May 29, 1962 L. G. COLE 3,036,895

FLUID ANALYSIS

Filed July 27, 1959

FIG_1

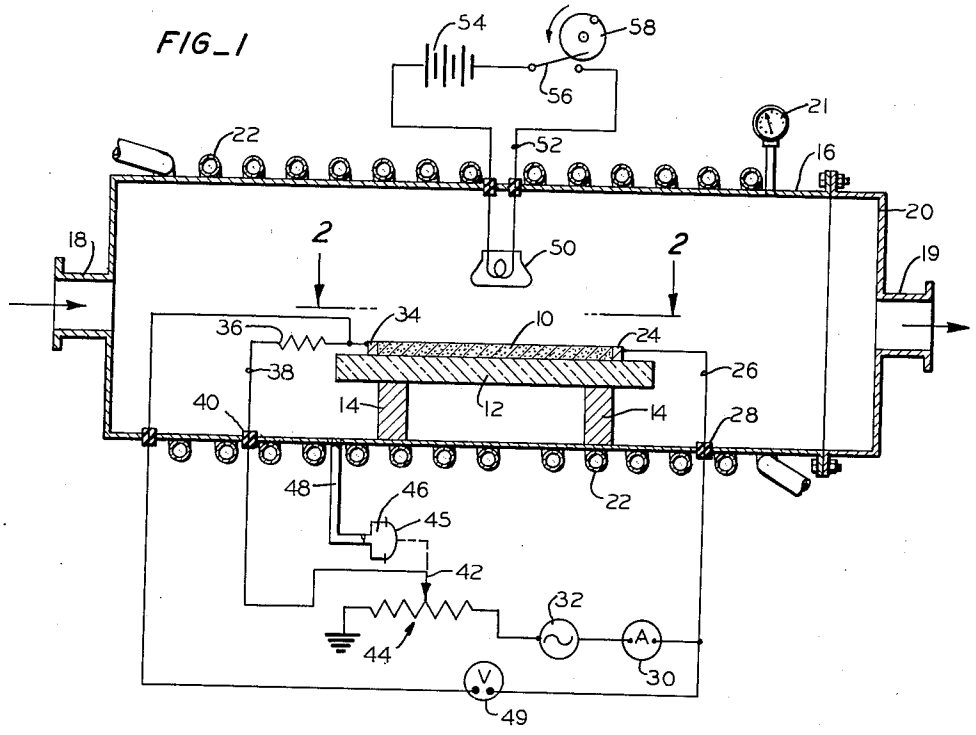


FIG_2

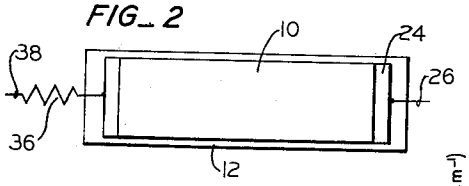


FIG_3

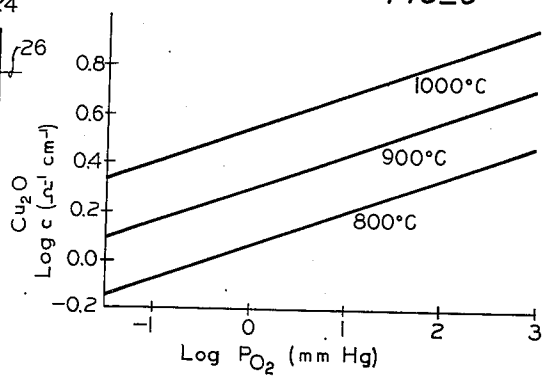
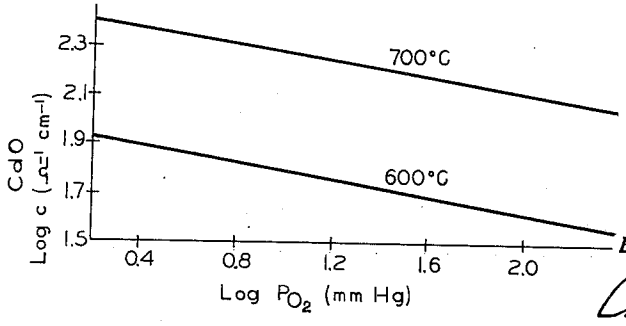


FIG_4



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FLUID ANALYSIS

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8 Claims. (Cl. 23—232)

This invention relates to methods and apparatus for fluid analysis, and utilizes the variation in electrical conductivity of semiconductor material with changes in the composition of fluid surrounding the semiconductor.

In the field of solid state physics, solids are generally classified with respect to electrical conductivity as conductors, semiconductors, and insulators. The conductivity of conductors, such as metals, runs as high as 10^5 ohm^{-1} cm.$^{-1}$, and for insulators is as low as 10^{-16} ohm^{-1} cm.$^{-1}$. The conductivity of semiconductors lies between these two extreme ranges, and although there are no sharp dividing lines, semiconductors are generally regarded as having conductivities ranging between 10^2 to 10^{-10} ohm^{-1} cm.$^{-1}$.

The electrical conductivity of a material is defined by the following equation:

$$c=\frac{IL}{EA}$$

where:

c is the conductivity in ohm^{-1} cm.$^{-1}$,
I is the current in amps flowing through the material,
E is the voltage in volts across the material,
L is the distance in centimeters which the current travels through the material, and
A is the cross-sectional area in square centimeters of the material through which the current travels.

Conductors, of which metals such as copper and silver are good examples, are characterized by the presence of many so-called "free" electrons, which provide the means for conducting relatively large currents. Good insulators have virtually no free electrons, all of their outer electrons being tied up in interatomic bonds. Semiconductors are solid materials which are neither good insulators nor good conductors. Some so-called insulators become conductive at high temperatures when some "bound" electrons are thermally torn loose from their bonds and can move about in the solid and conduct electricity. Under these conditions, the insulator has become what is called an intrinsic semiconductor. Thus, there is no sharp distinction between insulators and intrinsic semiconductors. If the electron bonds are easily broken, then a noticeable amount of conduction occurs even at room temperature, and the material is classed as a semiconductor.

Germanium is a good example of a semiconductor. Its diamond cubic lattice requires four "shared-pair" electron bonds per atom, thus involving all of the available electrons, and therefore pure germanium is a good insulator at low temperatures. However, the electron bonds are relatively easily broken thermally, even at room temperature, producing intrinsic conduction. In addition, the conduction of germanium is also greatly increased by the presence of small quantities of impurities which can act as electron donors or acceptors to create excess electrons or "holes," and thereby increase the conductivity of germanium.

In the case of germanium, which has some "free" electrons due to thermal agitation, the addition of impurities such as phosphorus, antimony, or arsenic (each of which has five electrons in its outer shell for interaction with other atoms), creates an increase in the number of free electrons. On the other hand, if the impurity is boron, gallium, indium, or aluminum (three electrons in the outer shell), there is a decrease in free electrons. The conductivity of the germanium still can be markedly greater, or less, depending on the number of "holes" to a negative electron, i.e., a positive charge.

For the purpose of describing and claiming this invention, the term "semiconductor" is used to include only those materials whose conductivities are markedly affected by the presence of small quantities of impurities which act as electron donor or acceptors. Such a definition does not include materials with conductivities which may happen to lie in the so-called semiconductor range, due, say, to the absorption of water of hydration, which imparts conductivity through the mechanism of ionic mobility, as opposed to transfer of electrons or "holes."

In recent years, semiconductor materials have received considerable attention because of their use as transistors. It has been known for some time that the conductivity of a semiconductor is often dependent on its ambient atmosphere, and in fact, this has been considered a disadvantage of semiconductors, because changes in ambient atmosphere tends to effect unwanted changes in the electrical characteristics of the semiconductor. As a consequence, considerable precautions are often taken to protect the semiconductor bulk materials and surfaces from exposure to gaseous components which would alter the conductivity of the semiconductor material.

This invention takes advantage of this characteristic dependence of semiconductor properties on ambient atmospheric composition which has previously been considered a disadvantage, and puts it to use in gas analysis.

Briefly, this invention contemplates analyzing a fluid mixture having an unknown concentration of a component which can act as a semiconductor impurity to alter the number of free electrons available to carry current through the semiconductor. The semiconductor material includes a substance which enters into a thermodynamically reversible chemical reaction with the component in question. Depending on the temperature of the system, and the concentration of the component, the substance in the semiconductor and the component approach an equilibrium condition which establishes a characteristic electrical conductivity for the semiconductor.

Preferably, the conductivity of the semiconductor is calibrated by measuring the recording at or near the equilibrium condition for various concentrations of the component so that when the semiconductor is exposed to an unknown concentration of the component, its concentration can readily be determined by measurig the conductivity of the semiconductor.

As the concentration of the component around the calibrated semiconductor changes, a new condition of equilibrium is established or approached, thereby creating corresponding characteristic conductivity of the semiconductor, which can be measured to follow or detect the change in concentration of the component.

Since the conductivity of semiconductors depends on temperature, this parameter is either held constant or compensated for by suitable means as described below.

In some cases, the sample and semiconductor must be heated to a sufficient temperature to insure an equilibrium reaction between the component and the reacting substance in the semiconductor material. Also, the temperature is preferably at a suitable value to insure a significant change in conductivity as the concentration of the component is varied.

It is often desirable to have a meter, or other suitable device connected to the semiconductor to read directly the concentration of the component in a gas sample. The conductivity of the semiconductor depends on the absolute or "partial" pressure of the component, which in turn varies with the concentration of the component in the gas sample and with the total pressure of the sample.

For example, increasing the total pressure of a gas

sample of constant composition and concentration of the component, increases the absolute or "partial" pressure of the component, and changes the conductivity of the semiconductor. Therefore, to have the conductivity of the semiconductor be a reliable indication of component concentration, the total pressure of the gas sample is either measured, held constant, or compensated for as described subsequently, when the invention is used to determine concentration of a component in the sample.

Since the reaction of the component and the substance in the semiconductor is essentially a surface phenomenon, the ratio of the surface area of the semiconductor to its mass is made as high as practical to decrease the response time of the measurement. Also, alternating current may be used having a sufficiently high frequency to promote "skin effect" so that the conduction of electricity through the semiconductor is concentrated at the surfaces of the semiconductor.

In terms of apparatus, the invention contemplates a body of semiconductor material including a substance which enters into a thermodynamically reversible chemical reaction with the component, a source of electric current, a circuit connecting the material in series with the source, and means for indicating the conductivity of the material.

In the preferred embodiment, the apparatus includes a source of high frequency alternating current, means for changing current through the semiconductor to compensate for pressure variations in gas samples, and means for changing the resistance of the circuit to compensate for temperature changes.

These and other aspects of the invention will be more fully understood from the following detailed description taken in conjunction with the accompanying drawings in which:

FIG. 1 is a schematic sectional view of apparatus for analyzing gas in accordance with the invention;

FIG. 2 is a view taken on line 2—2 of FIG. 1;

FIG. 3 is a graph showing the variation of conductivity of cuprous oxide with oxygen pressure; and

FIG. 4 is a graph showing the variation in conductivity of cadmium oxide with oxygen pressure.

Referring to FIG. 1, a thin, elongated rectangular strip **10** of a semiconductor material is deposited on the upper surface of an insulator **12** which is supported by blocks **14** inside a sample chamber **16**. A sample inlet **18** and a sample outlet **19** are at opposite ends of the chamber. The outlet end of the chamber is closed by a removable plate **20**, and a pressure gauge **21** is connected to the chamber for measuring total gas pressure within the chamber. An external heating element **22** is coiled around the sample chamber so that the temperature in the chamber can be adjusted and controlled by suitable means (not shown).

A first electrode **24** across one end of the semiconductor is connected by an electric lead **26**, which passes through a first seal **28** in the wall of the sample chamber, in series with an ammeter **30** and one terminal of a source **32** of alternating current. The A.C. source is capable of generating at least 1000 c.p.s., and preferably about 1000K c.p.s. to promote "skin effect." A second electrode **34** is in contact with the other end of the semiconductor and is connected serially with a compensating resistor **36** located in the sample chamber, an electric lead **38** which extends through a seal **40** in the wall of the sample chamber, and with the movable contact **42** of a potentiometer **44** connected to the other terminal of the current source. The movable tap of the potentiometer is mechanically connected to a movable pressure-compensating diaphragm **45** sealed across an opening in a chamber **46**, which in turn is connected by a tube **48** to the interior of the sample chamber. A voltmeter **49** is connected across the semiconductor.

An electric lamp **50** is supported above the semiconductor by leads **52** sealed through the upper portion of the sample chamber and connected to opposite ends of an electrical power source **54**. A switch **56** connected to a rotatable crank **58** is adapted to make and break the lamp circuit as the crank is revolved.

The practice of the invention can be more fully understood from considering a specific example, say in the analysis of a gas sample for the concentration of oxygen, which is an electronegative element.

FIG. 3 shows how the conductivity of cuprous oxide, a semiconductor, depends on oxygen pressure. It is used to measure oxygen concentration as follows: An air sample at atmospheric pressure containing 20% O_2 (partial pressure of 152 mm. Hg) and 80% N_2 (partial pressure of 608 mm. Hg) is introduced to the sample chamber of FIG. 1, and the system is heated to 900° C. The oxygen in the gas and the cuprous oxide semiconductor reach equilibrium at a point which establishes a conductivity for the semiconductor as determined from the 900° C. curve of FIG. 3. Since the semiconductor is of a thin, flat shape with a large exposed area, equilibrium is quickly established. If required, an equilibrium reading is further speeded by using for the measurement an alternating current with a frequency of 5000 cycles per second, which increases the flow of current at the surfaces of the semiconductor, by the so-called "skin effect" phenomenon.

If some of the oxygen in the air sample is burned, and the combustion products removed, say to condition the gas for ammonia synthesis, and the resulting gas sample at atmospheric pressure is 1% O_2 (partial pressure of 7.6 mm. Hg) and 99% N_2, the conductivity of the semiconductor at 900° C. at equilibrium with the new sample is as shown on the 900° C. curve of FIG. 3. As can be seen from FIG. 3 and the foregoing examples, the concentration of oxygen can be followed over a wide range of composition using cuprous oxide.

Referring to FIG. 4, which shows the change in conductivity of cadmium oxide with the partial pressure of oxygen, it is apparent from the above explanation that oxygen concentration can also be measured using cadmium oxide as the semiconductor material.

It will be observed from FIG. 3 that the conductivity of the cuprous oxide increases with increasing oxygen pressure, while on the other hand, the conductivity of the cadmium oxide decreases with increasing oxygen pressure. Other semiconductor materials which increase in conductivity with increasing pressure of the electronegative element, and can be used to measure oxygen concentration, are NiO, UO_2, FeO, CoO, and thorium oxide. Another semiconductor which decreases with increasing pressure of the electronegative element, and can be used to measure oxygen concentration, is ZnO.

The conductivity of the semiconductor for each gas composition can be calculated from the known dimensions of the semiconductor, the current flowing through it, and the voltage drop across it. The oxygen concentration may be determined from its partial pressure, and the temperature and total gas pressure in the sample chamber. However, it is preferable for many applications to maintain a fixed voltage across the semiconductor and hold the pressure and temperature in the sample chamber at a known and fixed value so the ammeter can be calibrated to read directly in oxygen concentration. If it is inconvenient to hold the temperature and pressure exactly constant, the temperature compensating resistor **36** and pressure compensating diaphragm are preselected to compensate automatically for variations in temperature and pressure. For example, the resistor has a positive thermal coefficient of resistance so that as temperature rises, its resistance increases to compensate for the increase in the conductivity of the semiconductor due to the temperature rise. Thus, the ammeter reading is held constant. The reverse procedure occurs if the temperature should fall below a desired value. If the total pressure in the sample chamber should change, say in-

crease, the diaphragm expands to reduce the voltage applied to the semiconductor, assuming that the conductivity increases with increasing gas pressure as is the case for cuprous oxide, and the ammeter reading is thereby kept constant. If a material such as cadmium oxide is used as the semiconductor (conductivity decreases with increasing pressure), the diaphragm connection with the potentiometer tap is reversed from the position shown in FIG. 1 so that the voltage applied across the semiconductor is increased as pressure increases, thereby holding the ammeter reading constant for a given oxygen concentration. In addition, the position of the potentiometer tap with respect to the linkage connecting it to the diaphragm is adjustable so that any desired operating voltage can be selected. The pressure compensation feature can be omitted if pressure is held constant, or if only the absolute pressure of the oxygen is of interest its concentration need not be known.

In a fashion similar to that indicated above for oxygen, the absolute pressure or concentration of iodine vapor is determined by using a semiconductor made of CuI, and the concentration of sulphur vapor is measured by using a semiconductor made of Cu_2S, both of these semiconductors increasing in conductivity with increasing pressure of the respective electronegative element. AgS can also be used as the semiconductor material to determine the concentration of sulphur vapor, but in this case, the conductivity of the semiconductor decreases with increasing concentration of the electronegative element in the gaseous phase. The concentration of gaseous hydrides can be measured in accordance with this invention by using zinc oxide as the semiconductor material.

The above examples demonstrate that by modifying the chemical composition of the semiconductor, or by altering the impurity electron acceptor or donor by exposure to variable ambient atmosphere, a transducer of a semiconducting material is produced which can detect gaseous halides, hydrides, oxides, sulphides, etc., by conducting the operation at a temperature dictated by the thermodyamic function for the particular reaction involved. In other words, if the concentration of the material to measured is high, say being in the range from 1 to 40%, it is desirable to operate the transducer semiconductor at a relatively high temperature so the decomposition of the solid in the semiconductor exhibits a higher proportion of dissociated ions and hence excess carrier of species opposite to that in the ambient atmosphere whose component is being detected, so that wide variations in composition can be accommodated without a disproportionate change in conductivity of the solid material.

Conversely, at relatively low concentrations, marked influence on conductivity is achieved by selecting the operating temperature to yield the largest compositional change per unit change in ambient atmosphere concentration of the species being detected. This is possible because the conductivities of the semiconductors do not obey the thermodynamic functions established for pure binary multi-phase systems, and in fact, can even have temperature inversions of conductivity depending on the composition of the gas. Fortunately, the most desirable temperature levels are easily selected empirically by conducting sample runs at various known concentrations for the particular systems under consideration.

In this last respect, a single transducer can be made to be selectively sensitive to various gaseous components by simply varying its operating temperature. Some transducer elements are insensitive to water vapor in a given temperature range, and yet exhibit a very marked dependence of conductivity on water concentration above and below that range. In the temperature range of insensitivity to water vapor, the transducer is sensitive to oxygen concentration, and therefore the determination of oxygen can be made without the interference of water vapor, inasmuch as the contribution to conductivity by water vapor in this intermediate region is essentially zero.

Hydrohalogens are detected by exposing the hydrohalogen and semiconductor element to a temperature which is sufficiently high to insure at least partial thermal decomposition of the hydrohalogen, and then detecting the halogen in its elemental state. For chlorine, bromine and iodine, the operating temperatures are reasonably low. However, the detection of hydrogen fluoride by decomposition techniques is difficult because of its high thermodynamic stability, and in this case, a hydrogen salt of a fluoride, e.g., KHF_2, is used to detect the hydrogen fluoride without requiring its thermal decomposition.

In an alternate procedure for measuring oxygen concentration, anthracene is used as a semiconductor material, because its photoconductivity is a function of oxygen concentration. When anthracene is radiated with light in the visible region, its conductivity increases, apparently as the result of the photo-oxidation of the surface by exposure to oxygen. The reaction does not take place in the dark, and in fact, the oxide formed in the presence of light is unstable and dissociates in the dark, thus providing an effective means for re-establishing an initial condition. For example, referring to FIG. 1, if the semiconductor material is anthracene and a gas mixture containing oxygen is to be analyzed, the crank 58 is rotated at a suitable rate to irradiate the anthracene with visible light energy modulated at a frequency which is sufficiently slow to permit the oxide formed in the light to be destroyed by the reduction in radiant energy. Thus, as the anthracene is irradiated with light, oxidation takes place and increases the conductivity of the anthracene by an amount proportional to the oxygen present in the gas sample. Then the lamp is turned off, the oxidation process reverses, reducing the conductivity of the anthracene. The anthracene is now in condition for another burst of light and oxidation in proportion to the amount of oxygen in the sample.

Hydrogen gas concentrations are measured as described above by detecting change in conductivity of zinc oxide on exposure to various concentrations of hydrogen.

I claim:

1. The method of analyzing a gas having an unknown concentration of a component which acts as a semiconductor impurity, the method comprising the steps of exposing a semiconductor material which enters into a thermodynamically reversible chemical reaction with the impurity component to various known gaseous concentrations of the impurity component, maintaining the semiconductor at a temperature to effect a thermodynamically reversible reaction with the impurity component, passing electric current through the semiconductor, recording the electrical conductivity of the semiconductor when exposed to the various known concentrations of the impurity component, exposing the semiconductor to the gas having an unknown concentration of the component, and recording the electrical conductivity of the semiconductor when in contact with the gas whereby the unknown concentration of the impurity component may be determined.

2. The method of analyzing a gas having an unknown concentration of a component which acts as a semiconductor impurity, the method comprising the steps of exposing a semiconductor material which enters into a thermodynamically reversible chemical reaction with the impurity component to various known gaseous concentrations of the impurity component, maintaining the semiconductor at a temperature to effect a thermodynamically reversible reaction with the impurity component, passing alternating electric current through the semiconductor at a sufficiently high frequency to produce a substantial skin effect, recording the electrical conductivity of the semiconductor when exposed to the various known concentrations of the impurity component, exposing the semiconductor to the gas having an unknown concentration of the component, and recording the electrical conductivity of the semiconductor when in contact with the gas

whereby the unknown concentration of the impurity component may be determined.

3. The method of analyzing a gas having an unknown concentration of a component which acts as a semiconductor impurity, the method comprising the steps of exposing a semiconductor material which enters into a thermodynamically reversible chemical reaction with the impurity component to various known gaseous concentrations of the impurity component, maintaining the semiconductor at a substantially constant temperature to effect a thermodynamically reversible reaction with the impurity component, passing electric current through the semiconductor, recording the electrical conductivity of the semiconductor when exposed to the various known concentrations of the impurity component, exposing the semiconductor to the gas having an unknown concentration of the component, and recording the electrical conductivity of the semiconductor when in contact with the gas whereby the unknown concentration of the impurity component may be determined.

4. The method of analyzing a gas having an unknown concentration of a component which acts as a semiconductor impurity, the method comprising the steps of exposing a semiconductor material which enters into a thermodynamically reversible chemical reaction with the impurity component to various known gaseous concentrations of the impurity component at a substantially constant pressure, maintaining the semiconductor at a temperature to effect a thermodynamically reversible reaction with the impurity component, passing electric current through the semiconductor, recording the electrical conductivity of the semiconductor when exposed to the various known concentrations of the impurity component, exposing the semiconductor to the gas at the said substantially constant pressure and having an unknown concentration of the component, and recording the electrical conductivity of the semiconductor when in contact with the gas whereby the unknown concentration of the impurity component may be determined.

5. The method of analyzing a gas having an unknown concentration of a component which acts as a semiconductor impurity, the method comprising the steps of exposing a semiconductor material which enters into a thermodynamically reversible chemical reaction with the impurity component to various known gaseous concentrations of the impurity component, maintaining the semiconductor at a temperature to effect a thermodynamically reversible reaction with the impurity component, passing electric current through the semiconductor, recording the electrical conductivity of the semiconductor when exposed to the various known concentrations of the impurity component, exposing the semiconductor to the gas at varying pressure having an unknown concentration of the component, changing the current flowing through the semiconductor as the unknown gas pressure changes to compensate for the change in conductivity of the semiconductor due to pressure changes, and recording the electrical conductivity of the semiconductor when in contact with the gas whereby the unknown concentration of the impurity component may be determined.

6. The method of analyzing a gas having an unknown concentration of an oxygen component which acts as a photosensitive semiconductor impurity, the method comprising the steps of exposing an anthracene photosensitive semiconductor material which enters into a thermodynamically reversible chemical reaction with the oxygen component to various known gaseous concentrations of the oxygen component, exposing the anthracene semiconductor to light, maintaining the anthracene semiconductor at a temperature to effect a thermodynamically reversible reaction with the oxygen component, passing electric current through the anthracene semiconductor, recording the photoconductivity of the anthracene semiconductor when exposed to the various known concentrations of the oxygen component, exposing the anthracene semiconductor to the gas having an unknown concentration of the oxygen component, and recording the photoconductivity of the anthracene semiconductor when in contact with the gas whereby the unknown concentration of the oxygen component may be determined.

7. The method according to claim 6 which includes the step of shining light pulses on the semiconductor material.

8. Apparatus for measuring the concentration of a component in a fluid, the apparatus comprising a body of semiconductor material including a substance which enters into a thermodynamically reversible chemical reaction with the component, a source of electric current, a circuit connecting the material in series with the source, means independent of the semiconductor body responsive to pressure changes in the fluid for automatically changing current through the body, and means for indicating the conductivity of the material.

References Cited in the file of this patent

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,036,895 May 29, 1962

Leland G. Cole

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 2, line 47, for "measurig" read -- measuring --; column 8, line 42, after "material." insert the following claim:

> 9. Apparatus for measuring the concentration of a component in a fluid, the apparatus comprising a body of semiconductor material including a substance which enters into a thermodynamically reversible chemical reaction with the component, a source of electric current, a circuit connecting the material in series with the source, means responsive to the temperature of the semiconductor body for automatically changing the resistance of the circuit independent of the semiconductor body, and means for indicating the conductivity of the material.

in the heading to the printed specification, line 7, for "8 Claims." read -- 9 Claims. --.

Signed and sealed this 16th day of October 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents