Feb. 2, 1971 J. L. TEAL ET AL 3,560,156
DETERMINING THE OXYGEN DEMAND OF COMBUSTIBLE MATERIALS IN AQUEOUS DISPERSIONS
Filed May 3, 1965 2 Sheets-Sheet 1

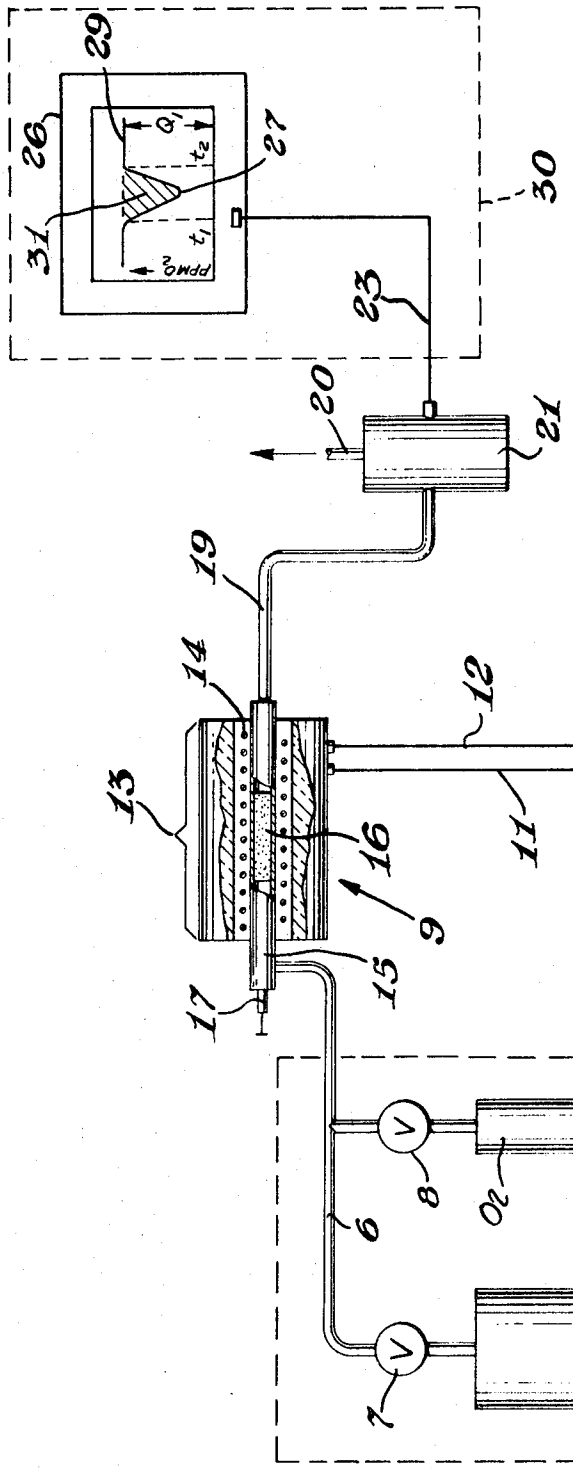

Fig. 1

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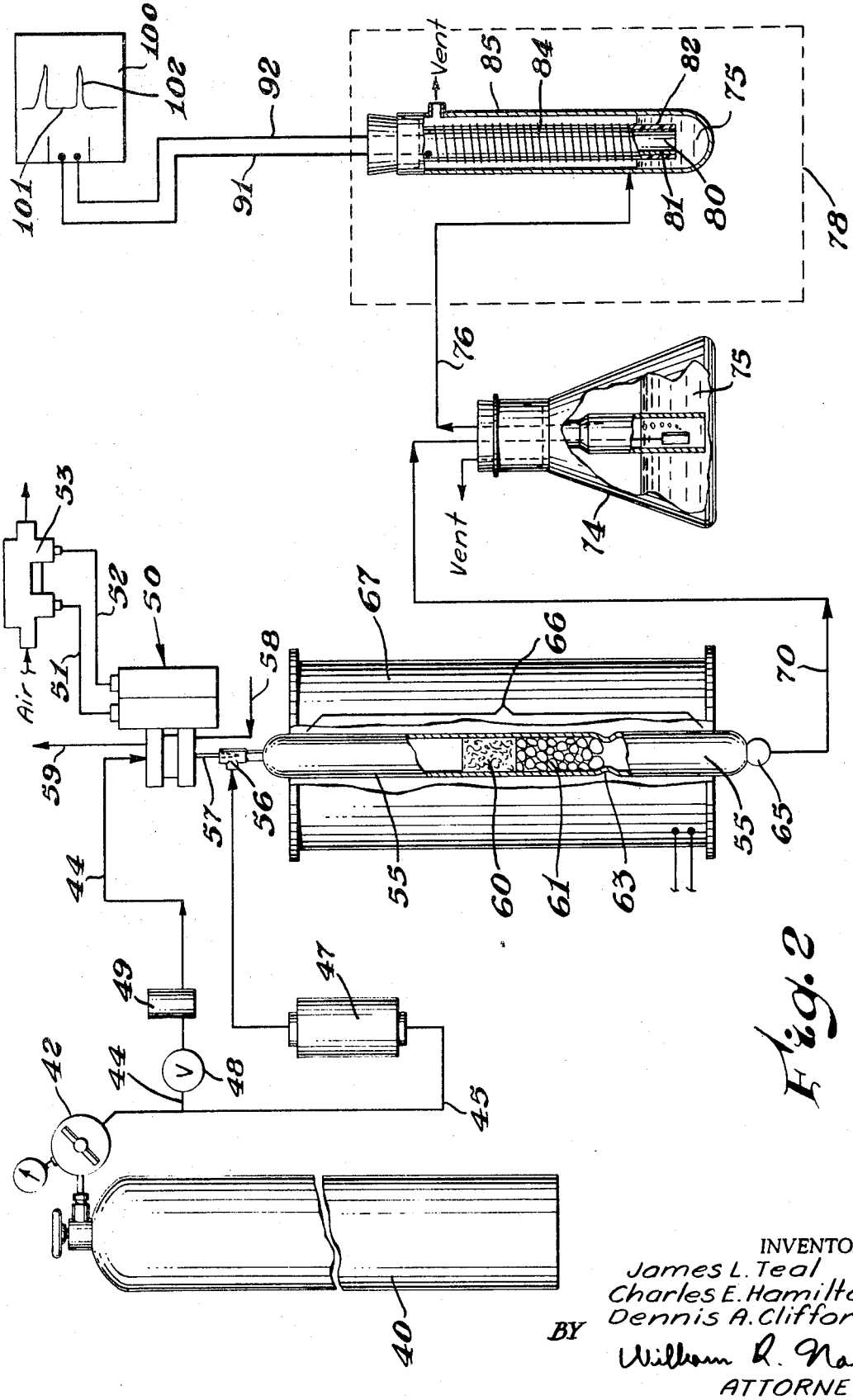

Fig. 2

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DETERMINING THE OXYGEN DEMAND OF COMBUSTIBLE MATERIALS IN AQUEOUS DISPERSIONS

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U.S. Cl. 23—230 6 Claims

ABSTRACT OF THE DISCLOSURE

Determining the oxygen demand of combustible materials in aqueous dispersions, comprising the steps of flowing a feed gas stream composed of an inert gas containing oxygen into a confined, heated combustion zone, at a constant rate. The feed gas stream is passed through a combustion supporting, porous catalyst bed in the combustion zone which is heated to a combustion supporting temperature and then is fed into a detector for small amounts of free oxygen. A small amount of a dilute aqueous dispersion of a combustible material is injected into the feed gas stream within the combustion zone upstream from the catalyst bed. The resulting gaseous product is then swept from the combustion zone into the oxygen detector by the continuing pressure of the feed gas stream. Since the feed gas stream contains only a small amount of oxygen, very small amounts of combustible materials in the aqueous dispersion produce a large percentage deviation in the oxygen content of the effluent gas from the combustion zone.

The present invention concerns a novel analytical apparatus for determining the oxygen demand of aqueous dispersions of combustible materials.

Water pollution control is a problem of long standing and ever increasing importance as population and industry continue to grow in relation to water resources. At the threshold of the overall problem of pollution control is the measurement of pollution itself. One of the parameters useful for this purpose is the ozygen demand of pollutants. Today this parameter is usually measured by means of a chemically promoted wet oxidation process. For a description of this technique see "Standard Methods for the Examination of Water and Waste Water," 11th ed. (1960), pp. 399–402. While good results can be obtained by the skillful practice of this method, it is cumbersome and time consuming. Its usefulness is also limited by the presence in many waste streams of certain combustible materials not readily subject to wet oxidation by chemical means. Moreover, the presence of chlorides in many waste streams interferes with the use of the wet oxidation method.

"Combustible material," as used herein, refers to any composition of matter whether solid, liquid or gas which can be chemically reacted with gaseous oxygen under the influence of heat. The terminology "aqueous dispersion" includes solutions and suspensions of combustible material.

In view of the above desiderata, an object of the present invention is to provide a method for rapidly determining the oxygen demand of aqueous dispersions of combustible material. Most especially, it is an object to provide a fast method for determining the oxygen demand of dilute dispersions of combustible pollutants as in waste waters. A further object is to provide an apparatus capable of carrying out the aforesaid methods.

The above objects, and other benefits, as will become apparent hereinafter, are accomplished in accordance with the present invention.

The process of the invention comprises the steps of flowing a feed gas stream composed of an inert gas containing at least about 10 and up to about 10,000, preferably however, no more than about 1,000, parts per million, by volume, of oxygen into a confined, heated combustion zone, at a constant rate. Within the combustion zone, the feed gas stream is passed through a combustion supporting, porous catalyst bed. The combustion zone is heated at a combustion supporting temperature. From the heated combustion zone, the gas stream is fed into a detector for small amounts of free oxygen. Having established a feed gas stream, flowing through the heated combustion zone and catalyst bed, and thence into the quanitative continuous oxygen detector, a small amount of a dilute aqueous dispersion of a combustion material is injected into the gas stream within the combustion zone upstream from the catalyst bed. The resulting gaseous product is then swept from the combustion zone into the oxygen detector by the continuing pressure of the feed gas stream.

The temperature of the combustion zone is maintained within the range from about 600 to about 1200° C. Although some oxidation catalysts permit the use of lower temperatures within the range of 600 to 800° C., best results are achieved using platinum as the catalyst and heating the combustion zone at a temperature within the range from about 800 to about 1000° C. Higher temperatures can be used if desired but there is no apparent advantage in doing so.

The oxygen extracted from that initially available in the feed gas stream, as the result of the oxidation of combustible material injected as an aqueous dispersion, is correlative with a characteristic of the signal produced by the oxygen detector. Since the feed gas stream contains only a small amount of oxygen, very small amounts of combustible materials in the aqueous dispersion produce a large percentage deviation in the oxygen content of the effluent gas from the combustion zone. Thus, the method of the invention is highly sensitive to small variations in the oxygen demand of dilute aqueous dispersions of combustible materials.

A most convenient characteristic of the signal, from the standpoint of ease of measurement, is its amplitude or deviation from the signal corresponding to the oxygen content of the combustion zone effluent under steady state conditions, or in other terms, the oxygen content of the feed gas stream. This deviation may be indicated graphically. Also, the area under a curve formed by a tracing or continuous plot of the signal can be used as the signal characteristic to be correlated with the oxygen content.

Thus when reproducible conditions are used, such that one analysis is comparable with a second analysis, the measured signal characteristic of the oxygen detector, is readily calibrated against results obtained using aqueous dispersions of combustible materials of known oxygen demand to determine the oxygen demand of unknown dispersions.

Either the signal amplitude or area under the curve can be measured by suitable electronic devices coupled to a conventional graphic recorder. Illustratively, a graphic integrator is one means for producing a recorded measurement. Calibration of the measured value can be accomplished visually or by appropriate electrical circuitry such as will be apparent to those skilled in the art.

Reproducibility essential to this mode of operation requires keeping parameters such as sample size, combustion temperature, gas flow rate, oxygen content of the feed gas stream, catalyst type and equipment design either essentially identical or functionally equivalent. Whether this condition is met is readily ascertained by repeated analysis of a given dispersion of combustible material under a

given set or range of operating conditions. If, for each analysis, the measured signal characteristic achieves an essentially constant value, the process may be assumed to be reproducible. In any event, the equipment should be calibrated from time to time during use with a standard dispersion of combustible material of known oxygen demand.

As employed herein, the useful determination described as "total oxygen demand" refers to the amount of oxygen that will have to be supplied to the dispersion to convert the combustible materials therein to their corresponding oxidation products. Any dissolved and otherwise unreacted oxygen is gasified upon injection of the sample into the combustion zone and this oxygen detracts from the measured or apparent chemical oxygen demand of the combustible materials. Thus, the measurement of the invention is said to define the total oxygen demand of the dispersion.

Consideration of apparatus suitable for performing the above method will provide further amplification of the invention. In the attached drawings FIG. I is a schematic illustration of essential basic components of an analyzer of the invention. FIG. II is a more detailed illustration of an automated embodiment of the invention for application to aqueous dispersions of combustible materials.

Referring to FIG. I, the elemental components of the apparatus comprise a dilute oxygen feed stream supply means **2**, which in this particular illustration is composed of an arrangement of an inert gas supply tank **3** and an oxygen supply tank **4** integrally feeding a feed gas line **6**. Nitrogen and oxygen are metered into the feed stream line **6** through pressure and flow control valves **7** and **8**. Line **6** feeds the mixed gas stream into a confined combustion zone defined by that portion of the combustion tube **15** within the heating zone **13** of an electric furnace **9**. Within the heated combustion zone is a gas permeable, catalyst bed **16** of an oxidation supporting catalyst. The temperature of the heating zone **13** is controlled by a variable power control **10** through the electrical input lines **11** and **12** which are connected to the terminals of a resistance heating coil **14**.

Injection of the aqueous dispersion to be analyzed is accomplished by suitable injection means such as the illustrated syringe **17**. The trajectory for sample injection is such that the sample will be deposited within the heating zone **13** on the upstream side of the catalyst bed **16**.

Gaseous effluent from the heating zone **13** flows through the gas line **19** into a continuous, quantitative, oxygen detector **21** and exhausts through vent **20** to the atmosphere. The oxygen detector **21** produces an electrical signal fed through an electrical connection **23** to read out means **30** which in this instance is a graphic recorder **26**.

The signal which may be measured as voltage or current, is proportional to, and therefore correlative with, the oxygen content of the gaseous effluent. If desired, the recorded signal can be calibrated for direct reading of the signal as the oxygen content of the effluent gas stream.

The total oxygen demand (TOD) is defined according to the formula:

$$TOD = Q_1(t_2 - t_1) - \int_{t_1}^{t_2} Q(dt)$$

wherein Q is a function of t, which is time, and Q_1 is the oxygen content of the feed gas stream, or in other terms the oxygen content of the effluent gas under steady state conditions. t_1 and t_2 are the times of sample injection and return of the oxygen content of the effluent gas to that of the feed gas stream, respectively. A graphic illustration of the value of the above equation solved for TOD is shown in FIG. I by the shaded area **31** between the base line **29** representing the oxygen content of the feed gas stream and curve **27** plotted by the graphic recorder **26** between t_1 and t_2.

Alternately, variations in the oxygen content of the gaseous effluent from the combustion zone, as the result of oxygen used to oxidize combustible material present in the injected aqueous dispersion, are reflected in the amplitude or displacement of the curve **27** from the recorder base line **29**. In fact, the displacement of the recorded curve **27** from the base line **29** is directly proportional to the amount of oxygen used in the combustion of the sample, i.e., the total oxygen demand of the aqueous dispersion.

While a graphic recorder **26** is the illustrated readout means **30**, any convenient technique and corersponding mechanism, including such appropriate electronic signal measuring means as will be apparent to those skilled in the art, can be used for the readout of the signals generated by the oxygen detector.

In practice, the total oxygen demand values are usually obtained by calibrating the graphic deviations for unknown dispersions of combustible materials against a calibrating curve based on data obtained for samples of dispersions of combustible materials having known oxygen demands. For the calibration technique to work effectively, care should be exercised, as mentioned previously, to insure functionally equivalent operating conditions.

Means for supplying the dilute oxygen feed stream can take any of several possible forms in addition to that specifically illustrated. For instance, the oxygen and inert gas can be premixed and the mixture supplied to the combustion zone from a storage cylinder. This mode is shown in FIG. 11. In another mode of operation, a a stream of inert gas in constantly and uniformly diluted with oxygen generated as required by controlled electrolysis of water, or by a controlled oxygen liberating chemical reaction. The carrier gas can be any of the essentially inert gases such as helium and argon. However, for convenience and economy, nitrogen is the preferred carrier gas.

The flow rate of the gas stream can vary within broad limits. In practice, the gas flow rate should be adjusted to produce conveniently measurable and recordable, signal deviations. Good results are achieved employing gas flow rates of from 50 up to 250 cubic centimeters (STP) per minute. It should be noted that knowledge of the actual flow rate is not necessary to the invention so long as the flow rate can be controlled to constant and predetermined levels.

The temperature required to effect combustion can be generated by any convenient furnace, but preferably an electrical furnace is used. Such a furnace permits more accurate temperature control and uniform heat distribution throughout the combination zone. The temperature in such a furnace, for instance, can be controlled by means of a voltage control on the power source for the furnace.

The combustion zone is conveniently defined by a tubular quartz conduit such as a Vycor fused silica and quartz tube. However, any inert material which retains its shape and is essentially inert to oxygen and steam at elevated combustion supporting temperatures will suffice as the material of construction for the combustion conduit. In most operations, the combustion zone should not exceed a cross sectional area of about 12 square centimeters and a total volume of about 200 cubic centimeters. The best dimensions in these regards will vary with changes in sample size, gas flow rates, catalyst bed size and the combustion temperature.

As stated above, the process of the invention utilizes a gas permeable combustion supporting catalyst bed in the combustion zone. The catalyst bed is positioned within the heating zone at some distance downstream from the inlet for the dilute oxygen feed stream so as to define a sample expansion zone within the combustion zone upstream from the catalyst bed. This distance is such that upon vaporization of the injected aqueous sample,

flash back, i.e., flow of the vapors against the direction of flow for the dilute oxygen feed stream is effectively maintained within the heated combustion zone. Deleterious flash back may be evidenced by the formation of condensate in conduits used to confine and supply the dilute oxygen feed stream to the combustion zone. The optimum volume of the sample expansion zone will be determined, in any given piece of apparatus, at least in part, by the sample size, permeability of the catalyst bed and temperature of the heated combustion zone. For example, the heated sample expansion zone should be at least about 5 cubic centimeters for an aqueous sample size of about 1 microliter up to 10 microliters. Larger samples will necessitate correspondingly larger sample expansion zones.

Suitable catalyst materials for the gas permeable, combustion supporting catalyst bed include solid platinum metal, palladium, rhodium, osmium and ruthenium metals.. Usually these metals are obtained in the form of wire or gauze, but particulate forms thereof are also useful. Other catalysts are the particulate oxides of certain metals such as nickel and cobalt. At high enough temperatures, siliceous materials become catalytic for the purposes of the invention.

If desired, the catalytic material may be supported on a base such as asbestos or quartz fiber. In general, any combustion supporting catalyst can be used. "Combustion supporting" means herein that the catalyst holds oxygen in such a form that upon contact thereof with a reducing material the oxygen is available for reaction.

The catalyst bed is essentially a loosely packed bed of one or more suitable catalyst materials, or when the catalysts exist in the form of wire or gauze, the bed is essentially a lightly compacted maze of such materials. In any event, it is sufficiently permeable to gas flow, that upon injection and vaporization of the sample to be analyzed, excessive back pressure is avoided. The length of the catalyst bed may be varied considerably, but desirably, the bed is at least about 5 centimeters long to ensure reproducible combustion.

Although the invention is not predicated upon an understanding or a theoretical explanation of the basis for operability of the invention, the following explanation of the function of the catalyst with reference to the analysis of aqueous dispersions of combustible materials, may provide basis for optimizing its performance.

It is believed that upon injection of an aqueous dispersion of combustible materials into the heated combustion zone, water vapor dilutes and envelops most of the combustible materials. Non-vaporizable materials such as inorganic refractory components of waste streams will, of course, largely remain at the site of sample vaporization. Under these conditions, gaseous oxygen within the combustion zone may not achieve sufficient contact with combustible vapors to accomplish efficient oxidation thereof for the purposes of the invention. This conclusion is substantiated by removing the catalyst bed from the combustion zone of an otherwise operable instrument. In such event, too little oxidation is observed in terms of the measured differential of oxygen content between that of the input feed gas stream, and that of the gaseous effluent containing the oxidation products. When the catalyst is present in the combustion zone, however, combustible materials gasified upon injection of the aqueous dispersion, are more effectively, if not completely oxidized by oxygen held in the catalyst bed.

Since under this hypothesis, the required oxygen is supplied from that held in the catalyst bed, the initial gaseous effluent from the combustion zone immediately after injection of the sample to be analyzed is not likely to reflect a significant decrease in oxygen content. It is not until the continually flowing feed gas stream, which sweeps the gasified combustible materials and the oxidation products thereof through the system, is denuded of oxygen as a result of restoring the oxygen held by the catalyst bed under steady state conditions, that a significant decrease in the oxygen content occurs in the gaseous effluent from the combustion zone. If this explanation is accepted, it becomes apparent that best results under the invention will be achieved with a catalyst characterized by the ability to give up and then rapidly recover oxygen.

Aqueous dispersions of combustible materials are readily injected into the combustion zone by any one of several means. One suitable injection means is a syringe as shown in FIG. I. Another injection means utilizes gas pressure as the source of the injecting force. A preferred method is to drop a small liquid sample into a vertically aligned combustion zone as shown in FIG. II.

A number of devices are known for quantitatively determining the oxygen content of gas streams. Illustrative of such devices and techniques are those shown in U.S. Pats. 2,651,612, 2,805,191, 2,992,170, 3,005,758, 3,076,-929, and 3,088,809. Preferred for use in the present invention are detectors which have a high sensitivity for low concentrations of gaseous oxygen. Such a detector is the Hersch electrolytic oxygen detection cell as taught in U.S. Pat. 2,805,191. The Hersch cell is most useful inasmuch as it produces a rapid response with high accuracy or reproducibility. Generally useful, however, are any oxygen detectors which measure from about 10 up to 10,000 parts per million of oxygen as the dilute phase in a gas stream.

In order that the useful life of the Hersch type oxygen detector be extended and its operation be improved, it is desirable to scrub the effluent gas stream to free it of CO_2 and other acid gases. This is conveniently accomplished by bubbling the effluent gas through an alkali metal hydroxide bath confined within a gas scrubber.

As a further illustration of the invention, refer to FIG. II which depicts an automated total oxygen demand apparatus for the analysis of aqueous dispersions. In this embodiment, a mixed gas stream of nitrogen and oxygen was supplied from a gas cylinder **40** equipped with a pressure regulating valve **42**. Connecting the gas cylinder with the combustion tube **55** was gas line **45**. This connected with an injection T **56**, which was seated in the end of the combustion tube **55**. In this line was a rotameter **47** to measure the gas flow rate. Just ahead of the rotameter **47**, the gas line **45** was tapped for gas line **44**. This diverted a small amount of the mixed gas to the sample injection means **50**. A Beckmann model LG–4 liquid injection valve was the actual injection means used. The flow rate in line **44** was controlled by valve **48** and measured by a bubbler flow meter **49**. The sample injection means **50** was operated by means of air pressure applied intermittently through lines **51** and **52**. The sample injection means **50** was fed a continuous stream of the aqueous dispersion to be analyzed through line **58**. The unused portion of the stream was wasted through line **59**. Application of the air pressure was accomplished through a timed solenoid actuated pneumatic valve **53**.

