853 --; column 2, line 54, after "induction" insert -- heating --.

Signed and sealed this 7th day of January 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents