US 20170003246A1

(19) **United States**

(12) **Patent Application Publication**

(10) **Pub. No.: US 2017/0003246 A1**

(43) **Pub. Date: Jan. 5, 2017**

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(54) **OXYGEN SENSOR FOR CO BREAKTHROUGH MEASUREMENTS**

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(21) Appl. No.: **14/788,203**

(22) Filed: **Jun. 30, 2015**

Publication Classification

(51) **Int. Cl.**

G01N 27/407 (2006.01)

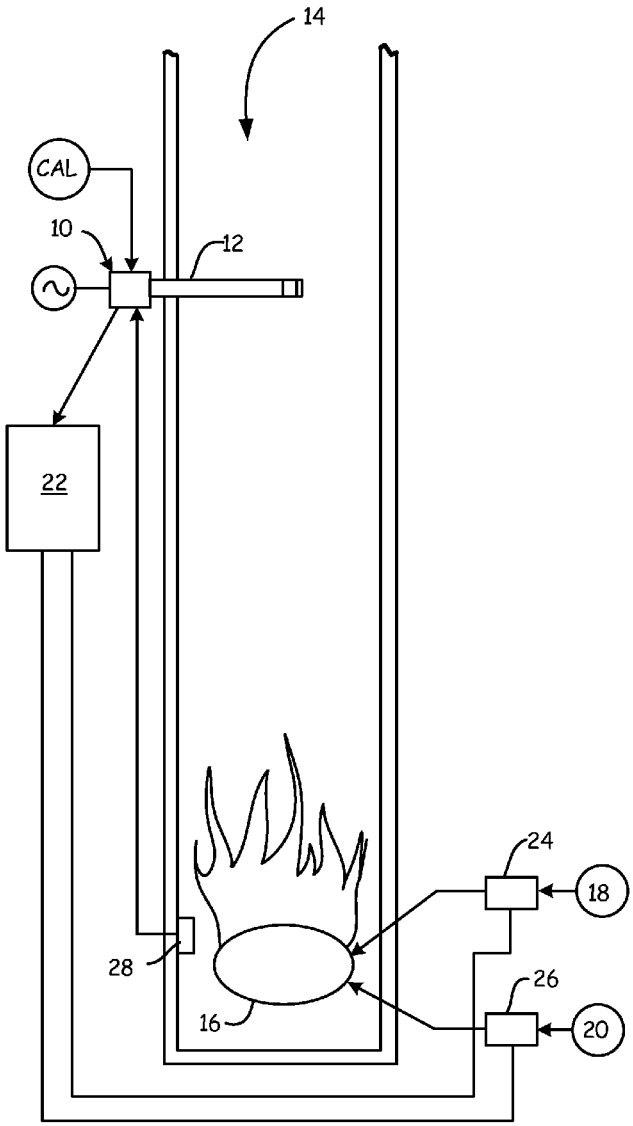
G01N 27/416 (2006.01)

(52) **U.S. Cl.**

CPC ***G01N 27/4073*** (2013.01); ***G01N 27/416*** (2013.01)

(57) **ABSTRACT**

A sensor system configured to detect oxygen in an exhaust stream of an industrial process is provided. In one embodiment, the sensor system comprises a probe with an oxygen-detecting sensor, wherein the oxygen-detecting sensor detects a concentration of oxygen in the exhaust stream. The system may also comprise a catalytic converter located on the probe near the sensor, wherein the catalytic converter is configured to convert carbon monoxide to carbon dioxide. The system may also comprise a signal detector configured to detect a change in oxygen concentration indicative of a carbon monoxide breakthrough.