Injection of the sample was accomplished through a stainless steel needle **57** which, with the aid of slight gas pressure provided through line **44**, dropped the sample into the combustion tube **55** through the injection T **56**.

Within the combustion tube **55**, which was a quartz tube, was a catalyst bed composed of a quartz wool plug **60** and, beneath this plug, a bed of platinum gauze balls **61**. The bed of platinum gauze balls **61** was seated against a slight indentation **63** in the wall of the combustion tube **55**. The bottom of the combustion tube **55** was connected through a balljoint **65** with the effluent gas line **70**. This line transmitted the effluent gas from the combustion zone **66** within the electric furnace **67** to a gas scrubber **74**, which removed carbon dioxide from the effluent gas in 25 weight percent aqueous potassium hydroxide **75**. This scrubber discharged humidified and

carbon dioxide free gas to an electrolytic oxygen detector **78** through gas line **76**.

The oxygen detector **78** was constructed as taught by Hersch in U.S. Pat. 2,805,191. Specifically, a lead foil **81** was wrapped around in inert plastic core **80**, one inch in diameter. The foil **81** was covered by a bibulous membrane **82** in the form of a water swellable ethylcellulose film. A silver wire **84** was wrapped around the membrane and the assembly placed in a tube **85** about ¼ full of 25 weight percent aqueous potassium hydroxide **75**. Connecting wires **91** and **92** attached respectively to the lead foil **81** and silver wire **84** carried the signal output of the cell. The wires **91** and **92** were electrically connected to an amplifying graphic recorder **100**.

Using the above apparatus, a feed gas stream was provided as nitrogen containing 200 parts per million, by volume, of oxygen. The gas entered the combustion tube **55** at a constant rate of about 120 cc. per minute (STP). Some gas flowed through line **44** and thence through the injection means **50** at the rate of approximately one bubble per second. The furnace temperature was brought up to 900° C. Once the gas flow rates and temperature had been stabilized, a 19 microliter sample of the aqueous dispersion to be analyzed was injected into the combustion zone. This was accomplished with the illustrated solenoid controlled pneumatic liquid injection means **50**. As the gas flow continued after sample injection, the oxygen detector sensed and the recorder depicted a drop in oxygen content of the effluent gas from the combustion zone. This was recorded as a departure **102** from the base line **101**. The amplitude of this departure was ascertained and using previously generated calibrating data, obtained under the same operating conditions, the amplitude was found to represent the theoretical total oxygen demand of the aqueous sample of combustible material analyzed.

In the above manner a number of aqueous dispersions of combustible materials were analyzed for their total oxygen demand. The results of these analyses, as compared with their theoretical oxygen demand, are reported below. The theoretical oxygen demand was calculated according to the equation:

$$C_nH_mO_xN_y+\left(n+\frac{m}{4}+\frac{y}{2}-\frac{x}{2}\right)O_2\rightarrow nCO_2+yNO+m/2H_2O$$

TABLE

	Disperse combustible material [1]	Observed mg./l. TOD [2]	Calculated mg./l TOD
Run No.:			
1	Acetic acid	99.8	100.0
2	Phenol	99.6	100.0
3	Triethylene glycol	98.8	100.0
4	Dipropylene glycol	99.4	100.0
5	Bromo-n,n,diethyl aniline	97.6	100.0
6	Ammonium chloride	99.5	100.0
7	Sodium sulfate	0	0
8	Sodium phosphate	0	0
9	Sodium chloride	0	0
10	Ferrous chloride	0	0
11	Ferric chloride	0	0
12	Phosphoric acid	0	0

[1] Runs 7-12 actually contained no combustible material. The results show the effectiveness of the method when materials with no TOD are present.
[2] Milligrams perliter of total oxygen demand.

