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[54] **APPARATUS FOR MEASURING NITROGEN OXIDE CONCENTRATIONS**
6 Claims, 2 Drawing Figs.

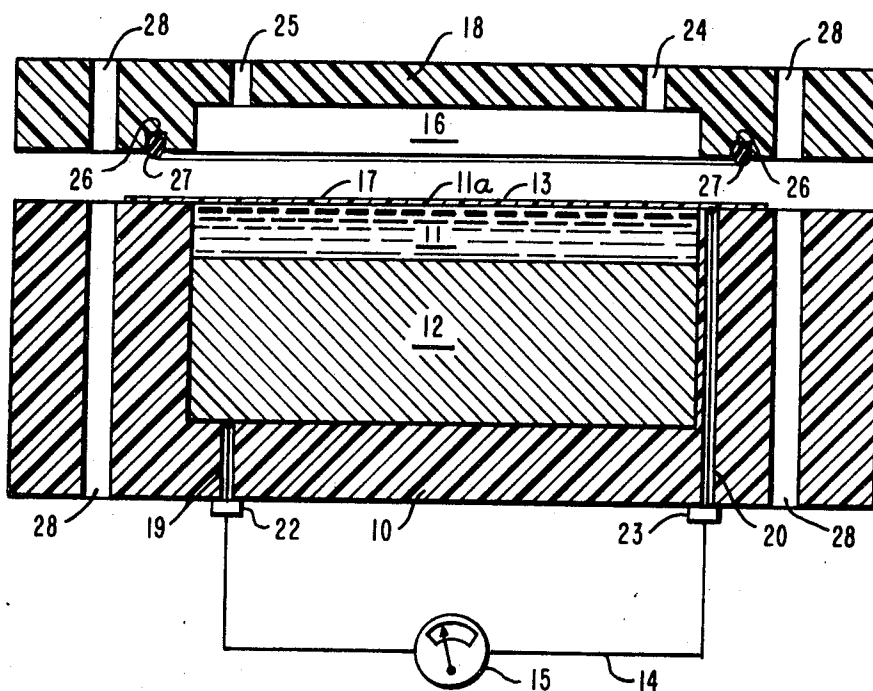
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195

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ABSTRACT: Nitrogen oxide concentrations present in a gaseous mixture are rapidly and continuously monitored by measuring the current passing between an inert metallic sensing electrode and a counter electrode which electrodes are in contact with an aqueous electrolyte solution and at which sensing electrode the oxides are electrooxidized. The sensing electrode is composed of an inert metal, whereas the counter electrode is composed of an electroactive material which is capable of being electrochemically reduced when electrically interconnected with the sensing presence in the presence of the aqueous electrolyte solution.



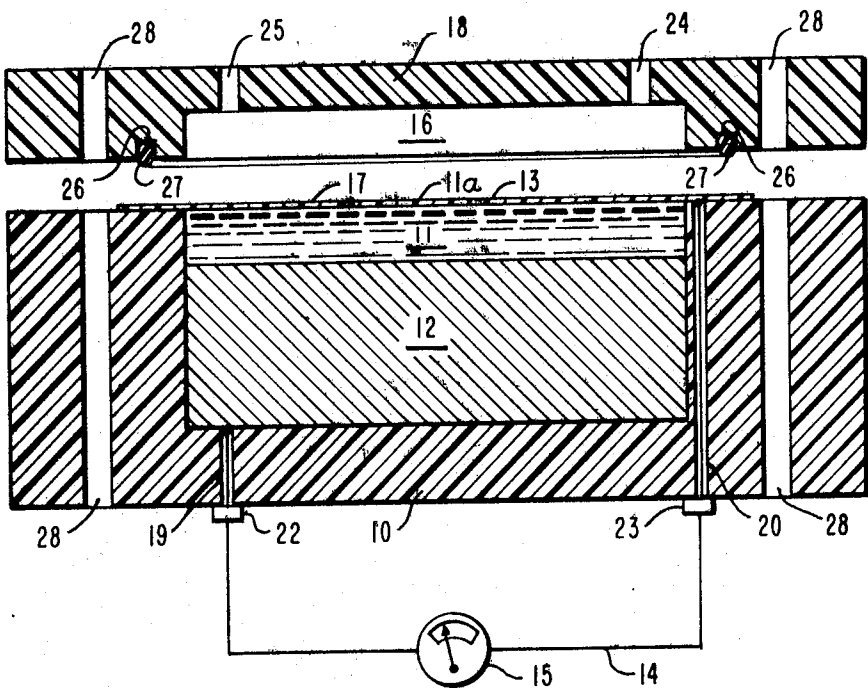


FIG. - 1

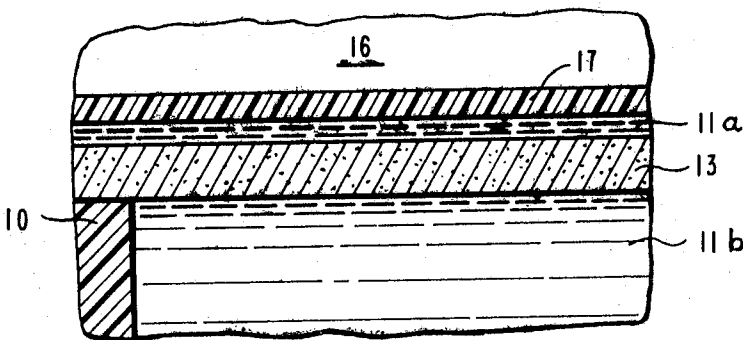


FIG. - 2

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APPARATUS FOR MEASURING NITROGEN OXIDE CONCENTRATIONS

BACKGROUND OF THE INVENTION

The oxides of nitrogen have become a serious atmospheric pollutant especially in areas in which there is a relatively high density of automobiles. It has been found that the exhaust of internal combustion engines which burn hydrocarbon fuels such as gasoline expel rather high concentrations of these nitrogen oxides into the atmosphere, and due to the catalytic action of sunlight, a number of rather complex compounds are formed. The presence of significant concentrations of these oxides causes serious problems of atmospheric pollution, commonly referred to as smog, especially in large metropolitan areas in which automobiles are a major mode of transportation. This atmospheric contamination is being more and more seriously regarded in attempts to check or otherwise reduce the serious effects caused by such atmospheric pollutants. It is well appreciated that the presence of such conditions as smog are extremely undesirable from a health standpoint, with eye and lung irritations being the most obvious problems. It is further known that this atmospheric contamination also inhibits and destroys plant growth as well. Aside from being one of the major contributors to smog, the oxides of nitrogen are themselves extremely dangerous and poisonous. Accordingly, the importance of being able to continuously monitor the concentrations of these compounds is readily evident.

Although a number of nitrogen oxide analyzers are presently available, these instruments are less than satisfactory for a number of reasons. These analyzers incorporate coulometric, colorimetric, electrical and thermal conductivity as well as infrared and ultraviolet absorbance methods of analysis. Such instruments are generally of high cost and bulkiness, thereby inhibiting their widespread use and acceptance. In addition, many of these analyzers can only be operated by skilled technical personnel often requiring a number of steps in effecting the analysis as well as critical calibration procedures and handling of chemical solutions. Further, instrumental response is often slow.

Nitrogen dioxide concentrations may be measured by indirect electrolytic reaction in a coulometer in which iodide or bromide ions are oxidized to iodine or bromine respectively. The iodine or bromine is then cathodically reduced by controlled potential electrolysis with the resulting current being proportional to the nitrogen oxide present. However, this method of analysis is severely limited because of nonspecificity, continued maintenance requirements and poor response times. Ozone interferes with the reactions and must be removed by chemical filters which require frequent maintenance and/or replacement. Further, the iodide or bromide solutions require constant replenishment with storage problems of these corrosive solutions being undesirable. The slow response time of such a coulometer has been reported to be as high as 15 to 25 minutes for a 90 percent response.

Colorimetric analysis relies on the nitrogen oxides absorption in a chemical reagent which thereby changes color and is photometrically measured. Some disadvantages include considerable maintenance, poor response and bulky apparatus. Reagent solutions must be stored and constantly pumped and samples require rigorous conditioning to remove interfering species. Response time of such instruments is of the order of 15 minutes for 90 percent response. The size and operation of the instrument is such as to discourage its use outside the laboratory.

Electrical and thermoconductivity analyzers, although requiring less maintenance, are highly nonspecific, and are only suited to the measurement of laboratory samples which have been conditioned to remove interfering species.

Perhaps the most suitable analyzers presently available are those utilizing photometric means in which the infrared and ultraviolet absorbance properties of nitrogen dioxide and nitric oxide are monitored. With proper filter selection, such an instrument can be made specific for the nitrogen oxides.

However, the size of the analyzer makes it bulky to handle thereby discouraging its use as a portable type instrument. Further, samples must be carefully handled and continuously conditioned in order to eliminate foreign particles which settle out at the cell windows and thereby affect the sensitivity of the instrument. In addition, changes in light source intensity and detector tube sensitivity also affect the measurements thereby necessitating frequent calibration checks.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a schematic cross section of the transducer of the invention; and

FIG. 2 shows an enlarged detailed view of a broken away portion of the sensing electrode area of FIG. 1.

DESCRIPTION OF THE INVENTION

It is to the elimination of the problems generally associated with the above-noted methods of analyzing for nitrogen oxides that the present invention is directed. The most important nitrogen oxides present in the atmosphere are nitric oxide and nitrogen dioxide and it is to the analysis of these oxides that the invention is generally directed. However, it will be appreciated that other oxides such as nitrous oxide may also be monitored by proper selection of electrolyte and counter electrode materials within the scope of the disclosure. Specifically, the apparatus of the invention for measuring nitrogen dioxide and nitric oxide concentrations present in a gaseous mixture comprises a transducer having a sensing electrode and a counter electrode which contact an aqueous electrolyte solution. The transducer is constructed in such a manner that the sensing electrode, at which the nitrogen oxides are electrooxidized, is located between the surface of the electrolyte which is in contact with the oxide-containing atmosphere and the counter electrode. In this manner, as the gaseous mixture is diffused into the electrolyte at the gas-electrolyte interface, the oxide molecules will contact the sensing electrode and thereupon be electrooxidized to nitrate ions. At the same time, the counter electrode, which is in contact with the electrolyte solution and interconnected with the sensing electrode so as to allow a current to flow therebetween, is electroreduced to consume negative ions to balance those produced by oxidation at the sensing electrode.

Initially, the operation of the transducer of the invention will be more readily appreciated and understood by referring to the schematic representation of the device as shown in the accompanying drawings.

FIG. 1 shows a schematic cross section of a preferred construction of the transducer utilized in the invention whereas FIG. 2 illustrates, in detail, a portion of the device at the sensing electrode. Each of these drawings may be referred to in the following description. The electrolyte solution 11 is contained in a suitable vessel 10 in which is present a counter electrode 12 and a sensing electrode 13. The vessel 10 may consist of any suitable material such as plastic, glass, etc. which is preferably impact resistant and shatterproof. A means for passing a current between the sensing and counter electrodes comprises a conductive wire 14. The wire 14 is attached to terminals 22 and 23 located on the exterior of the vessel 10 with the terminals 22 and 23 being interconnected to the respective electrodes via conduits 19 and 20. It will be appreciated that other suitable means for electrically connecting the electrodes may be used which allows a current flow, which current is caused by electrons generated at the sensing electrode at which an electrooxidation reaction occurs. In a preferred embodiment, as shown in the drawings, the surface of the electrolyte is covered with a semipermeable membrane 17 through which a gas may diffuse but which will prevent significant losses of electrolyte by evaporation or spillage. However, in a simplified device, the membrane may be eliminated and the electrolyte surface fully exposed to a gas. As the nitrogen oxide containing gas contacts the electrolyte surface, molecules will diffuse into the electrolyte with the oxide con-

centration initially entering the electrolyte solution being proportional to their partial pressures or concentrations within the atmosphere. Thereafter, as molecules of NO and NO₂ in solution in the electrolyte contact the surface of the sensing electrode 13, they become electrooxidized with the specific reaction depending on the type of or relative potential of electrolyte present and the material making up the counter electrode as will be more fully explained hereinafter. As the oxide electrooxidation producing nitrate ions (NO₃^{7E-}) occurs, a current generated between the sensing and counter electrodes is monitored by suitable means 15 which may include amplification equipment. Although the current will depend on the rate of oxide diffusion into the particular electrolyte, temperature and pressure variations, etc., it will be evident that the current in any event will be proportional to the concentration of atmospheric nitrogen oxides.

It is especially important that the nitrogen oxides present in electrolyte are essentially confined to the portion of the electrolyte 11a between the sensing electrode 13 and the electrolyte surface. Significant diffusion of oxides beyond the sensing electrode 13 and throughout the bulk of electrolyte 11b will be prevented during transducer operation since essentially all of the molecules contacting the sensing electrode 13 will become immediately electrooxidized. Accordingly, as the nitrogen oxide concentration within the portion of electrolyte contacting the sensing electrode 13 is continually diminished, more molecules diffuse to that portion of electrolyte and thereafter are electrooxidized. Thus, further oxide diffusion into the portion of electrolyte 11b between the counter and sensing electrodes is essentially prevented. It will be evident that nitrogen oxides present at the counter electrode 12 would become directly oxidized or reduced with no resulting current flowing between the counter and sensing electrodes from the reaction.

As previously noted, the vessel 10 may be open to the atmosphere or be constructed as shown in FIG. 1 whereby a cover 18 is present. Where such a cover is utilized, means for directing a gas into the sample gas space 16 such as a gas inlet 24 and outlet 25 are provided. The cover 18 may also be provided with a groove or slot 26 for seating a gasket or O-ring 27 which will complete the enclosure of the gas sample space 16 and confine the gas. The cover 18 and vessel 10 may additionally be provided with appropriate bore holes 28 through which bolts may be placed for securing the cover 18 to the vessel 10. Obviously, other means such as clamping devices and the like may also be used for this purpose. This type of construction is especially suited for directing gas streams such as automobile exhausts and the like to be analyzed.

It will be appreciated that the construction of the transducer disclosed herein may be used for analysis of a number of different gases and is not limited to nitrogen oxides. Thus, for example, the device may be utilized to monitor, for example, sulfur dioxide as disclosed in our copending application, Ser. No. 758,527, filed Sept. 9, 1968, concurrently herewith by proper selection of counter electrodes and electrolyte compositions.

The sensing electrode may consist of any noble metal which itself does not undergo electrochemical reaction within the electrolyte. Examples of suitable metals include gold, platinum, palladium, iridium and the like. The electrode itself may consist of a screen, foil, porous plaque or fabricated in such other suitable form as desired. In forming an electrode of such precious metals, as a practical manner it is often preferred to form a coating of the inert metal on relatively less expensive metallic substrate materials. Thus, for example, a sensing electrode consisting of a gold-plated copper or nickel expanded metal is found to be quite satisfactory. Further, it is preferred to fabricate this sensing electrode in a manner to expose a rather large electrode surface area to the electrolyte solution. Accordingly, fine screens or porous electrodes may be preferred.

The counter electrode consists of an electroactive material which is capable of being electroreduced when in contact with the electrolyte. Where the transducer is to act as an electroox-

idant type sensor, i.e., where nitric oxide and/or nitrogen dioxide is to be electrooxidized at the sensing electrode, the counter electrode must comprise a material which will accept the negative ions equivalent to the nitrate ions being generated at the sensing electrode by the electrooxidation reaction. In turn, the counter electrode material utilizes the electrons and itself is electroreduced combining with negative ions in solution to balance those generated by oxidation at the sensing electrode and neutralizing them to form an inactive salt. Various counter electrode compositions may be used which are chemically compatible with the electrolyte and relatively insoluble therein. The specific composition of the counter electrode will depend on how it is to be electroreduced with the specific material selected determined by the type of electrolyte and the possible presence of interfering species in the gaseous mixture to be analyzed.

The electrooxidation of diffused nitrogen dioxide in aqueous acid electrolyte solution at the sensing electrode is carried out at +0.80 volts (Stockholm Convention) relative to the standard hydrogen electrode, and which polarity is positive relative to the standard hydrogen electrode whereas nitric oxide electrooxidation occurs between +0.96 and +1.03 volts. The acid electrolyte in this electrooxidant type sensor is preferably dilute sulfuric acid although other acid solutions may be used. Accordingly, in analyzing gases containing mixtures of these oxides, an electroactive counter electrode composition must be one itself having a single standard reduction potential more positive than +1.03 volts at a positive polarity relative to the standard hydrogen electrode. Suitable materials include the metallic oxides, lead dioxide and manganese dioxide or other materials in the oxidized state which are chemically compatible with the acid electrolyte and which have a reduction potential greater than +1.03 volts with positive polarity relative to the standard hydrogen electrode. The electrooxidation reactions proceed readily in dilute acid electrolyte without significant interference by the presence of oxygen, carbon dioxide, carbon monoxide, water vapor, hydrocarbons, carbonyl compounds such as aldehydes and ketone in the diffused gaseous mixture. However, the presence of sulfur dioxide in the nitrogen oxide containing sample should be avoided since it will oxidize at a lower potential and interfere with the nitrogen oxide measurement. Although sulfur dioxide interference may not be serious in analysis of automobile exhausts, its presence in other gaseous samples and the concentrations thereof may readily be determined by the methods of analysis set forth in our aforementioned copending application. Thus, as the sulfur dioxide concentration is monitored in one transducer without nitrogen oxide interference by selecting suitable counter electrodes providing a lower oxidation potential, the instant sensor could be used to monitor both sulfur dioxide and nitrogen oxide concentrations. Accordingly, the difference between the monitor sensing sulfur dioxide exclusively and that analyzing the combined gases could be determined taking into consideration variations of instrument response, etc.

It will be evident to those skilled in the art that a number of counter electrode compositions which will be compatible with aqueous acidic electrolyte solutions may be selected. The counter electrode compositions disclosed herein are in no way to be considered exhaustive of those materials which may be used and are given only by way of example. However, selection of specific counter electrode compositions must be made so that the electrooxidation of nitrogen oxides in the particular electrolyte may be accomplished.

Again, as in the case of the sensing electrodes, a number of different techniques for fabricating the counter electrode may be used. Thus, the compositions may be plated or otherwise impregnated onto inert materials in such a manner as to allow maximum exposure of the electroactive material to the electrolyte solution. Where the apparatus is to be used for relatively long periods of time, it may be desirable to cover the counter electrode with a suitable ion-exchange or ion-selective membrane which will prevent the gradual buildup of dis-

solved metal ions originating from the counter electrode. The use of such a cover prevents possible changes of surface characteristics resulting from extensive buildup of ionic materials.

The gaseous mixture which is to be analyzed for nitrogen oxide according to the present invention may be exposed to the electrolyte solution in which it will be diffused by any suitable manner. Where an open vessel is used, gaseous diffusion at the electrolyte surface will readily take place by mere exposure to the nitrogen oxide containing atmosphere. Where an enclosed vessel is preferred, a space between the vessel wall and the electrolyte surface into which space gases may be directed is necessary. The gaseous mixture may then be pumped or otherwise fed into the space continuously or intermittently as desired. As previously noted, in order to prevent extensive electrolyte evaporation, a semipermeable membrane of an inert material which will not prevent or substantially impede gaseous diffusion of the nitrogen oxides into the electrolyte may be used to cover the surface of the electrolyte solution. For example, Teflon, polyethylene, polypropylene and the like are suitable where the particular material may be chosen for its relative impermeability to possible interfering gases. The membrane will also prevent loss of the electrolyte by spillage and will provide improved convenience since the device may be placed in any position during use or storage without significant loss of electrolyte.