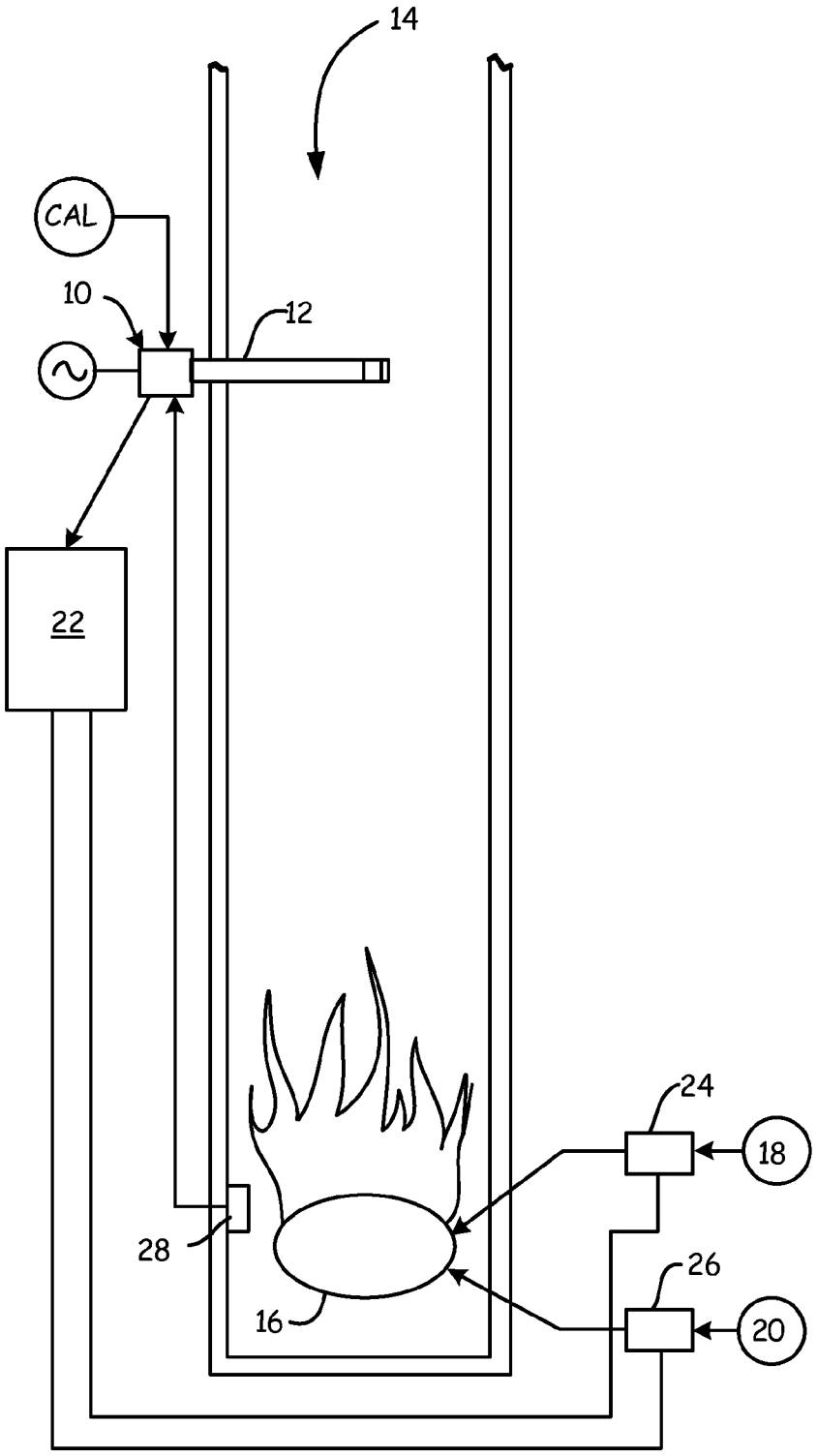


FIG. 1

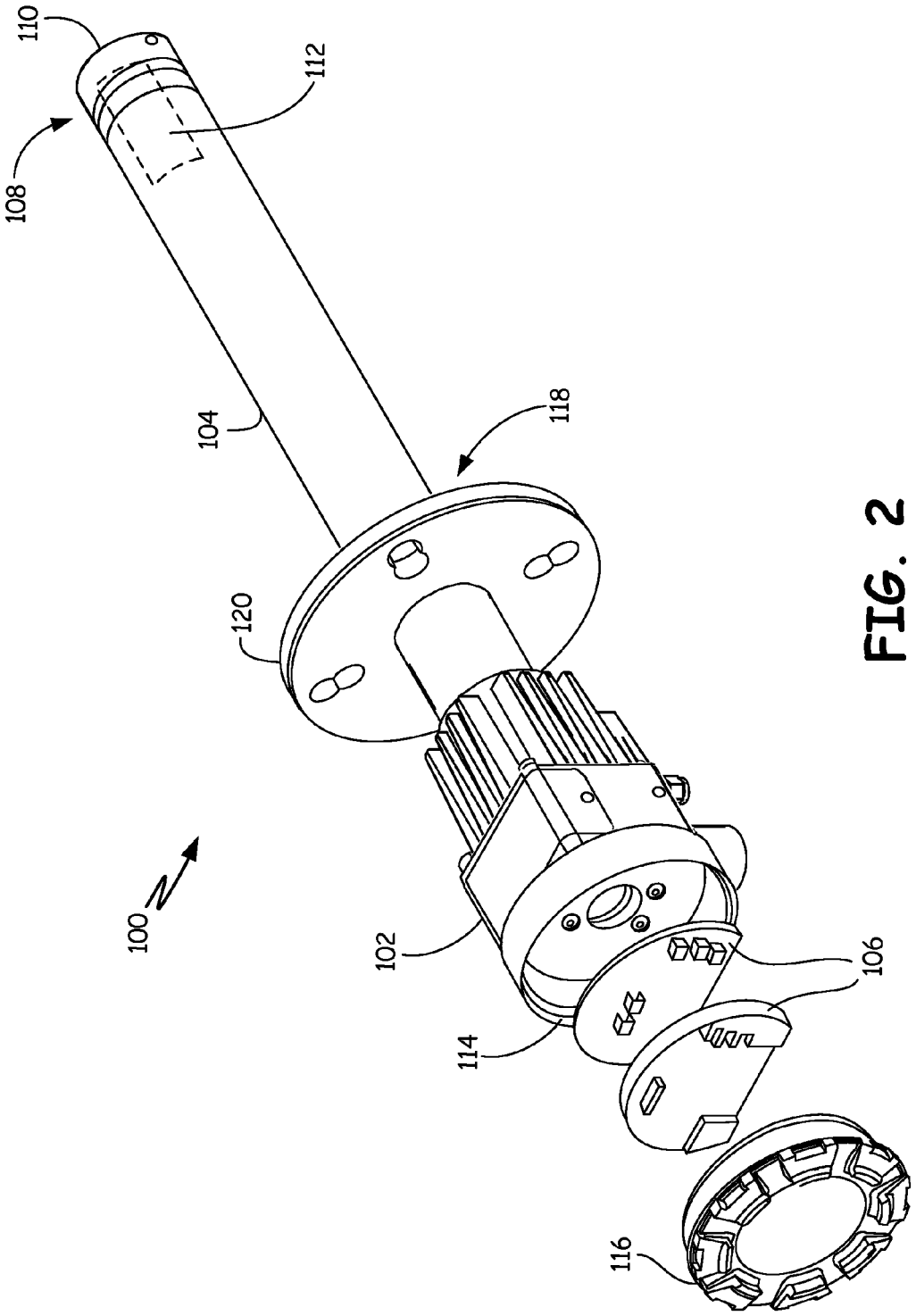


FIG. 2

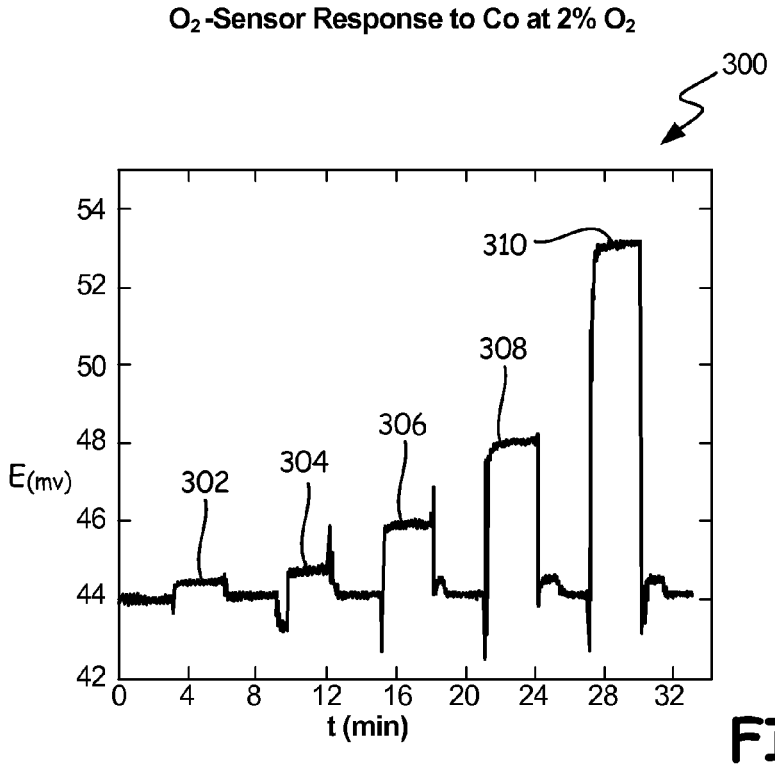

O_2-Sensor Response to Co at 2% O_2
300
310
308
306
304
302
$E_{(mv)}$
54
52
50
48
46
44
42
0
4
8
12
16
20
24
28
32
t (min)

FIG. 3A

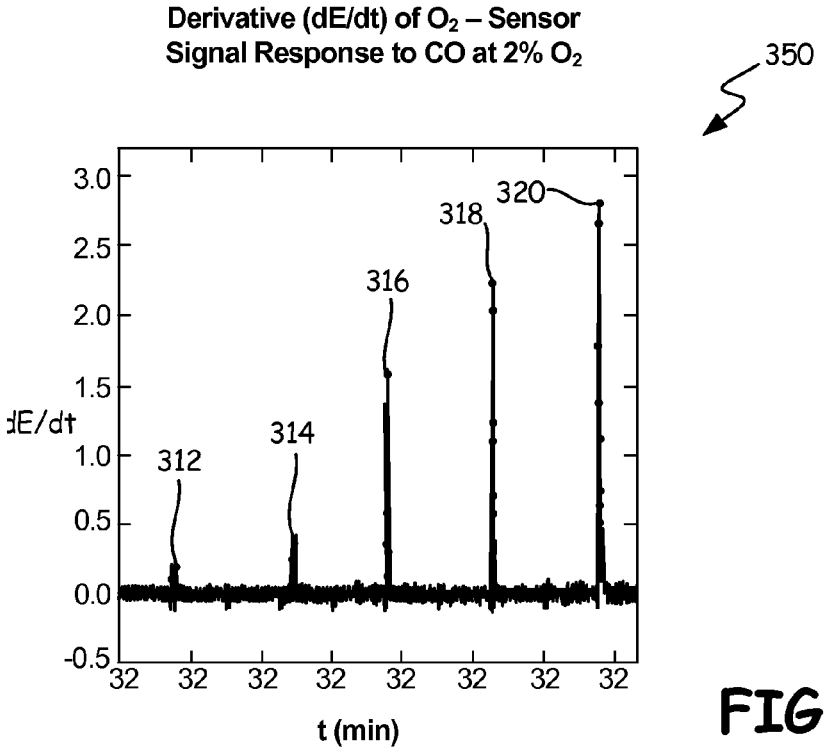

Derivative (dE/dt) of O_2 – Sensor Signal Response to CO at 2% O_2
350
320
318
316
314
312
dE/dt
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
32
32
32
32
32
32
32
32
t (min)

FIG. 3B

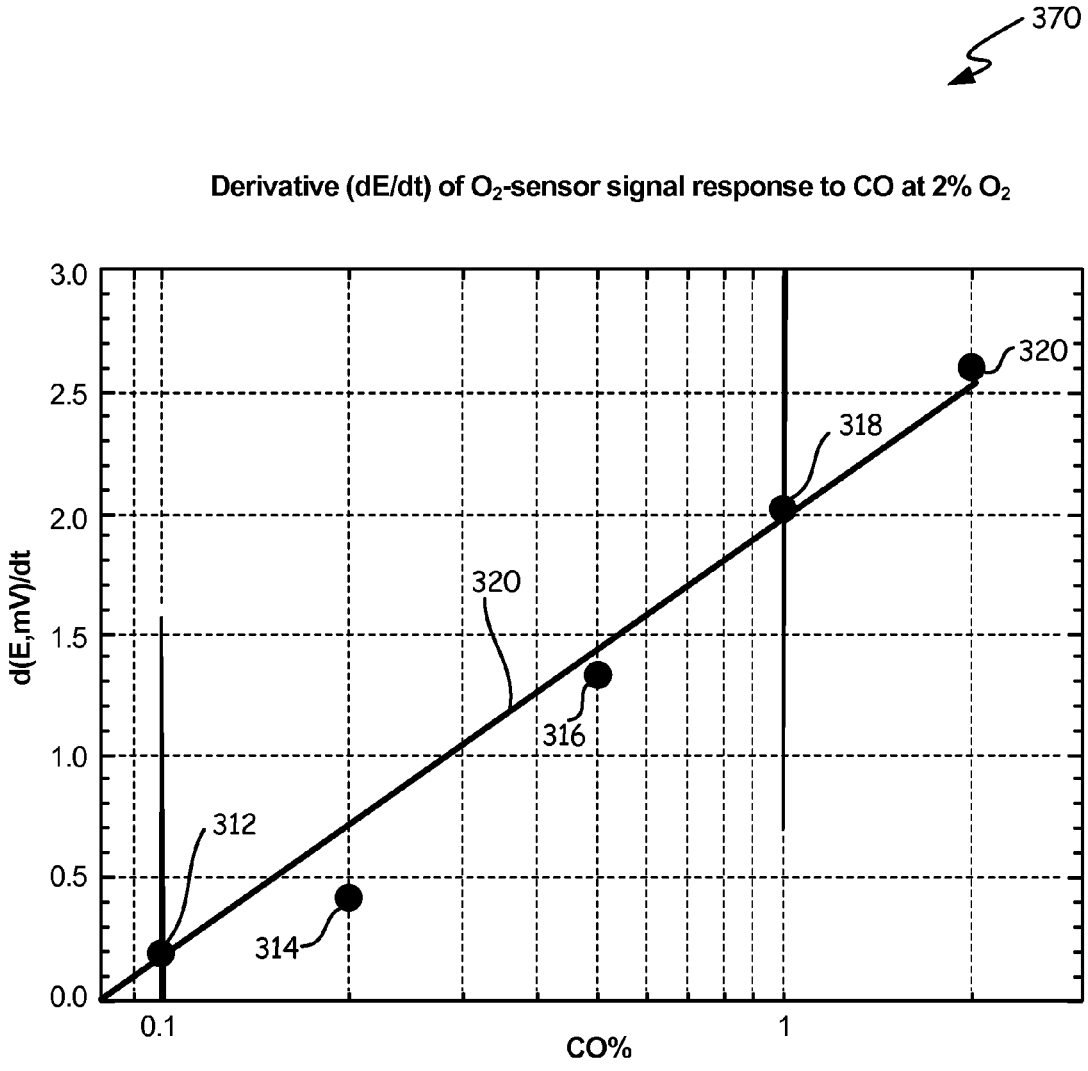

370
Derivative (dE/dt) of O_2-sensor signal response to CO at 2% O_2
3.0
2.5
2.0
1.5
1.0
0.5
0.0
d(E,mV)/dt
0.1
1
CO%
320
318
320
316
312
314

FIG. 3C

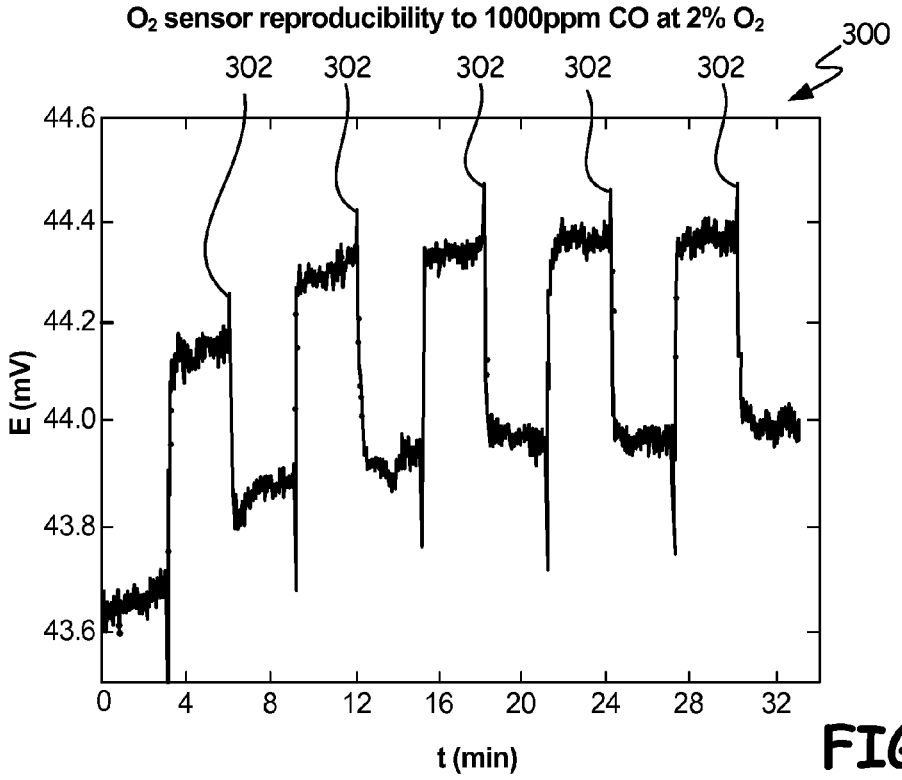

O2 sensor reproducibility to 1000ppm CO at 2% O2
300
302
302
302
302
302
44.6
44.4
44.2
44.0
43.8
43.6
E (mV)
0
4
8
12
16
20
24
28
32
t (min)

FIG. 3D

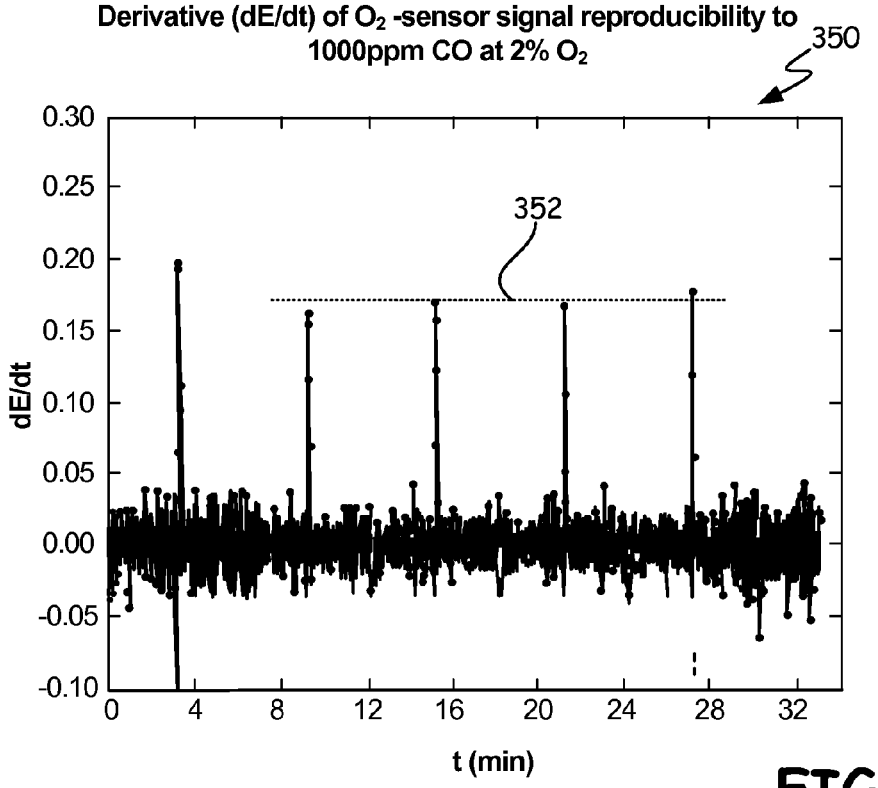

Derivative (dE/dt) of O2 -sensor signal reproducibility to 1000ppm CO at 2% O2
350
352
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
dE/dt
0
4
8
12
16
20
24
28
32
t (min)

FIG. 3E

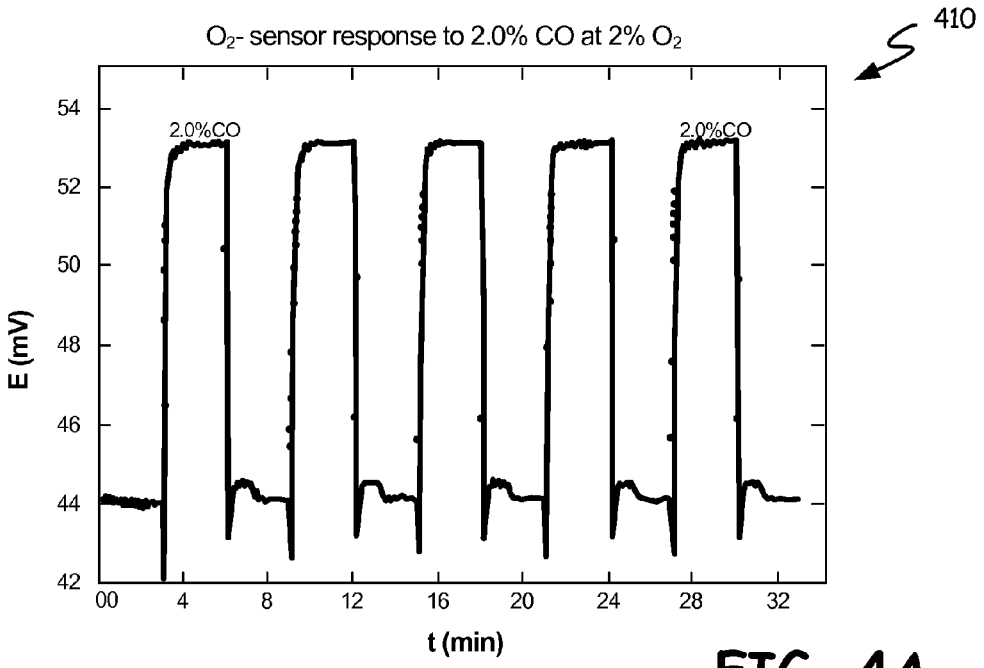

O_2- sensor response to 2.0% CO at 2% O_2
410
2.0%CO
2.0%CO
E (mV)
54
52
50
48
46
44
42
00
4
8
12
16
20
24
28
32
t (min)