What is claimed is:

1. A process for measuring the oxygen demand of an aqueous dispersion of combustible material which comprises the steps of:

(1) flowing a feed gas stream of an inert gas containing at least about 10 and up to about 10,000 parts per million by volume of oxygen at a constant rate through a confined combustion zone heated at a combustion supporting temperature within the range from about 600 to about 1200° C., and, within the combustion zone, flowing the feed stream through a combustion supporting catalyst bed,

(2) flowing the effluent gas from the combustion zone into a continuous quantitative detector for gaseous oxygen to produce an electrical signal which varies with the oxygen content of the effluent gas and,

(3) while continuing the above procedure, injecting a small amount of the aqueous dispersion of combustible material into the combustion zone upstream from the catalyst bed whereby an electrical signal correlative with the total oxygen demand of the aqueous dispersion is produced.

2. A process for measuring the oxygen demand of an aqueous dispersion of combustible material which comprises the steps of:

(1) flowing a feed gas stream of an inert gas containing at least about 10 and up to about 10,000 parts per million by volume of oxygen at a constant rate through a confined combustion zone heated at a combustion supporting temperature within the range from about 600 to about 1200° C., and, within the combustion zone, flowing the feed stream through a combustion supporting catalyst bed,

(2) flowing the effluent gas from the combustion zone into a continuous quantitative detector for gaseous oxygen to produce an electrical signal which varies with the oxygen content of the effluent gas and,

(3) while continuing the above procedure, injecting a small amount of the aqueous dispersion of combustible material into the combustion zone upstream from the catalyst bed,

(4) measuring the amplitude of the maximum deviation of the signal produced by the oxygen detector in step (3), with reference to that produced in step (2).

3. A process for measuring the oxygen demand of an aqueous dispersion of combustible material which comprises the steps of:

(1) flowing a feed gas stream of an inert gas containing at least about 10 and up to about 10,000 parts per million by volume of oxygen at a constant rate through a confined combustion zone heated at a combustion supporting temperature within the range from about 600 to about 1200° C., and within the combustion zone, flowing the feed stream through a combustion supporting catalyst bed,

(2) flowing the effluent gas from the combustion zone into a continuous quantitative detector for gaseous oxygen to produce an electrical signal which varies with to the oxygen content of the effluent gas and,

(3) while continuing the above procedure, injecting a small amount of the aqueous dispersion of combustible material into the combustion zone upstream from the catalyst bed,

(4) calibrating the difference between the electrical signal produced in step (2) and the maximum departture therefrom produced in step (3) to determine the total oxygen demand of the aqueous dispersion.

4. A process for measuring the oxygen demand of a dilute aqueous dispersion of combustible material which comprises the steps of:

(1) flowing a feed gas stream of nitrogen containing at least about 10 and up to about 10,000 parts per million by volume of oxygen at a constant rate through a confined combustion zone having a volume less than about 200 cubic centimeters heated at a combustion supporting temperature within the range from about 800 to about 1000° C., and, within the combustion zone, flowing the feed stream through a combustion supporting catalyst bed at least about 5 centimeters long,

(2) flowing the effluent gas from the combustion zone into a continuous electrolytic detector for small amounts of gaseous oxygen to produce an electrical

signal which varies with the oxygen content of the effluent gas and,

(3) while continuing the above procedure, injecting a small amount of the diluent aqueous dispersion of combustible material into the combustion zone upstream from the catalyst bed,

(4) calibrating the difference between the electrical signal produced in step (2) and the maximum departure therefrom produced in step (3) as the total oxygen demand of the aqueous dispersion.

5. A method as in claim **4** where the dilute aqueous dispersion contains less than 1 percent by weight of combustible material.

6. A method as in claim **4** wherein a flow rate of the feed gas stream is within the range from about 50 up to about 250 cubic centimeters (STP) per minute.

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U.S. Cl. X.R.

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