Monitoring of the current passing between the sensor electrode and the counter electrode may be accomplished by any suitable means. Although the current is directly proportional to the partial pressure of nitrogen oxides present in the atmosphere diffusing into the electrolyte solution due to the relatively low current intensity, appropriate electronic amplification will be useful. Further, equipment calibrated to read directly in parts-per-million nitrogen oxide is effective in continually monitoring the output voltage of the amplifier although other suitable means may be selected.

The following example is given to illustrate the manner in which the invention is carried out. It is to be understood that the example is given by way of illustration only and is not intended to limit the invention to any particular or specific materials or conditions set forth therein.

EXAMPLE

A counter electrode was prepared by mixing 6.8 grams of reagent grade lead dioxide, 0.8 grams polypropylene powder and 0.4 grams carbon black. Approximately 4 grams of this mixture was spread evenly in a mold 1 1/4 inch by 1 1/4 inch by one-fourth inch deep having removable bottom and top plates. A flat piece of platinum mesh 1 1/4 inch by 1 1/4 inch by 0.004 inches thick was placed in intimate contact with the powder and the assembly pressurized 6,000 p.s.i.g. for 5 minutes in a hydraulic press at a temperature of 150° C. Thereafter, the mold was removed from the press and cooled. The sensor electrode consisted of a 3-inch diameter circular plate of gold. The electrodes were commonly wired to electronic current amplification equipment and were assembled in a plexiglass container to which an aqueous solution of 1N sulfuric acid was carefully added to avoid trapped air bubbles. The gold electrode was covered with a 1/4-mil-thick Teflon membrane and

the entire assembly made secure. Into the airspace above the membrane was continually passed an atmospheric gaseous mixture containing nitric oxide and nitrogen dioxide through an inlet tube extending from the exterior of the plexiglass container. The gas exited from the enclosure through a similar projection tube opposite the inlet tube. Diffused nitric oxide and nitrogen dioxide oxidation immediately took place at the sensor electrode producing negatively charged nitrate ions with concomitant reduction of the lead dioxide counter electrode composition in which equivalent sulfate ions already present in the electrolyte are consumed to produce inactive lead sulfate and water. The current caused by the simultaneous reactions was continuously monitored while the nitrogen oxide concentrations of the gaseous mixture entering the analyzer was changed. Initially, the response time of the apparatus to indicate 90 percent of the actual initial nitric oxide and nitrogen dioxide concentration of 100 p.p.m. was about 10 seconds. Thereafter, the total concentration of both oxides was changed to 50 p.p.m. with the recovery time of the analyzer in registering the change in concentration being about 15 seconds.

We claim:

1. A transducer for measuring the concentration of nitrogen oxides in a gaseous sample comprising:

a confined volume of aqueous acid electrolyte having an active surface for receiving nitrogen oxide molecules from said gas sample to be dissolved in said electrolyte;

a sensing electrode immersed in said electrolyte adjacent the active surface consisting of a chemically inert material for contacting the nitrogen oxides dissolved in said electrolyte for electrooxidation to produce nitrate ions;

means, including a counterelectrode of a material selected from the group consisting of manganese dioxide and lead dioxide immersed in said electrolyte and spaced from said sensing electrode on the side opposite said active surface of the electrolyte, electrically coupled to said sensing electrode for maintaining said sensing electrode at a predetermined positive potential in excess of 1.03 volts relative to the standard hydrogen electrode but less than a selected level at which other gases in the sample may be oxidized by said sensing electrode; and,

indicator means electrically coupled for measuring the amplitude of the current flow between said sensing electrode and said counterelectrode.

2. The transducer of claim 1 wherein: the surface of said sensing electrode consists of a material selected from the group consisting of gold, platinum, palladium and iridium.

3. The transducer of claim 1 wherein: said counterelectrode consists of manganese dioxide.

4. The transducer of claim 1 wherein: said counterelectrode consists of lead dioxide.

5. The transducer of claim 1 further comprising membrane means for covering said active surface and confining said electrolyte consisting of a membrane material readily permeable to the diffusion of nitrogen oxides therethrough and relatively impermeable to said electrolyte.

6. The transducer of claim 5, wherein: said membrane material is selected from the group consisting of Teflon and polyethylene.

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