FIG. 4A

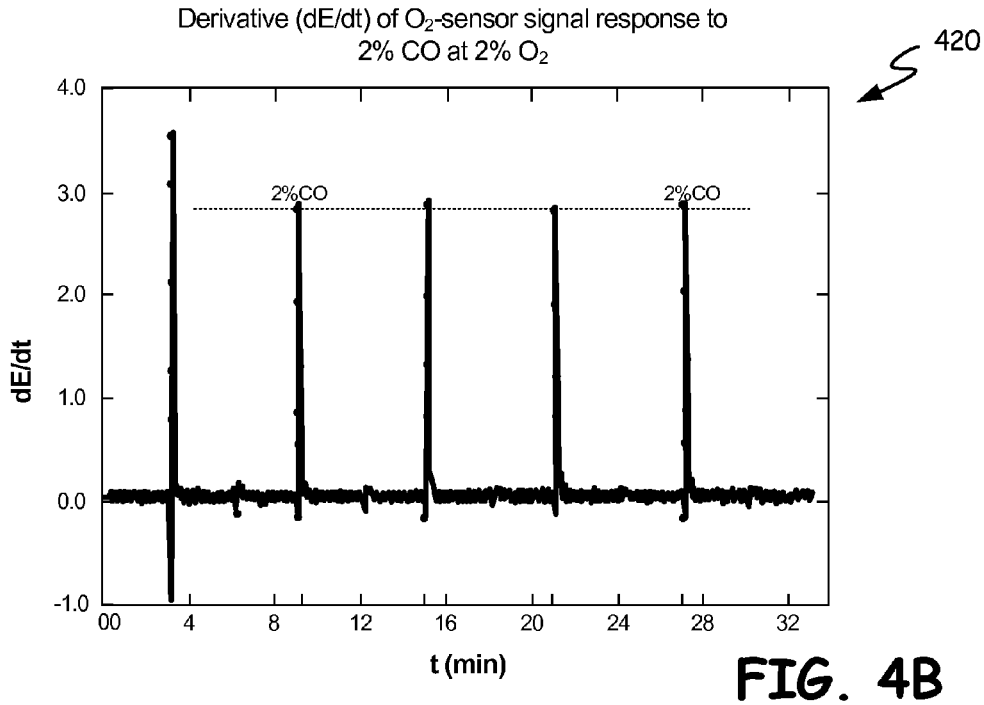

Derivative (dE/dt) of O_2-sensor signal response to 2% CO at 2% O_2
420
2%CO
2%CO
dE/dt
4.0
3.0
2.0
1.0
0.0
-1.0
00
4
8
12
16
20
24
28
32
t (min)

FIG. 4B

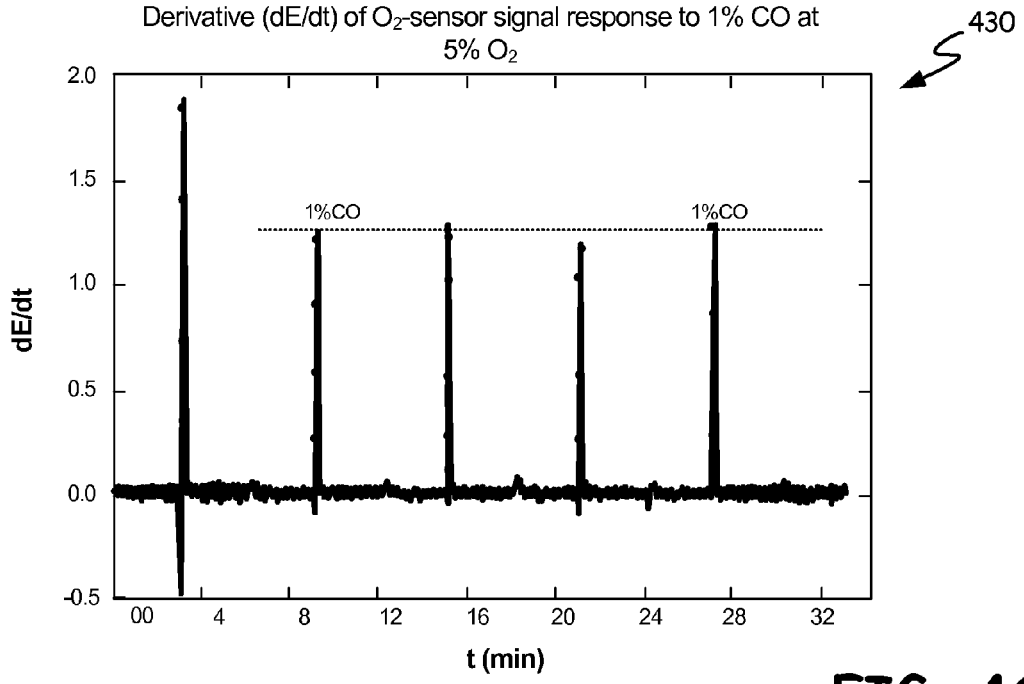

Derivative (dE/dt) of O_2-sensor signal response to 1% CO at 5% O_2
430
2.0
1.5
1.0
0.5
0.0
-0.5
dE/dt
1%CO
1%CO
00
4
8
12
16
20
24
28
32
t (min)

FIG. 4C

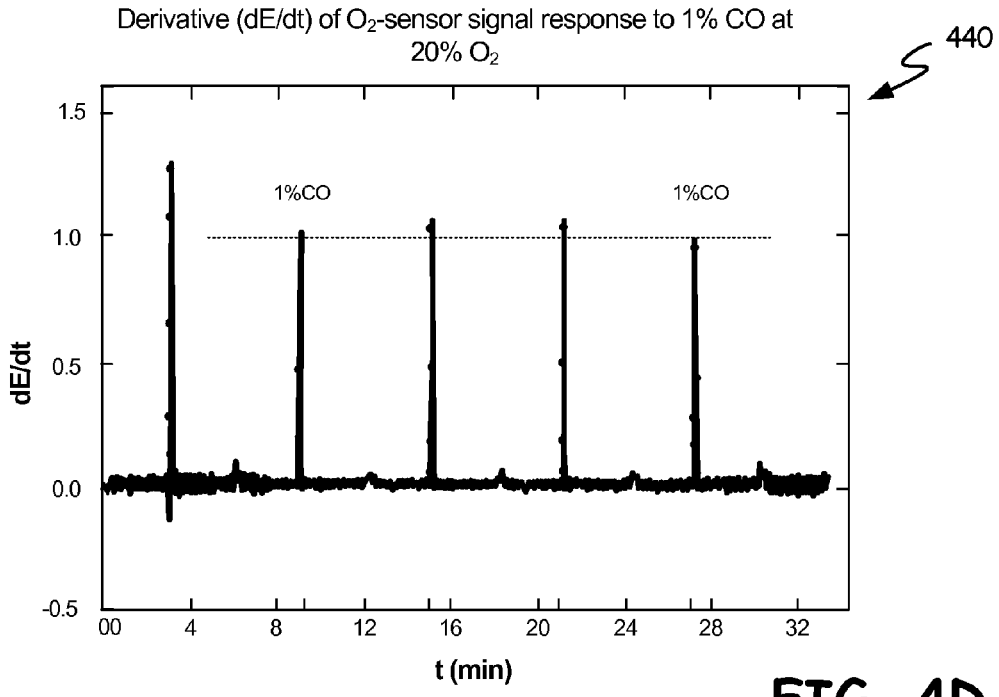

Derivative (dE/dt) of O_2-sensor signal response to 1% CO at 20% O_2
440
1.5
1.0
0.5
0.0
-0.5
dE/dt
1%CO
1%CO
00
4
8
12
16
20
24
28
32
t (min)

FIG. 4D

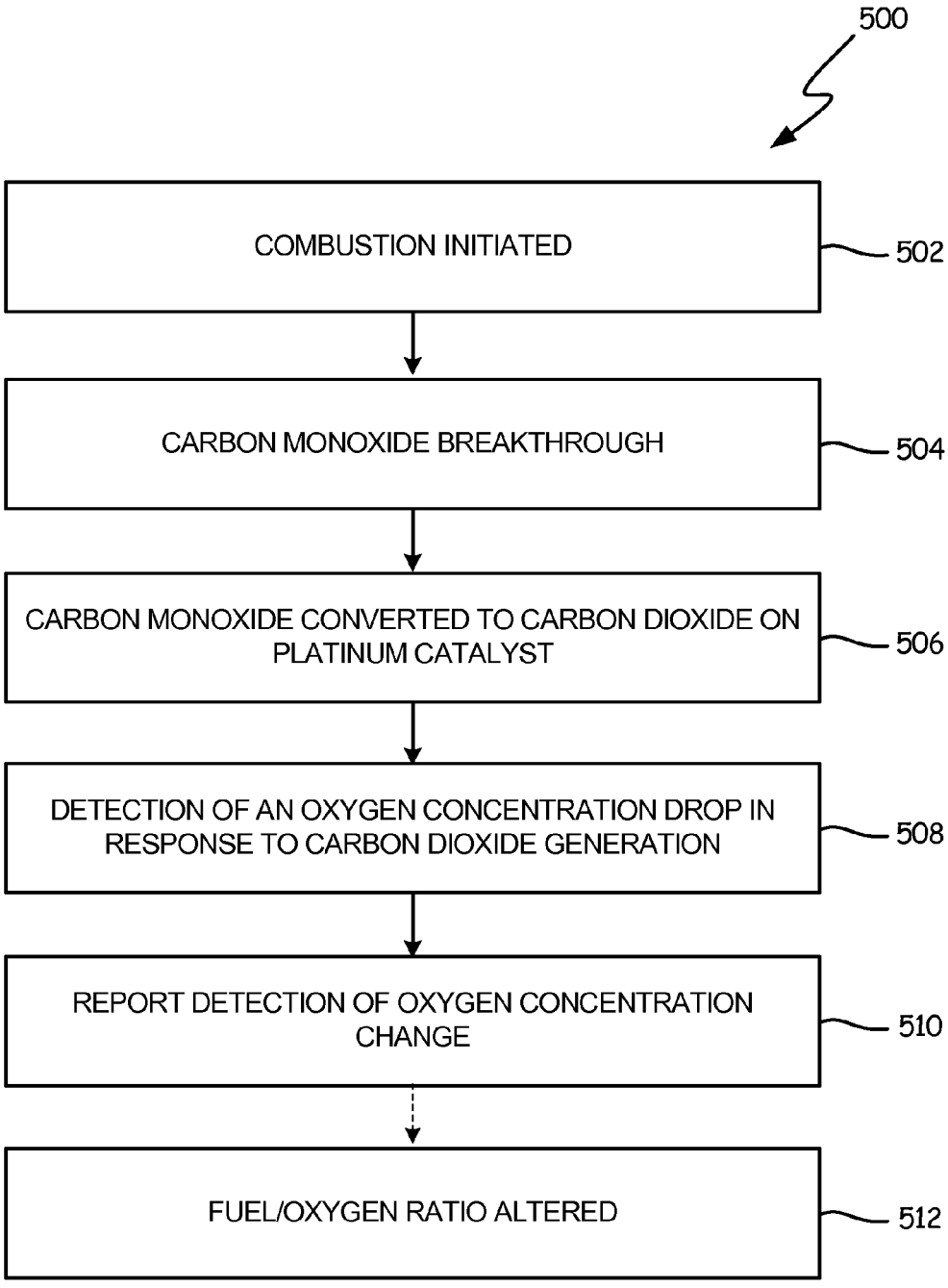

500
COMBUSTION INITIATED
502
CARBON MONOXIDE BREAKTHROUGH
504
CARBON MONOXIDE CONVERTED TO CARBON DIOXIDE ON PLATINUM CATALYST
506
DETECTION OF AN OXYGEN CONCENTRATION DROP IN RESPONSE TO CARBON DIOXIDE GENERATION
508
REPORT DETECTION OF OXYGEN CONCENTRATION CHANGE
510
FUEL/OXYGEN RATIO ALTERED
512

FIG. 5A

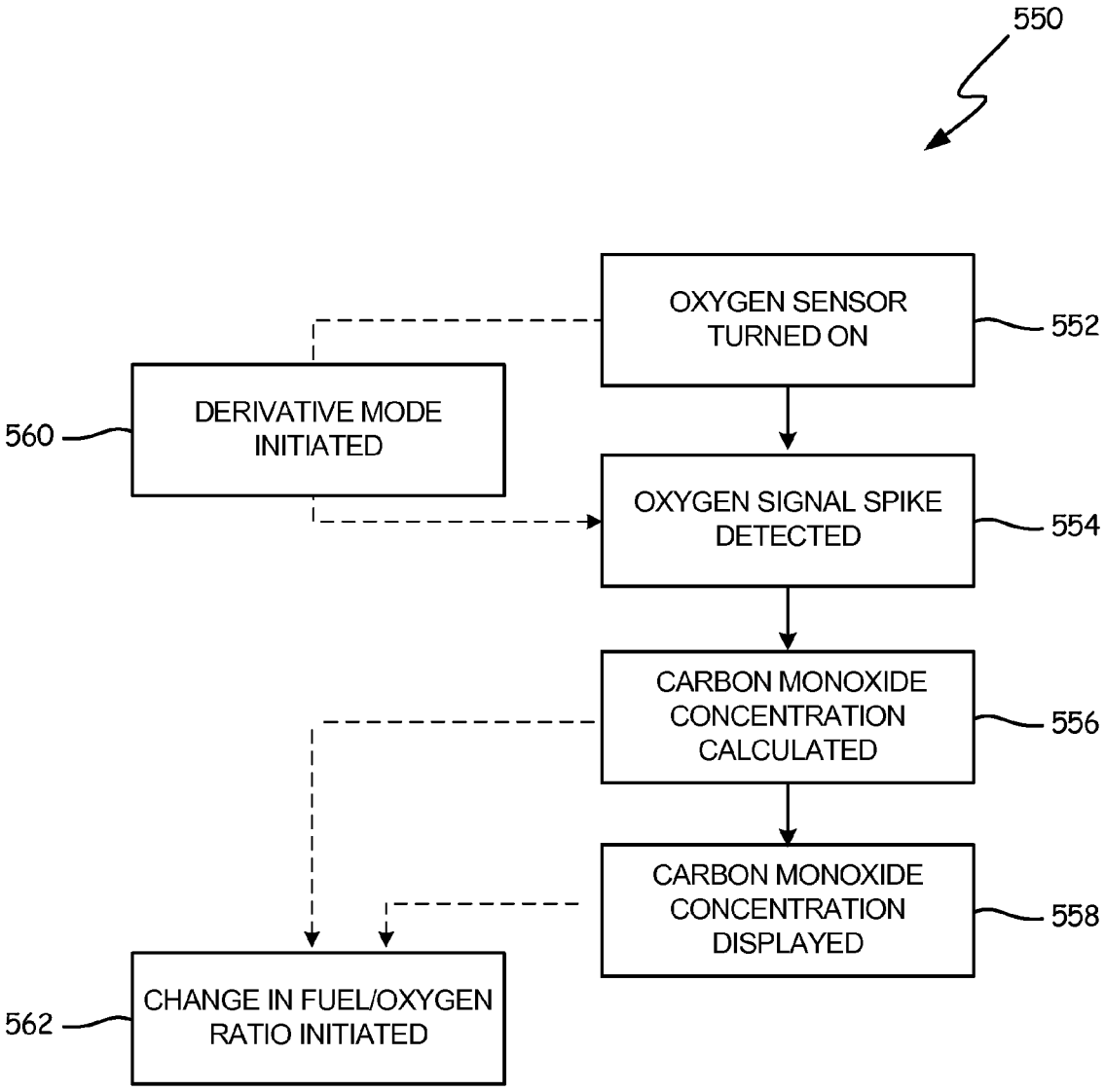

550
OXYGEN SENSOR TURNED ON
552
DERIVATIVE MODE INITIATED
560
OXYGEN SIGNAL SPIKE DETECTED
554
CARBON MONOXIDE CONCENTRATION CALCULATED
556
CARBON MONOXIDE CONCENTRATION DISPLAYED
558
CHANGE IN FUEL/OXYGEN RATIO INITIATED
562

FIG. 5B

OXYGEN SENSOR FOR CO BREAKTHROUGH MEASUREMENTS

BACKGROUND

[0001] The process industries often rely on energy sources that include one or more combustion processes. Such combustion processes include operation of a furnace or boiler to generate steam or to heat a feedstock liquid. While combustion provides relatively low cost energy, combustion efficiency is sought to be maximized. In addition, flue gases from industrial processes exiting smokestacks are often regulated, and the amount of dangerous gases often must be minimized. Accordingly, one goal of the combustion process management industry is to maximize combustion efficiency of existing furnaces and boilers, which inherently also reduces the production of greenhouse and other regulated gases. Combustion efficiency can be optimized by maintaining the ideal level of oxygen in the exhaust or flue gases coming from such combustion processes.

[0002] In-situ or in-process analyzers are commonly used for the monitoring, optimization, and control of the combustion process. Typically, these analyzers employ sensors that are heated to relatively high temperatures and are operated directly above, or near, the furnace or boiler combustion zone. Known process combustion oxygen analyzers typically employ a zirconium oxide sensor disposed at an end of a probe that is inserted directly into a flue gas stream. As the exhaust, or flue gas, flows into the sensor, it diffuses into proximity with the sensor. The sensor provides an electrical signal related to the amount of oxygen present in the gas.

SUMMARY

[0003] A sensor system configured to detect oxygen in an exhaust stream of an industrial process is provided. In one embodiment, the sensor system comprises a probe with an oxygen-detecting sensor, wherein the oxygen-detecting sensor detects a concentration of oxygen in the exhaust stream. The system may also comprise a catalytic converter located on the probe near the sensor, wherein the catalytic converter is configured to convert carbon monoxide to carbon dioxide. The system may also comprise a signal detector configured to detect a change in oxygen concentration indicative of a carbon monoxide breakthrough. These and various other features and advantages that characterize the claimed embodiments will become apparent upon reading the following detailed description and upon reviewing the associated drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] FIG. **1** is a diagrammatic view of an in-situ process oxygen analyzer/transmitter with which embodiments of the present invention are particularly applicable.

[0005] FIG. **2** is a diagrammatic perspective view of a combustion oxygen transmitter with which embodiments of the present invention are particular applicable.

[0006] FIGS. **3**A-**3**E are graphical representations of CO measurements using an oxygen sensor in accordance with an embodiment of present invention.

[0007] FIGS. **4**A-**4**D are graphical representations of an oxygen sensor response to carbon monoxide in accordance with an embodiment of present invention.

[0008] FIGS. **5**A and **5**B illustrate exemplary methods of measuring the concentration of carbon monoxide utilizing an oxygen sensor in accordance with an embodiment of present invention.

DETAILED DESCRIPTION

[0009] FIG. **1** is a diagrammatic view of an in-situ process oxygen analyzer transmitter installation with which embodiments of the present invention are particularly applicable. Transmitter **10** can be, for example, a Model **6888** oxygen transmitter available from Rosemount Analytical Inc., of Solon, Ohio (an Emerson Process Management company). Transmitter **10**, in one embodiment, includes probe assembly **12** that is substantially disposed within stack or flue **14** and measures oxygen content of the flue gas related to combustion occurring at burner **16**. In one embodiment, burner **16** is operably coupled to a source of air or oxygen source **18** and source **20** of combustion fuel. Each of sources **18** and **20** are controllably coupled to burner **16** in order to control the combustion process, in one embodiment. Transmitter **10** measures the amount of oxygen in the combustion exhaust flow and provides an indication of the oxygen level to combustion controller **22**, in one embodiment. Controller **22** controls one or both of valves **24** and **26** to provide closed loop combustion control. In one embodiment, controller **22** operates automatically, such that an indication of too much or too little oxygen in the exhaust flow results in a change in the amount of oxygen or fuel provided to the combustion chamber. In one embodiment, the oxygen analyzer transmitter may also include a calibration line with calibration gases **28**, connected to transmitter **10**.

[0010] FIG. **2** is a diagrammatic perspective view of a combustion oxygen transmitter with which embodiments of the present invention are particularly applicable. Transmitter **100** includes housing **102**, probe body **104**, and electronics **106** with a protective cover **116**. Probe **104** has a distal end **108** where a diffuser **110** is mounted. The diffuser **110** is a physical device that allows gaseous diffusion therethrough, but otherwise protects components within probe **104** from solid particles like fly ash. Specifically, diffuser **110** protects from the dust a measurement cell, or sensor **112**, illustrated in phantom in FIG. **2**.

[0011] Housing **102** has a chamber **114** that is sized to house electronics **106**. Additionally, housing **102** includes internal threads that are adapted to receive and mate with external threads of cover **116** to make a hermetic seal. Additionally, housing **102** includes a bore or aperture therethrough allowing electrical interconnection between electronics **106** and measuring cell or sensor **112** disposed within distal end **108** of the probe **104**.

[0012] Probe **104** is configured to extend within a flue, such as flue **14**. Probe **104** includes a proximal end **118** that is adjacent to flange **120**. Flange **120** is used to mount or otherwise secure the transmitter **100** to the sidewall of the duct. When so mounted, transmitter **100** may be completely supported by the coupling of flange **120** to the duct wall.

[0013] Electronics **106** provide heater control and signal conditioning, resulting in a linear 4-20 mA signal representing flue gas oxygen concentration. Preferably, electronics **106** also includes a microprocessor that is able to execute programmatic steps to provide the functions of diffuser diagnostics. However, in some embodiments, transmitter **100** may simply be a "direct replacement" probe with no electronics and thus sending raw millivolt signals for the

sensing cell and thermocouple providing indications representative of the oxygen concentration and cell temperature respectively. In embodiments where a "direct replacement" probe is used, the probe is coupled to a suitable analyzer such as the known Xi Operator Interface available from Rosemount Analytical Inc. The Xi Operator Interface provides a backlit display, signal conditioning and heater control within a NEMA 4X (IP 66) housing.

[0014] Ideally, combustion in an industrial process is perfect, and fuel and oxygen combust to create carbon dioxide and water, according to Equation 1 below, where the stoichiometric amount of carbon dioxide and water produced is dependent on the type of fuel used in a specific industrial process.

$$\text{Fuel}+O_2 \rightarrow CO_2+H_2O \qquad \text{Equation 1}$$

[0015] Often, however, combustion in industrial processes is not perfect and, in addition to carbon dioxide and water, excess oxygen exists in the exhaust. In one embodiment, while the industrial process is in a regular operating mode, an oxygen sensor, for example, oxygen transmitter **100** with probe **104**, measures the remaining oxygen gas in the exhaust of a the combustion process. Additionally, as is often the case, incomplete combustion occurs according to Equation 2 below.

$$\text{Fuel}+O_2 \rightarrow CO_2+H_2O+(CO+NO_x+SO_x)_{incomplete\ products} \qquad \text{Equation 2}$$

[0016] In an imperfect combustion, fuel comes into the industrial process with some contaminants and reacts to form, primarily carbon dioxide, CO_2, and water H_2O, with traces of other gases such as sulfur dioxide, nitrogen oxides, which come from the fuel impurities, as well as nitrogen oxidation. Additionally, when insufficient oxygen is provided to the industrial process, carbon monoxide forms as part of the incomplete combustion. The stoichiometric point, e.g. the ratio of fuel to oxygen with the highest efficiency and lowest emissions is very difficult to achieve in real combustion because of imperfect fuel to air uniformity, and of the fuel energy density and fuel to air flow variation.

[0017] Typically, flue gas oxygen excess concentration is 2-3 percent for gas burners and 2-6 percent for coal fired boilers and oil burners. The most efficient combustion may occur, in one embodiment, between 0.75 percent and 2 percent oxygen excess. While good combustion control can be accomplished with oxygen measurement alone, combustion efficiency and stability can be improved with the concurrent measurement of carbon monoxide, CO. As shown above in Equation 2, carbon monoxide is often a result of incomplete combustion of the fuel and oxygen supply and, therefore, a good first indicator that incomplete combustion is occurring in the process.

[0018] The development of carbon monoxide often occurs when the oxygen level is below a required amount for the industrial process to complete Equation 1 above. As carbon monoxide is a dangerous by-product of an incomplete combustion, its presence in exhaust gas may be regulated and an industrial process may be designed to include a catalytic converter to allow for conversion of carbon monoxide to carbon dioxide, according to Equation 3 below.

$$CO+\frac{1}{2}O_2 \leftarrow \rightarrow CO_2 \qquad \text{Equation 3}$$

[0019] In one embodiment, the excess oxygen is sampled periodically by probe **104** throughout combustion. In one embodiment, the excess oxygen is sampled by probe **104** almost continually throughout a combustion process. The oxygen sensor output may be reported on an attached display, in one embodiment. The oxygen sensor output may also be transmitted to a database for storage. In another embodiment, the oxygen sensor output may be attached to an alarm system wherein certain maximum or minimum threshold oxygen concentrations may trigger a process alarm or an alert to a process engineer that a threshold has been surpassed. In one embodiment, the alert may be sent through text message, e-mail or another wireless-based delivery mechanism. In another embodiment, the alert may be an audiovisual alert within the industrial process, and may result in either a light being activated, a sound being emitted, or a combination of alert mechanisms that a threshold has been surpassed.

[0020] In another embodiment, oxygen transmitter **100** is coupled to controllers **24** and **26** such that readings from the oxygen transmitter can trigger automatic changes in the ratio of oxygen to fuel entering the industrial process. For example, upon a reading indicative of a rich exhaust mixture, indicating a high amount of unburned fuel and low remaining oxygen, the transmitter **100** may trigger controller **24**, allowing more oxygen into the system, and/or may also trigger controller **26** inputting a lower amount of fuel into the system. The system may be calibrated, in one embodiment, to automatically adjust controllers **24** and **26** until a lean mixture is achieved. In one embodiment, a lean mixture is defined as a mixture of fuel and oxygen sufficient to convert the fuel into water and carbon dioxide without any incomplete combustion products.

[0021] In one embodiment, transmitter **100** is based on electrochemical zirconia-based cell technology. In one embodiment, the probe **104** is based on a solid-state electrochemical cell consisting of at least one zirconia ceramic located between an exhaust gas sample on one side, and a reference sample on the other side, wherein gas permeable electrodes are located on either side of the zirconia ceramic. The zirconia-based sensor **104** measures a concentration of remaining oxygen in the exhaust gas by measuring an output voltage across the zirconia ceramic, corresponding to a quantity of oxygen in the exhaust of the industrial process measured against a quantity of oxygen in a reference sample. The voltage measured corresponds to a concentration differential of oxygen between the two samples and, therefore, to an amount of oxygen consumed in a combustion reaction according to Equation 1 above. In one embodiment, the reference sample contains air of substantially atmospheric quality.

[0022] The oxygen sensor readings may depend logarithmically on the oxygen concentration according to the Nernst equation, Equation 4, below.

$$EMF=\frac{RT}{4F}\ln\left(\frac{P_{process}}{P_{ref}}\right)+C=0.0496\times T\times\log\left(\frac{P_{process}}{P_{ref}}\right)+C \qquad \text{Equation 4}$$

[0023] Zirconia based electrochemical oxygen sensors are widely used in industrial applications for oxygen measurements. In one embodiment, the sensor **104** works at temperatures in the 650-800 degree C. ranges and above, and measures the excess oxygen remaining after combustion. The response of the sensor to the differential oxygen concentration with a fixed oxygen partial pressure on the reference electrode, for example, fixed by using air can be calculated by using equation 4 above. In Equation 4, C is the constant related to the reference/process side temperature variation and thermal junctions in the oxygen probe, R is the universal gas constant, T is the process temperature, measured in degree Kelvin, and F is the Faraday constant.

[0024] In the combustion process, carbon monoxide is often the first indicator of an incomplete combustion. Operation at near trace CO levels of about 100 to 200 ppm and a slight amount of excess air would indicate the combustion conditions near the stoichiometric point with the highest efficiency. While there are many CO sensors available for applications ranging from workspace safety to exhaust gas analysis, the high temperature of typical industrial processes presents a difficulty in providing a reliable in-situ CO measurement for a combustion process.

[0025] A number of studies have been done on chemical gas sensors based on semiconducting oxides that are now used worldwide for combustible gas detection. This type of sensor, known as the Taguchi sensor, employs a solid state device made of sintered n-type metallic oxide (iron, zinc, and tin families), but poor selectivity and insufficient long term stability have been the major difficulties of these semiconducting sensors in the process environment.

[0026] Infrared absorption techniques relying on measuring the infrared light absorption would mostly require the flue gas conditioning system and thus add a relatively large expense to an industrial process. New, very sophisticated, and highly promoted tunable diode laser spectroscopy uses much more powerful laser light, is more reliable, and does not require a flue gas preconditioning. Unfortunately, fouling at a heavy particulate load, wide background radiation from the fireball, and required temperature and pressure compensation, as well as very high price, limit this technology to the applications in the chemical industry and for applications requiring high temperatures, such as combustion related processes. Currently, the only in-situ CO probe available on the market, and based on mixed potential zirconia technology was developed for very clean gas combustion application.

[0027] In one embodiment, the solid state potentiometric gas sensor for the oxygen measurements in the process comprises an oxide ion conducting ceramic in the form of a tube, disc or thimble, and two metallic or oxide catalytic electrodes that are exposed to the process and reference gases, respectively. In one embodiment, the ionic conducting ceramic is mostly a doped zirconia but could be stabilized cerium or bismuth oxide or any other oxide ion conducting solid electrolyte. The process reference electrodes are in one embodiment platinum, but any other electron conducting metal or metal oxide or mixed conducting pure or composite material could also be used. The oxygen sensor's process electrode is exposed to the flue gas, and the oxygen sensor is in an oxidizing environment in the regular potentiometric mode precisely measuring excess oxygen concentration in the combustion process flue gas. The highest peak of the derivative of the oxygen sensor signal is used as an additional carbon monoxide sensing output. The oxygen sensor, in one embodiment, is calibrated using fixed CO concentrations. This may correlate, for example, to the results shown in FIGS. **3** and **4**. The measured oxygen sensor raw mV signal is used to calculate an oxygen concentration according to equation 4, the Nernst equation, and the highest peak of the derivative of the oxygen sensor signal is applied for carbon monoxide breakthrough calculation using developed carbon monoxide algorithm validated with the carbon monoxide calibration gases. An additional oxygen sensor signal noise reduction, could be applied, in one embodiment, to remove the parasite electrical spikes in the industrial application that may alter oxygen and carbon monoxide measurements.

Oxygen Sensor Detecting Carbon Monoxide

[0028] Carbon monoxide is known to be one of the first products of an incomplete combustion to appear in a process. The presence of carbon monoxide results in a decrease in oxygen concentration as the carbon monoxide breaking through in the combustion process will, in one embodiment, be immediately converted to carbon dioxide, according to Equation 3 above, on a platinum electrode catalyst that is located on the sensor **112**. In one embodiment, the platinum electrode catalyst is located very close to the oxygen-sensing portion of sensor **112**. This will result in the oxygen concentration being significantly reduced near the oxygen-sensing electrochemical cell, as a result of the catalytic conversion of carbon monoxide to carbon dioxide, resulting in a sudden increase in the raw mV signal produced by sensor **112**. This will result in the oxygen sensor output signal indicating an immediate reduction in oxygen concentration, especially in the milliseconds after carbon monoxide breakthrough in a combustion scenario. This may trigger, as indicated above, an alert provided to a process engineer, or it may trigger a change in the ratio of fuel and oxygen sources **20** and **18**, respectively, through alteration of controls **26** and **24**, respectively.

[0029] The detection of a drop in concentration of oxygen gas in the exhaust provides a quantitative indication of carbon monoxide that was present in the exhaust gas prior to the conversion and, therefore, an indication of the concentration of carbon monoxide produced as a result of the combustion. As can be seen from Table 1 below, CO presence is reducing the oxygen signal by almost 50 percent of the CO concentration, with CO conversion rate varying between 80 to 100% at 1000 ppm CO to 60 to 100% at 2% CO.

TABLE 1

OXYGEN SENSOR PROBE RAW mV SIGNAL REDUCTION

	[CO] (%)							
	0.1		0.5		1.0		2.0	
$[O_2]$ (%)	ΔE_t (mV)	ΔE_m (mV)	ΔE_t (mV)	ΔE_m (mV)	ΔE_t (mV)	ΔE_m (mV)	ΔE_t (mV)	ΔE_m (mV)
2	0.55	0.43	2.9	1.8	6.3	3.9	15.1	9.1
3	0.36	0.30	1.9	1.3	4.0	2.8	8.8	6.4
4	0.25	0.24	1.4	1.0	2.9	2.2	6.3	4.9
5	0.22	0.20	1.1	0.8	2.3	1.8	4.9	3.9
20.9	0.05	0.05	0.26	0.26	0.53	0.52	1.06	1.05

[0030] In Table 1 the change in sensor signal is theoretical ΔE_t and calculated assuming 100% CO combustion by the platinum catalytic converter. The measured signal change ΔE_m being close to theoretical change ΔE_t, Table 1 does prove the effectiveness of an oxygen sensor, such as probe **112**, to detect carbon monoxide in an industrial environment.

Examples of Carbon Monoxide Detection with an Oxygen Sensor

[0031] FIGS. **3**A-**3**E are graphical representations of CO measurements using an oxygen sensor in accordance with an embodiment of the present invention. Specifically, FIGS. **3**A-**3**E illustrate the responses of an oxygen sensor **112** to the presence of carbon monoxide at various levels of oxygen over time in an industrial process. More specifically, FIGS. **3**A and **3**D illustrate a direct sensor response. FIGS. **3**B, **3**C and **3**E illustrate the derivative of the oxygen sensor signal response to carbon dioxide.

[0032] FIG. **3**A illustrates the oxygen sensor **112** response to carbon monoxide in an environment with a two percent oxygen concentration over a period of time, with time on the X axis, and the response of the oxygen sensor, in mV, shown on the Y axis. At around four minutes, a spike **302** is shown that corresponds to roughly 1000 ppm presence of carbon monoxide in the industrial process, as indicated by a reading of approximately 44.5 mV. At around ten minutes, a spike **304** corresponds to a 2000 ppm presence of carbon monoxide, as indicated by a reading of just under 45 mV. At around fifteen minutes, a spike **306**, corresponding to a 0.5% carbon monoxide concentration, results in a reading of approximately 46 mV. At around twenty one minutes, a spike of one percent carbon monoxide is detected, as indicated by a reading of approximately 48 mV. At around twenty seven minutes, a spike **310** is detected, indicating a two percent presence of carbon monoxide, with a corresponding reading of 53 mV by the sensor **112**. As can be seen from FIG. **3**A, oxygen sensor raw mV signal is highly sensitive to carbon monoxide gas presence at 2% oxygen concentration, with a 9 mV change in sensor reading detected.

[0033] The sensor signal derivative over time, as shown in FIG. **3**B, is also presented, with time on the x-axis and the derivative value on the y-axis. The highest peak value of the derivative dE/dt is logarithmically dependent on the carbon monoxide concentration in the range between 1000 ppm and 2% carbon monoxide. At approximately 4 minutes, a spike **312** is shown, corresponding to a concentration of approximately 1000 ppm carbon monoxide, with a reading of approximately 0.2. At approximately ten minutes, spike **314** indicates a carbon monoxide concentration of approximately 2000 ppm, resulting in a reading of approximately 1.0 by the sensor **112**. At approximately fifteen minutes, spike **316** indicates a carbon monoxide concentration of 0.5%, resulting in a reading of approximately 1.5 by the sensor **112**. At approximately twenty-one minutes, spike **318** indicates a carbon monoxide concentration of approximately 1% carbon monoxide, resulting in a reading of approximately 2.2 by the sensor **112**. At approximately twenty-seven minutes, spike **320** indicates a carbon monoxide concentration of 2%, with a reading of approximately 2.7 by the sensor **112**.

[0034] In one embodiment, sensor **112** outputs the raw mV data graphically, as shown in FIG. **3**A. In another embodiment, sensor **112** outputs the derivative dE/dt value graphically, as shown in FIG. **3**B. In another embodiment, sensor **112** outputs a current carbon monoxide concentration, calculated from either the data obtained from the sensor, for example as shown in FIG. **3**A or FIG. **3**B. In another embodiment, detection of a minimum threshold of carbon monoxide concentration in the exhaust gas triggers a change in the ratio of fuel to oxygen input into the industrial process. In another embodiment, detection of a minimum threshold concentration of carbon monoxide in the exhaust gas triggers an alert.

[0035] FIG. **3**C illustrates a graphical representation **370** of the derivative of the O_2 sensor signal response shown in FIG. **3**B, with the carbon monoxide concentration presented logarithmically on the x-axis, and the dE/dt values obtained on the y-axis. Equation 5, shown below, is also shown as line **320**. Equation 5 has an R value of 0.9912.

$$\frac{dE}{dt} = 1.97 + 1.948 \times \log[\%\ CO] \qquad \text{Equation 5}$$

[0036] FIG. **3**D illustrates the reproducibility of the oxygen sensor **112** to repeated carbon monoxide breakthroughs of 1000 ppm, in an environment with 2% oxygen. Indications **302** are shown as occurring roughly at four minutes, nine minutes, sixteen minutes, twenty one minutes and twenty-seven minutes. As shown in FIG. **3**D, the raw mV value of oxygen sensor **112** may exhibit slight drifting in the response to the presence of 1000 ppm carbon monoxide.

[0037] FIG. **3**E illustrates the increased reproducibility of detected carbon monoxide using the derivative of the oxygen sensor signal, with repeated 1000 ppm carbon monoxide breakthroughs occurring at nine, fifteen, twenty one and twenty seven minutes all resulting in a detected reading of approximately 0.17, as represented by bar **352**. Additionally, the derivative of the oxygen sensor signal highest peak is shown at 1000 ppm carbon monoxide with about a 70 ppm carbon monoxide error as shown in FIG. **3**E.

[0038] FIGS. **4**A-**4**D are graphical representations of an oxygen sensor response to carbon monoxide. FIG. **4**A illustrates a graph **410** showing the reproducibility of detecting a 2% carbon monoxide concentration, with peaks at approximately four, nine, fifteen, twenty one and twenty seven minutes all resulting in a detected reading of approximately 52 mV. FIG. **4**B illustrates a graph **420** showing the reproducibility of the derivative of the oxygen sensor response at detecting a 2% carbon monoxide concentration, with peaks at approximately four, nine, fifteen, twenty one and twenty seven minutes all resulting in a detected reading of approximately 2.8, with an error rate in detection of approximately ±0.02% CO, or a 1% error rate. FIG. **4**C illustrates a graph **430** showing the reproducibility of the derivative of the oxygen sensor response at detecting a 1% carbon monoxide concentration in a 5% oxygen environment, with peaks at approximately nine, fifteen, twenty one and twenty seven minutes all resulting in a detected reading of approximately 1.3. FIG. **4**D illustrates a graph **440** showing the reproducibility of the derivative of the oxygen sensor response at detecting a 1% carbon monoxide concentration in a 20% oxygen environment, with peaks at approximately four, nine, fifteen, twenty one and twenty seven minutes all resulting in a detected reading of approximately 1.0.

[0039] Thus, FIGS. **3**A-**3**E and FIGS. **4**A-**4**D show that, through the use of a zirconia electrochemical oxygen sensor, and the derivative of the sensor signal response, reliable

carbon monoxide measurements can be provided in a variety of carbon monoxide breakthrough scenarios.

Methods of Detecting Carbon Monoxide

[0040] FIGS. **5**A and **5**B illustrate exemplary methods of measuring development of carbon monoxide utilizing an oxygen sensor. FIG. **5**A illustrates an exemplary method **500** of detecting and displaying a carbon monoxide breakthrough using an oxygen sensor. In one embodiment, the oxygen sensor may include the zirconia-based electrochemical cell described above.

[0041] Method **500** starts in block **502** with a combustion initiating in an industrial process. Method **500** continues with a carbon monoxide breakthrough occurring as shown in block **504**. In one embodiment it may be minutes, hours, or longer between a combustion process starting and a carbon monoxide breakthrough occurring. Method **500** continues, in one embodiment, with the produced carbon monoxide being converted to carbon dioxide on a catalyst. In one embodiment, the catalyst is a platinum-based catalyst. In one embodiment, this occurs as described above with respect to Equation 3. As the carbon monoxide is converted to carbon dioxide, the measured oxygen concentration in the exhaust gas drops. This drop is detected in block **508** by the probe **104**. In one embodiment, the detection is reported in block **510**. In one embodiment, as illustrated by method **500**, a concentration of carbon monoxide is not calculated as part of the detection process. In an optional embodiment, the method **500** moves on to block **512**, where the fuel to oxygen input ratio is altered. This alteration may happen, in one embodiment, automatically, upon the detection of carbon monoxide. In one embodiment, this may result in additional air or oxygen being input to the system through source **18**. In one embodiment, this may result in reduced fuel being input to the system through source **20**.

[0042] FIG. **5**B illustrates a method **550** for calculating the carbon monoxide concentration in an exhaust stream using oxygen sensor **112**. Method **550** starts in block **552** with the oxygen sensor **112** provided to an industrial process environment. Then, in block **554**, an oxygen signal spike is detected, for example, any oxygen signal spike is shown in any of FIGS. **3** and **4**. In one embodiment, the sensor **112** operates in a normal, and not a derivative sensing mode. In another embodiment, sensor **112** operates in either a normal or a derivative sensing mode, and the derivative sensing mode is optionally initiated in block **560**. In one embodiment, the oxygen sensor may detect both an oxygen sensor signal response and a derivative of the oxygen sensor signal response. However, in another embodiment the sensor may only detect the derivative of the oxygen sensor signal response.

[0043] The method then moves on to block **556** wherein a carbon monoxide concentration is calculated based at least in part on Equation 4, described above. The method may then continue, in one embodiment to block **558** where the detected carbon monoxide concentration is displayed, for example, on a connected computer or other display device. Additionally, in another embodiment, displaying the carbon monoxide concentration may comprise sending an alert to a process engineer, for example using wireless or other technology. This may trigger an indication to an operator of the industrial process that there has been a carbon monoxide breakthrough and that fuel to air ratios may need to be changed. The alert could be triggered visually, audibly, or through another means of notification. Additionally, in another embodiment, detection of a carbon monoxide breakthrough may result in an automatic change in the fuel to oxygen ratio, as indicated in block **562**.

[0044] Although the present invention has been described with reference to preferred embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

What is claimed is:

1. A sensor system configured to detect oxygen in an exhaust stream of an industrial process, the sensor system comprising:

a probe with an oxygen-detecting sensor, wherein the oxygen-detecting sensor detects a concentration of oxygen in the exhaust stream and outputs a signal corresponding, at least in part, to the detected concentration of oxygen;

a catalytic converter located on the sensor, wherein the catalytic converter is configured to convert carbon monoxide to carbon dioxide; and

a signal detector configured to detect a change in oxygen concentration indicative of a carbon monoxide breakthrough.

2. The sensor system of claim **1**, wherein detection of the carbon monoxide breakthrough triggers an alert.

3. The sensor system of claim **1**, wherein detection of the carbon monoxide breakthrough triggers a change in a current fuel to oxygen ratio input to the industrial process.

4. The sensor system of claim **1**, and further comprising:

a transmitter configured to transmit an indication of the detected carbon monoxide breakthrough.

5. The sensor system of claim **1**, wherein the oxygen-detecting sensor comprises an electrochemical zirconia-based cell, and wherein the electrochemical zirconia-based cell measures a voltage across electrodes separating a reference gas from the exhaust stream.

6. The sensor system of claim **1**, wherein the catalytic converter comprises a platinum catalyst.

7. The sensor system of claim **1**, wherein the signal detector is further configured to calculate a concentration of carbon monoxide in the exhaust stream, at least based in part on the detected change in oxygen concentration.

8. A method for detecting carbon monoxide in an exhaust stream of an industrial process, the method comprising:

detecting an abrupt change in oxygen concentration in the exhaust stream of the industrial process, wherein the detected abrupt change is indicative of a carbon monoxide breakthrough and wherein the detection is completed utilizing an oxygen sensor; and

calculating a concentration of carbon monoxide in the exhaust stream at least in part using the detected change in oxygen concentration.

9. The method of claim **8**, and further comprising:

reporting the detected change in oxygen concentration.

10. The method of claim **8**, and further comprising:

reporting the calculated change in carbon monoxide concentration.

11. The method of claim **8**, and further comprising:

altering an existing fuel-to-oxygen ratio based at least in part on the detected concentration of carbon monoxide to a new fuel-to-oxygen ratio.

12. The method of claim **8**, and further comprising:
transmitting an indication of the calculated carbon monoxide concentration.

13. The method of claim **8**, and further comprising:
triggering an alert indicating that carbon monoxide is present within the exhaust stream of the industrial process.

14. The method of claim **8**, wherein calculation the concentration of carbon monoxide is based on a derivative of the oxygen-sensor signal.

15. The method of claim **8**, wherein the oxygen sensor comprises a zirconia-based electrochemical cell.

16. A method for detecting carbon monoxide, the method comprising:
detecting a sudden change in oxygen concentration, based at least in part by signals output from an oxygen sensor, wherein the sudden change in oxygen concentration is indicative of a carbon monoxide breakthrough;
calculating a derivative of the signals output from the oxygen sensor; and
determining a concentration of carbon monoxide based at least in part on the derivative of the signals output from the oxygen sensor.

17. The method of claim **16**, and further comprising:
reporting the calculated concentration of carbon monoxide.

18. The method of claim **16**, and further comprising:
transmitted an indication of the calculated concentration of carbon monoxide.

19. The method of claim **16**, and further comprising:
changing a current fuel-to-oxygen ratio at least in part based on the determined concentration of carbon monoxide.

20. The method of claim **16**, wherein the oxygen sensor comprises an zirconia-based electrochemical cell.

21. A sensor system for detecting gas in an exhaust stream of an industrial process, the sensor system comprising:
a probe with an oxygen-detecting sensor, wherein the oxygen-detecting sensor is configured to detect a concentration of oxygen in the exhaust stream and provide a signal corresponding, at least in part, to the detected concentration of oxygen;
electronics operably coupled to the oxygen-detecting sensor, the electronics being configured to detect an abrupt change in oxygen concentration in the exhaust stream of the industrial process, wherein the detected abrupt change is indicative of a carbon monoxide breakthrough and wherein the detection is completed utilizing the oxygen-detecting sensor; and
wherein the electronics are further configured to calculate a concentration of carbon monoxide in the exhaust stream at least in part using the detected change in oxygen concentration.

22. A sensor system for detecting gas in an exhaust stream of an industrial process, the sensor system comprising:
a probe with an oxygen-detecting sensor, wherein the oxygen-detecting sensor is configured to detect a concentration of oxygen in the exhaust stream and provide a signal corresponding, at least in part, to the detected concentration of oxygen;
electronics operably coupled to the oxygen-detecting sensor, the electronics being configured to calculate a derivative of the signals provided from the oxygen-detecting sensor and to determine a concentration of carbon monoxide based at least in part on the derivative of the signals provided by the oxygen-detecting sensor.

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